ADSORPTION OF POLYELECTROLYTES AT LIQUID – LIQUID INTERFACES AND ITS EFFECT ON EMULSIFICATION

(with a summary in Dutch)

J. Th. C. BÖHM

*Department of Physical and Colloid Chemistry, Agricultural University,
Wageningen, The Netherlands*

(Received 11–XII–1973)

2045762

CONTENTS

1. INTRODUCTION

1.1. POLYMER ADSORPTION

Ever since antiquity natural water-soluble polymers such as proteins, gums, starches and their derivatives have been widely used at interfaces. Their function and structure were often unknown. However, with the development of research on natural and synthetic polymers and their applications in technology during the past twenty-five years the knowledge of their properties at interfaces has been increased.

Polymers adsorb at almost any interface. Due to the sum effect of all monomeric units the decrease in free energy upon adsorption per polymer molecule becomes very high. The mechanism of attachment of segments to the interface can have various origins such as electrostatic interaction, VAN DER WAALS forces of attraction, chemical, hydrogen and hydrophobic bonding. JENKEL and RUMBACH (1951) were the first to propose a model for the adsorption of polymers. They stated that only a part of the segments is really in contact with the interface (train segments), the other part being present in loops or tails. This picture is now generally accepted and explains why the amount of polymer adsorbed per unit area is usually several times higher than the amount of monomers that can be accommodated in the monolayer.

As a consequence of all of this, polymers adsorb normally irreversibly. Statistically it is very unlikely that all adsorbed segments would desorb simultaneously. Moreover, polymer adsorption is a time-dependent process. When a polymer molecule reaches the interface it adsorbs but not instantly in the most advantageous conformation. Exchange of adsorbed against non-adsorbed segments remains possible and this process gives rise to a growing amount of polymer at the interface. Eventually, a steady-state value of the adsorption will be reached, usually in the order of hours. The final conformation depends on many factors such as polymer concentration, molecular weight, the quality of the solvent and the way of adsorption. PATAT et al. (1964) and STROMBERG (1967) extensively reviewed the adsorption of polymers with special emphasis on the liquid-solid interface.

The theoretical formulation of polymer adsorption, based on the loop-train model, has been worked out by FRISCH and SIMHA (1954, 1955 and 1957), SILBERBERG (1962, 1967, 1968 and 1970) and by HOEVE (1965, 1966, 1970 and 1971). Although there is no mutual agreement between these theories they predict similar trends that are more or less in satisfactory agreement with the experimental results. These theories are restricted to flexible homopolymers, whereas in experiments this condition is not always fulfilled. Blockpolymers and proteins can adsorb in conformations deviating considerably from those predicted for flexible homopolymers.

The stability of colloidal dispersions is usually strongly affected if polymers are present on the surface of the particles. Interpretation of the action of the adsorbed polymer on the stability of the dispersion solely on basis of the DLVO theory (DERYAGIN and LANDAU, 1941; VERWEY and OVERBEEK, 1948) is not possible. Additional interaction contributions should be taken into account (e.g. HESSELINK, 1971; EVANS and NAPPER, 1973). By adsorption of polymers a bridging between the particles can occur if the loops of the molecules anchor onto a second particle. This results in an extra attraction free energy due to the gain in segmental adsorption free energy. On the other hand the number of possible conformations of a loop, and hence its entropy, is reduced by this bridging. This leads to an entropic repulsive contribution to the free energy. Moreover, an osmotic free energy contribution, due to the increasing segment concentration between the particles must be taken into account. As even negatively charged suspensions can be flocculated[1] by negative polyelectrolytes, these additional interaction contributions can be the major factors in the flocculation by polymers.

The wide application of polymers as stabilizers or destabilizers of solid dispersions in liquids is based on these additional interaction contributions. An example of the stabilizing action of polymers is the coating of granulated food, to be added, for example, to drinking water for cattle. The destabilizing action of polymers on solid dispersions in liquids is widely used in the industrial production of metals, in soil engineering, in water purification and in paper production. In these fields polymers are known as flocculants and especially cationic flocculants are of growing interest. The properties of such systems depend on the ratio of dispersion to polymer and the mixing procedure. If covered and naked particles are mixed, the loops of the adsorbed molecules attach to the naked particles and a so-called bridged system with a network between the particles is obtained. Flocculation of this system is now more likely. However, if completely covered particles approach each other entropic repulsion between the adsorbed layers would prevent bridging and the stability of the dispersion is now increased (FLEER and LYKLEMA, 1973). In the production of beer there is also an example of the action of polymers at the liquid-solid interface. During the storage of beer, proteins are responsible for the nonbiological clouding by a complex formation with tannins. Finely divided modified silica, added to the beer, can prevent this clouding and has a so-called stabilizing effect. Its action can be explained essentially in that the silica selectively adsorbs the high molecular weight proteins.

Hitherto, applications at the liquid-solid interface have been reported. In beer technology also an example of an application of polymer adsorption at the liquid-gas interface is known. A desirable characteristic of beer is the for-

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1. In agreement with FLEER et al. (1972) we distinguish between flocculation (aggregation of colloidal particles by polymers and coagulation (aggregation by electrolytes)

mation of stable foam upon pouring. Addition of a chemically modified starch improves this foam stability considerably without affecting the taste. Also in many non-food products the quality of foams has been improved by addition of synthetic polymers. The action of polymers at the liquid-air interface (and also at the liquid-liquid interface) is, that the polymer reduces the drainage and promotes the stability to rupture of thin films.

In the study to be described in this thesis, the liquid-liquid (L/L) interface is emphasized. Polymers are widely used at the L/L interface as emulsifiers or/and stabilizers. An emulsion is a dispersion of liquid droplets in another liquid, the two of which are immiscible. Examples of applications of emulsions in which polymers are used as emulsifier or stabilizer are sprays, cosmetics, pharmaceutics and especially food products. The dispersed phase of milk consists of fat globules surrounded by an adsorbed layer of mainly proteins and lecithin. In many other emulsified food products it is the adsorbed amount and the kind of the proteins that determine the properties of the products. In ice-creams, for example, addition of polymeric emulsifiers improves the whipping quality of the mixture and the production of a smooth texture, giving a stiff dry product. Usually the emulsifiers or stabilizers in food products are mixtures of several compounds, but their main ingredients are proteins or gum-like substances. As their physico-chemical properties are very complicated, model substances are more suitable to investigate the emulsifying and/or stabilizing capacity of proteins at L/L interfaces.

1.2. POLYMERS AT LIQUID-LIQUID INTERFACES

The topic of the study to be described is polymers at L/L interfaces. Technically speaking, this system has a disadvantage as compared with the liquid-solid (L/S) interface in that direct determination of the adsorbed amount per unit area Γ is not well feasible, since as a rule the interfacial area is too small. Emulsification of the system would solve this problem but creates a new problem namely the role of the polymer as emulsifier. An additional measurable parameter in the L/L system is the interfacial tension γ. However, the relation between the bulk concentration c_p, γ and the adsorbed amount of polymer per unit area Γ is ambiguous because of the irreversible nature of the adsorption. The well-known GIBBS equation may not be applied. This explains why in studies, concerning the properties of polymers at L/L interfaces, the interpretations are mainly qualitative and comparative. Moreover, use of *spread* monolayers is not very helpful for understanding the relation between γ and Γ for *adsorbed* layers, because the conformation of the polymer molecules in the interfacial layer differs much for the two systems. All this indicates that there is no simple technique to obtain information on the conformation of polymers at L/L interfaces. On the other hand, the practical importance of such systems is important enough for further investigations.

In general γ decreases upon adsorption of polymers. From investigations at the L/S interface it can be deduced that the number of train segments per unit area increases with adsorption (e.g. STROMBERG et al., 1965; KILLMANN et al., 1973). Moreover, it has been found by radioactivity measurements at the air-water interface that γ can still decrease, even if the adsorbed amount remains constant (e.g. ADAMS et al., 1971). This indicates a reconformation of the molecule with an increasing number of train segments. It is therefore reasonable to assume as a first approximation that the reduction of γ is primarily related to the number of segments being adsorbed in the first layer and not to the total amount of adsorbed polymer. LANKVELD and LYKLEMA (1972) stated this already on account of the adsorption of polyvinyl alcohol (PVA) at the paraffin oil-water interface. We shall adopt this idea as a working hypothesis and investigate its validity in due course.

As polymers are often used as emulsifiers we are also interested in the behaviour of polymers at disturbed interfaces. A disturbed interface is subject to expansion and/or compression during the time that adsorption takes place. One must always realize that the findings about the behaviour of polymers at undisturbed interfaces cannot be directly compared with the behaviour at disturbed interfaces. In order to explain the emulsifying behaviour of an interfacially active compound and the stability of emulsions it is more valuable to use dynamic techniques than equilibrium techniques (LUCASSEN and V. D. TEMPEL, 1972a). LUCASSEN (1968) has developed a method for measuring surface tension changes, caused by local periodic area variations. The response of this surface tension change on the area variation is called the surface dilational modulus ε and it reflects the effectivity by which the uniformity of the surface tension is recovered after disturbance of the surface. At L/L interfaces this modulus is probably reflected in the behaviour during emulsification. Due to agitation the interface is disturbed continuously and the dispersed phase breaks up into smaller units. Adsorption of an emulsifying agent at this disturbed interface and its effectiveness to reduce the interfacial tension gradients at these interfaces determine the coalescence behaviour of the newly created units.

If coalescence of droplets after finishing emulsification is absent, the final dispersity reflects the behaviour during emulsification. If polymers are used as emulsifying agents this stability is usually very high. KITCHENER and MUSSELL-WHITE (1968) stated that the almost infinite stability to coalescence after finishing emulsification for such systems is correlated with the visco-elastic properties of the polymers in thin films, but KANNER and GLASS (1969) also mention examples that disagree with that conclusion. Nevertheless, it can be concluded that in general with polymers as the emulsifying agents the obtained dispersity reflects the emulsification process.

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1.3. Outline of this study

This study was undertaken to gain more insight into the behaviour of synthetic polyelectrolytes at undisturbed and disturbed L/L interfaces. LANKVELD and LYKLEMA (1972) already investigated the properties of an uncharged polymer (PVA) at the same L/L interface. As polyelectrolytes retain many of the properties of uncharged polymers and can be modified by charging dissociable groups or by changing the ionic strength of the solution, this study provides an interesting extension of the study of PVA at L/L interfaces.

To achieve a basic understanding of emulsification with polymeric emulsifiers such as proteins and synthetic polyelectrolytes it is necessary to investigate their physico-chemical properties at an interface between oil and water. In order to understand these interfacial phenomena at a disturbed interface, first the simpler system of an undisturbed interface has been considered. We wonder to what extent these interfacial tension measurements at an undisturbed interface are related to emulsion properties. The experiments at undisturbed interfaces imply interfacial tension measurements at the oil-water interface at which the polyelectrolyte adsorbs or has been adsorbed. Several parameters have been investigated, such as time of adsorption, polyelectrolyte concentration, charge density of the polyelectrolyte chain, ionic strength of the solution, nature of the counterion and effect of spreading the polyelectrolyte compared with adsorption from solution. Extensive attention has been paid to the effect of the chemical constitution and to the conformational transition of the polyelectrolytes in solution. Also changes of conditions after adsorption have been performed. Since polymer adsorption is normally irreversible upon dilution the properties of the adsorbed layer depend on its history and one can get additional information by changing the conditions after adsorption. For polyelectrolytes not only concentration variations, but also pH changes and ionic strength variations are possible. JAFFÉ and RUYSSCHAERT (1964) used this idea to obtain information about the reversibility of polyelectrolyte adsorption at a L/L interface. As the dynamic interfacial properties of the polyelectrolytes are probably reflected in the properties of the emulsions stabilized by polyelectrolytes the dynamic technique as developed by LUCASSEN (1968) has been used, although at the air-water interface.

The properties of the emulsions, which have been investigated concern the dispersity and the rheology of the emulsions and the adsorption of the polyelectrolytes at the emulsified interface. As the stability to coalescence after finishing emulsification is very high for these emulsions we concerned our attention to the emulsifying capacity of the polyelectrolytes as a function of the parameters mentioned before. With the information obtained by these experiments it has been tried to gain more insight into the mechanism of emulsification and to explain the rheological behaviour of the emulsions.

Polyacrylic acid, polymethacrylic acid and the copolymers of the monomeric acids with their methyl esters have been chosen as the polyelectrolytes. These are weak polyelectrolytes. As in the study of the properties of polyelectrolytes

the charge of the macromolecule is an important parameter, it is obvious to choose model substances for which the charge is controlled by the pH. Moreover, polymethacrylic acid and its copolymer of the methyl ester show a conformational transition in bulk as a function of the charge density of the chain (MANDEL and STADHOUDER, 1964). To some extent these synthetic polyelectrolytes may serve as a model for the more practically applied systems with proteins at the L/L interface, although they lack the ampholytic character. Especially the differences in the chemical constitution of the polyelectrolytes and the conformational transition are valuable contributions in terms of this model.

2. CHARACTERIZATION OF MATERIALS

2.1. PARAFFIN

In our model system paraffin was selected as the oil phase. It is virtually insoluble in water. For the interfacial tension measurements (chapter 3 and 4) we used liquid paraffin, laboratory grade ex J. T. BAKER chemicals Co, Deventer, Netherlands. For emulsion experiments (chapter 5 and 6) we always used liquid paraffin ex MERCK A.G., Darmstadt, DBR., with a density of 880 kg m^{-3}. The viscosity of both paraffins was about 0.08 N s m^{-2}.

The interfacial tension, measured against distilled water was 51.0 ± 0.8 mN m^{-1} for the different samples. The paraffin was used for experiments only if the interfacial tension did not decrease by more than 1.5 mN m^{-1} in 24 hours.

2.2. POLYELECTROLYTES

We decided to study the following model substances of which the structural formulae are collected in fig. 2.1.:
1. the copolymer of methacrylic acid and the methyl ester of methacrylic acid (PMA-pe).

This copolymer is commercially available. We used Rohagit S, low viscosity grade ex RöHM A.G., Darmstadt, DBR. The number ratio between the monomeric substances of these polymers is always about 2. By titration and elementary analysis we have checked the composition and found 67% acid groups confirming the above ratio.
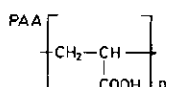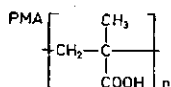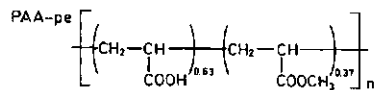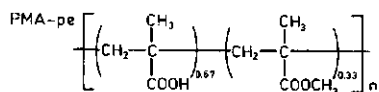
FIG. 2.1. Structural formulae of the polyelectrolytes used in this study. For abbreviations see section 2.2.

2. the copolymer of acrylic acid and the methyl ester of acrylic acid (PAA-pe). The fraction of acid groups is 0.63. For further details we refer to section 2.2.1.
3. polymethacrylic acid (PMA).
4. polyacrylic acid (PAA).

The polyelectrolytes mentioned under 2 till 4 have been prepared by us. Henceforth we shall use the given abbreviations for these polyelectrolytes.

Most of the experiments have been carried out with PMA-pe. A great advantage of this polyelectrolyte with respect to the more hydrophilic PMA and PAA is its pronounced surface or interfacial activity, even when it is completely charged. SCHWARZ (1962) has summarized the emulsifying capacities of several hydrophilic colloids and he concluded that predominantly hydrophilic polyelectrolytes are inadequate emulsifiers.

PMA, PAA and PAA-pe have been mainly used for the sake of comparison, notably to investigate the influence of the ester and methyl groups on the interfacial properties.

2.2.1. *Synthesis and properties*
1. PMA-pe

This commercial polyelectrolyte has been prepared by a perl polymerization of the two monomer components as described by DBP 947115 (1956). About two thirds of the methyl methacrylate monomer was saponified with NaOH. After saponification H_2SO_4 was added to make the monomer insoluble. After addition of the initiator (dibenzoylperoxide) the mixture of the thus obtained methacrylic acid and the unmodified methyl methacrylate is polymerized for 2 hours at 74 °C. The product is purified by washing with water. By changing the amount of NaOH per unit monomer, the ratio of both monomers in this polymer can be varied.

A detailed description of this polymer has been given by VÖLKER (1961a, 1961b). For commercial use the monomer ratio of 2 is very advantageous, because in this special case the polyelectrolyte is also soluble as Ca^{2+} salt, whereas a lower or higher ratio makes the polyelectrolyte very sensitive to Ca^{2+} ions (DBP 950182, 1956). The degree of polymerization of Rohagit S, low viscosity grade, is about 1000 (RÖHM A.G., 1972). We tried to check this value by means of viscosity measurements (see section 2.4.). PMA-pe does not dissolve in water but only in alkaline solutions. In order to prepare PMA-pe solutions the following procedure has been adopted: to a weighed amount of PMA-pe the alkaline solution is slowly added under constant stirring. Especially the first part of this solution must be added very slowly. This dissolution procedure can be accelerated by heating to about 70 °C. To avoid degradation of the polyelectrolyte this process should be carried out in the dark (VÖLKER, 1961a). After complete neutralization ($\alpha=1$) has been reached it is possible to decrease the degree of neutralization by adding HCl without precipitation. Thus it is even possible to obtain a PMA-pe solution of $\alpha=0$. However, if the same dissolution procedure has been followed at higher ionic strength the limiting value

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of α is not so low. For example in 0.2 M NaCl the lowest attainable value of α is about 0.08. The procedure described is applicable to a Na^+PMA-pe solution. In order to prepare a $Ca^{2+}PMA$-pe solution a different procedure has to be followed. Weighed amounts of dry PMA-pe and dry $Ca(OH)_2$ are mixed and the solution must be prepared by slowly adding water and stirring. Again α can be reduced to about 0.10 by addition of HCl after completion of this process.

The preparation of PMA-pe of different degrees of esterification has also been tried both by esterification of PMA (MANDEL and STADHOUDER, 1964) and by saponification of the complete ester of PMA (polymethyl methacrylate, PMMA). This saponification is very difficult to carry out and depends on the stereo-regularity of the starting material (SELEGNY and SEGAIN, 1971). The rate of saponification decreases from isotactic to syndiotactic PMMA. BEVINGTON and EBDON (1972) suggested that saponification is only possible for the middle monomer of an isotactic triade. Complete saponification was never attained. We also tried to saponify our PMA-pe, because it would be interesting to incorporate the effect of the degree of saponification in the interfacial experiments. In acetone/water (1/1 volume) with a fivefold amount of NaOH we could not detect any saponification, when the solution was kept at 40°C for two days. More rigorous conditions are not allowed, because of degradation of the polymer.

We have no specifications about the PMA-pe other than the information provided by the manufacturer. A random distribution of the monomers has been supposed. MARKERT and PENNEWISS (1970) paid attention to this subject, although their ways of copolymerization differ markedly from that of RÖHM. They found that the propagation parameters for the copolymerization of methacrylic acid and methyl methacrylate do not differ much from each other, so that no significant preference for the addition of certain radical components is to be expected.

2. PAA-pe

In contrast with the ester of PMA, this ester can be saponified very easily. There is no steric hindrance in this polymer. PAA-pe has been prepared by us by polymerization of the methyl ester of acrylic acid follwed by a partial saponification. KAWABE and YANAGITA (1969, 1971) have studied the kinetics of this saponification. The experimental details of the two steps are:

1. *Polymerization of methyl acrylate.*

Methyl acrylate (ex BDH) was distilled to remove the inhibitor. 150 ml (about 140 g) of the freshly distilled product was added to 1100 ml benzene analytical grade (ex MERCK) and 0.225 g α, α'-azobisisobutyronitrile ($M=164$) was also added. The solution was polymerized at 60°C in N_2 atmosphere for 18 hours. After polymerization the polymer was precipitated by adding an excess of methanol and purified by repeated precipitation from its acetone solution by an excess of methanol. The polymer obtained was dried in a vacuumoven at 40°C. The yield was 55%. The purity was estimated by complete saponification and titration with NaOH. The result was 83% purity. The remaining 17% is prob-

ably acetone, it is not likely that any monomer is left because the polymer has been intensively washed out with methanol. By vacuum drying a certain amount of solvent remains included.

2. *Saponification of the ester.*

To a solution of the ester in a water-acetone mixture (2:5 by volume) so much NaOH was added that upon complete saponification 37% of the ester group would remain. After saponification the final polyelectrolyte was precipitated by HCl, vigorously washed with distilled water to remove acetone and HCl, and finally freezedried. Titration of the freezedried product confirmed that the degree of esterification was indeed $37 \pm 1\%$ and that the purity of the product was 85%, the rest probably being water.

The molecular weight of the ester was estimated viscosimetrically and found to be $1.15 \cdot 10^5$ (see section 2.4.).

3. PAA and PMA

These polyelectrolytes have been prepared by solution polymerization in water. H_2O_2 was used as the initiator. 150 ml acrylic acid (ex BDH), freshly distilled under reduced pressure to remove the inhibitor and 120 g 30% H_2O_2 are added to 900 ml water. The mixture was polymerized for 6 hours at 80°C in N_2 atmosphere under constant stirring. Afterwards the polymerisate was dialyzed against water for 6 days to remove low-molecular weight substances (monomer and initiator). After evaporation till a small but viscous volume was left the polymer solution was freezedried. The purity of this product is 76.4%

PMA was prepared in an analogous way: 45 g methacrylic acid (ex FLUKA A.G.) freshly distilled under reduced pressure and 170 g 30% H_2O_2 were added to 350 ml water, after which the same procedure was applied. The achieved purity was 79.4%.

The relatively low purity of these polymers does not mean that they are

TABLE 2.1. Survey of the polyelectrolytes, used in this study with some properties. See also fig. 2.1.

poly-electrolytes	% acid groups	$\overline{M}_\eta$	determination[1]	parameters MARK-HOUWINK equation
PMA-pe	67.6	$\sim 10^5$	information manufacturer	–
PAA-pe	63.0	$1.15 \cdot 10^5$	acetone, 25° C [2]	$k = 1.98 \cdot 10^{-4}$ $a = 0.66$
PAA	100	$5.0 \cdot 10^5$	10^{-2} M HCl, 30° C	$k = 6.9 \cdot 10^{-4}$ $a = 0.50$
PMA	100	$0.51 \cdot 10^5$	$2 \cdot 10^{-3}$ M HCl, 30°C	$k = 6.6 \cdot 10^{-4}$ $a = 0.50$

notes: 1. see section 2.2.3.
2. estimated for polymethyl acrylate, assuming no degradation upon saponification.

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unsuitable for interfacial activity measurements. The impurity is probably just entrapped solvent, i.e. in this case water. SELIER (1965) found analogous results for the purity of his polyelectrolytes.

The molecular weights of both polymers were estimated viscosimetrically and found to be $5.0 \cdot 10^5$ for PAA and $0.51 \cdot 10^5$ for PMA, i.e. they differed by a factor of 10. Table 2.1. summarizes some data on these polyelectrolytes.

The polyelectrolytes are insoluble in paraffin. Aqueous solutions of 1000 ppm PMA-pe of $\alpha=0$ and $\alpha=1.0$ have been mixed with paraffin. Afterwards we measured the interfacial tension of this paraffin against distilled water. During the first 24 hours no significant decrease of interfacial tension was observed.

2.3. THE CONFORMATIONAL TRANSITION OF POLYMETHACRYLIC ACIDS AS STUDIED BY POTENTIOMETRIC TITRATIONS

2.3.1. *Introduction*

One of the main objects of our investigation is the influence on the polyelectrolyte adsorption of the degree of ionization of the polyelectrolyte and the ionic strength of the solution. In view of these parameters we have to pay attention to the conformational properties of the polyelectrolyte in solution. Potentiometric titration, as well as viscosimetry (see section 2.4.) are excellent methods to obtain this information. For proteins e.g. by the titration method the transformation from helix to random coil structure as a function of pH can be detected (HAMORI and SCHERAGA, 1967; NAGASAWA, 1970). LEYTE and MANDEL (1964) and MANDEL et al. (1967) reported on these potentiometric titrations for synthetic polyelectrolytes. Usually titration curves of synthetic polyelectrolytes do not indicate any conformational transition. However, PMA and its derivatives such as PMA-pe are characterized by a clear change in conformation at $0.1 < \alpha < 0.3$. This conformational transition makes these weak polyelectrolytes interesting model substances for proteins, even if the ampholytic character is absent. It also induced us to look for possible conformational transitions in the adsorbed state.

Following LEYTE and MANDEL we designated the two conformations as the a- and b-form. At low values of α the a-form predominates. Then, with increasing α, follows a transition region after which the polyelectrolyte is in the b-form. At all values of α there is a thermodynamic equilibrium between the two forms. The a-form is a compact, hypercoiled conformation, whereas the b-form is more extended. MANDEL and STADHOUDER (1964) mentioned its presence for PMA and PMA-pe, whereas the transition has not been observed with PAA or its derivatives. They only exist in the b-conformation. DUBIN and STRAUSS (1970) observed a similar transition for copolymers of maleic acid and alkyl vinyl ethers. The influence of the stereo-regularity on the transition has been shown by NAGASAWA (1970) and by LEYTE et al. (1972).

It is worth mentioning that this transition has been confirmed by other techniques, e.g. by calorimetry (CRESCENZI et al., 1972), viscosimetry (ARNOLD and

OVERBEEK, 1950; KATCHALSKY, 1951; SILBERBERG and MIJNLIEFF, 1970) and spectrophotometry (MANDEL et al., 1967).

For the physical interpretation of this transformation we refer to the discussion (section 2.3.4.) and to chapter 6.

2.3.2. *Theory*

The titration behaviour of a weak polyelectrolyte deviates from that of a weak electrolyte. The dissociation equilibrium of a carboxylic acid in aqueous solution can be written as:

$$-COOH \rightleftharpoons -COO^- + H^+ \qquad (2.1.)$$

with $\quad K_0 = [-COO^-] [H^+]/[-COOH] \qquad (2.2.)$

The brackets indicate activities. Equation 2.2. can be written as:

$$pH = pK_0 - \log[(1-\alpha')/\alpha'] \qquad (2.3.)$$

with $\quad pK_0 = -\log K_0 = 0.434 \, \Delta G^\circ/RT \qquad (2.4.)$
$\quad \alpha' \quad$ = degree of ionization (the prime is used to distinguish this quantity from the degree of neutralization).

where ΔG° is the standard free energy change of the dissociation process. In this derivation activity effects are neglected.

For an already charged polyelectrolyte, however, the dissociation of a carboxylic group depends on the additional work to remove a H^+ ion against the electrostatic forces arising from the presence of charged groups in the same molecule. It is customary to define an apparent ionization constant K:

$$pK = pH + \log[(1-\alpha')/\alpha'] = 0.434 (\Delta G^\circ + \delta G_{el}/\delta\alpha')/RT \qquad (2.5.)$$

where $\delta G_{el}/\delta\alpha'$ is the additional electrostatic free energy change per group. Again in eq. (2.5.) activity effects, other than the electrostatic ones, are neglected. Eq. (2.5.) indicates that this apparent K is a function of the degree of ionization. By combining equations 2.4. and 2.5. we find:

$$pH = pK_0 - \log[(1-\alpha')/\alpha'] + 0.434 (\delta G_{el}/\delta\alpha')/RT \qquad (2.6.)$$

This description of polyelectrolyte behaviour is based on a model, whereas e.g. FISCHER and KUNIN (1956) observed that the titration behaviour of many polyelectrolytes conforms to the empirical HENDERSON-HASSELBALCH (H-H) equation over a wide range of α' values. In formula:

$$pH = pK_{av} - n \log[(1-\alpha')/\alpha'] \qquad (2.7.)$$

in which pK_{av} and n are constants at a constant polyelectrolyte concentration and ionic strength.

Equations 2.5. and 2.7. are very suitable for analysing the potentiometric titration data of polyelectrolytes. One can obtain pK_0 from a plot of pK versus α' by extrapolation to $\alpha' = 0$. Moreover, G_{el} of a polyelectrolyte having a degree of ionization α' can be calculated from the area under the graph of a plot of

$pK - pK_0$ versus α'. In a plot of pH as a function of $\log[(1-\alpha')/\alpha']$ — a so-called H—H plot — deviations from linearity, e.g. an inflection point, indicate conformational transitions in the polyelectrolyte.

2.3.3. *Experimental*

The potentiometric titrations have been carried out with an Electrofact combined electrode 7GR221. Titrant was added from a buret into the titration vessel, containing 50 ml of polymer solution. All titrations were performed under nitrogen at room temperature (22 °C). One single titration took 5 hours. We used only NaOH as titrant, the molarity of which was adapted to the concentration of polymer to preclude differences in polymer concentration between different titrations. The difference between α' and α is only significant at low pH and rather low polymer concentration.

2.3.4. *Results and discussion*

Results are presented in fig. 2.2. as H—H plots. They demonstrate the differences between the polyelectrolytes and the effect of ionic strength. In agreement with cited literature we observe the conformational transition only for PMA and PMA-pe. It can be inferred from eq. (2.6.), that the higher the pH, at a
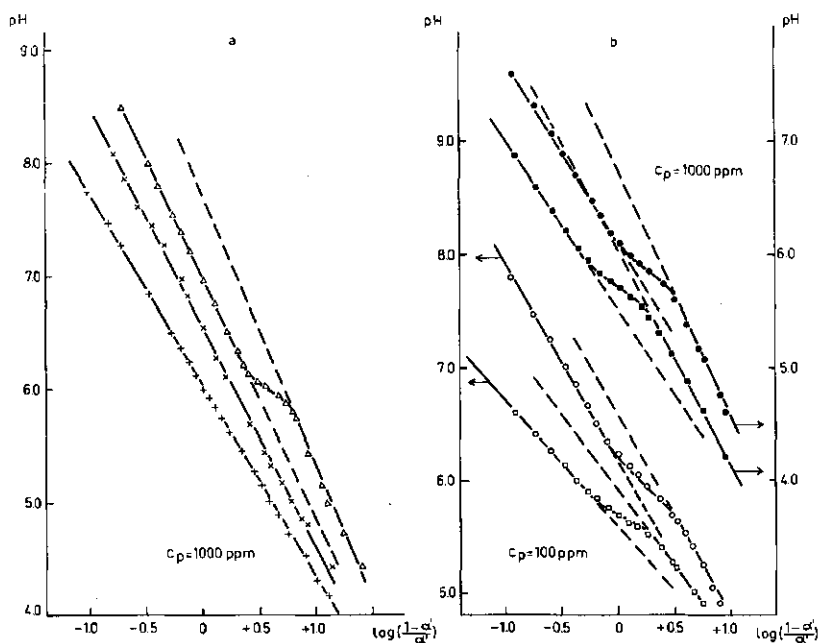

FIG. 2.2. HENDERSON-HASSELBALCH plots.
a. PAA-pe, 0.01 M NaCl (+); PAA, without NaCl (×); PMA, without NaCl (△).
b. PMA-pe, 0.02 M NaCl (○, ●); PMA-pe, 0.20 M NaCl (□, ■). Note shift of 2 pH units at $c_p = 1000$ ppm PMA-pe.

given value of $\log[(1-\alpha')/\alpha']$, the higher the additional electric work required to remove a H^+ ion from the chain to infinity $\delta G_{el}/\delta\alpha'$. From fig. 2.2. and eq. (2.6.) it can be concluded that $\delta G_{el}/\delta\alpha'$ increases with decreasing ionic strength. One would expect this trend. Moreover, $\delta G_{el}/\delta\alpha'$ is higher for PMA than for PAA. This indicates the effect of steric hindrance being higher for PMA than for PAA. A comparison between PAA and PAA-pe (or PMA and PMA-pe) is more complicated, because of the differences in ionic strength. For PMA-pe no significant influence of the polyelectrolyte concentration is observed. Extrapolation of the linear parts of the curves for PMA and PMA-pe allows us to make a comparison between the a- and b-conformation in the transition region. $\delta G_{el}/\delta\alpha'$ is considerably higher for the compact hypercoiled a-conformation than for the more extended b-conformation. From the slope of the curves it can be concluded that differences in $\delta G_{el}/\delta\alpha'$ are less pronounced at lower degree of ionization. It should be borne in mind that these comparisons are only possible if the pK_0 values are the same for all conditions (see equation 2.6.).

The H−H plots allow also the calculation of the fractional replacement of the a-form by the b-form as a function of pH in the transition region. Following LEYTE and MANDEL (1964) we assume that in the transition region the following linear combination may be written:

$$\alpha' = (1-v)\alpha'_a + v\alpha'_b \qquad (2.8.)$$

in which $v\ \ = c_b/c_p$

$\qquad c_b\ \ =$ polyelectrolyte concentration in b-conformation

$\qquad c_p\ \ =$ total polyelectrolyte concentration

$\qquad \alpha'_a =$ degree of ionization in the a-conformation

$\qquad \alpha'_b =$ degree of ionization in the b-conformation

Since α'_a and α'_b can be found as a function of pH from the lower and upper linear parts of the plots we can find v as a function of α'. Fig. 2.3. summarizes the results of these calculations for different experimental conditions. From these plots – and also already from the previous plots – we can conclude, that:

1. there is no significant influence of c_p on the transition region for both ionic strengths.

2. there is a shift in the transition region with ionic strength. This can be explained as follows: the transition of a- to b-conformation is promoted by increasing α', i.e. expansion of the coil by charging. At a given α' the expansion is less pronounced at higher ionic strength and hence the b-conformation can persist till higher α' values. In respect of the effect of ionic strength different authors have not arrived at the same conclusion. MANDEL and STADHOUDER (1964) found no salt effect on the location of the transition in $NaNO_3$ (up to 10^{-2} M). On the other hand, CRESCENZI et al. (1972) found a broadening and upward shift of the transition region with increasing concentration of NaCl (up to 0.5 M). This difference can be due to the different concentration regions used. The region studied by us (NaCl, up to 0.2 M) corresponds relatively better with that investigated by CRESCENZI et al. and so does our experimental found shift.
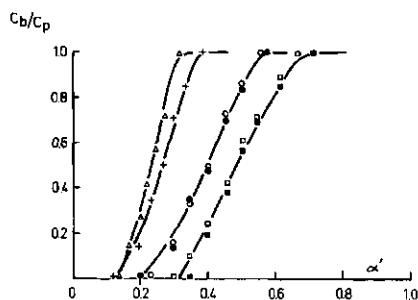
FIG. 2.3. Conformational transition in solution (a ⇄ b).
PMA-pe, 0.02 M NaCl, c_p = 100 ppm (○) and 1000 ppm (●).
PMA-pe, 0.20 M NaCl, c_p = 100 ppm (□) and 1000 ppm (■).
PMA, without NaCl, c_p = 1000 ppm (△).
PMA-pe, 0.02 M NaCl, if α' is based upon the total number of segments (+).

3. for PMA the transition takes place at a lower region of α' than for PMA-pe.

However, if α' is not based upon the total number of carboxylic groups as done, but on the total number of segments (carboxylic and ester groups) the shift is smaller and may be attributed completely to the difference in the ionic strength. MANDEL and STADHOUDER (1964) found even a complete merging of v as a function of α' for PMA's of different degrees of esterification at constant ionic strength, if α' was related to the total number of segments. It means that the occurrence of the a-conformation is not specifically due to the carboxylic groups, but to the methyl groups of PMA in the main chain.

About the origin of the existence of the compact state of PMA and PMA-pe at low degree of ionization, there is no complete agreement. It is certain that the methyl group in the main chain is a prerequesite but not the ester group or acid group. Intramolecular hydrogen bonding between COOH groups is excluded as a major factor because partial esterification of PMA does not influence the charge density at which the transition takes place. Two other possible factors are hydrophobic bonding and nearest-neighbour VAN DER WAALS forces of attraction between the $-CH_3$ groups of the main chain. From potentiometric and spectrophotometric results MANDEL et al. (1967) concluded, that the stabilization of the compact state is not primarily due to hydrophobic bonding, because in a water-methanol mixture with 40 % volume fraction of methanol the transition is still present. Our viscosimetric experiments of emulsions stabilized by PMA-pe in water-methanol mixtures as the continuous phase are in contradiction with this conclusion (see chapter 6). These emulsion experiments suggest the occurrence of hydrophobic bonding as the major factor.

2.4. CHARACTERIZATION OF PMA-PE BY VISCOSIMETRY

2.4.1. *Theory*

The viscosity-averaged molecular weight $\overline{M}_\eta$ is related to the intrinsic viscosity $[\eta]$ by the MARK-HOUWINK relation:

$$[\eta] = k \cdot \bar{M}_\eta{}^a \tag{2.9.}$$

in which k and a are constants. With the aid of this relation we estimated the molecular weight of our PAA, PMA and PAA-pe (see section 2.2.1.). The values of k and a for PAA, PMA and polymethyl acrylate are obtained from BRANDRUP and IMMERGUT (1965). For PMA-pe no values for these parameters are known. Hence, we tried to check the molecular weight, as given by the manufacturer, in a quite different way (FLORY and OSTERHELD, 1954).

The intrinsic viscosity in an arbitrary solvent is related to the intrinsic viscosity in a Θ-solvent through the expansion factor α_η:

$$\alpha_\eta{}^3 = [\eta]/[\eta]_\Theta \tag{2.10.}$$

where the subscript Θ refers to the Θ-condition. FLORY and OSTERHELD (1954) were able to check the molecular weights of their PAA samples by plotting $\alpha_\eta{}^5 - \alpha_\eta{}^3$ as a function of the reciprocal value of the ionic strength at different degree of ionization. In order to assess α_η, $[\eta]_\Theta$ has to be known as a function of the degree of ionization. To obtain $[\eta]_\Theta$ we followed FLORY and OSTERHELD, who stated that the unperturbed dimensions are unaffected by the degree of ionization and can be obtained simply by increasing the ionic strength at any degree of ionization. The same procedure has been followed by GREENE (1971). However, it should be mentioned that the theory of FLORY and OSTERHELD is open to doubt, since in this way they found their molecular weights too low by a factor of 2 till 3. The method of NODA et al. (1970) gives better results for polyelectrolytes, but is not applicable in our case, as more properties of the PMA-pe have to be known.

2.4.2. *Experimental*

The viscosity measurements were carried out in Ubbelohde-type viscometers, which were mounted in a water bath, thermostatted at $20.0 \pm 0.02\,^\circ\text{C}$. The elution times for water at this temperature were about 360.0 ± 0.2 sec. and sufficiently long to neglect kinetic energy corrections. The $[\eta]$ value was obtained by extrapolation of the viscosity ratio excess η_{sp}/c_p to infinite dilution. $[\eta]$ has been estimated for the following α values: 0.10, 0.30, 0.50, 0.70, 0.75, 0.90 and 1.0 at ionic strengths till 0.8 M NaCl. Dilution was done with a solution of fixed NaCl molarity. In some experiments it was checked that an isoionic dilution produces the same $[\eta]$ within the experimental error of 10%.

2.4.3. *Results and discussion*

In fig. 2.4. $[\eta]$ values for the various experimental conditions are collected. These experiments have been performed only for PMA-pe. In the region of $\alpha \leqslant 0.70$ the curves are sigmoid shaped. The low values of $[\eta]$ at low degree of neutralization agree with the existence of a compact conformation, as deduced from titration. For PAA and PMA, NODA et al. (1970) confirm the difference in viscosimetric behaviour at low α values. They found the same sigmoid shape for PMA, whereas for PAA the rise in $[\eta]$ in the region of low α is much more

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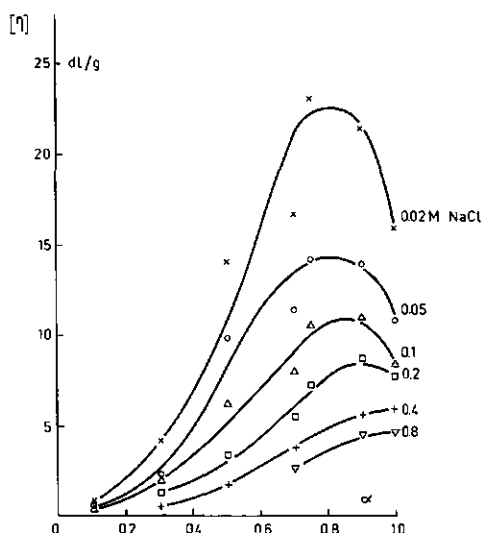
FIG. 2.4. Intrinsic viscosity of PMA-pe at different ionic strengths of NaCl.

pronounced. OHNO et al. (1973) find for a copolymer of maleic acid and styrene the similar sigmoid shape for $[\eta]$ as a function of α and moreover, as expected, the occurrence of an a-conformation for this polymer was also found by potentiometric titrations.

At high values of α (> 0.75) a decrease of $[\eta]$ has been observed, especially at low ionic strength. This phenomenon at $\alpha > 0.75$ is rather difficult to explain. One would expect $[\eta]$ to tend to a limiting value with increasing α. In the literature similar results have been found for other polyelectrolytes with hydrophobic groups (SHAREV et al., 1970; DUBIN and STRAUSS, 1970). SHAREV et al. noted that the maximum in $[\eta]$ as a function of α coincided with a maximum in emulsion stability as a function of α. DUBIN and STRAUSS found a significant maximum in $[\eta]$ for a copolymer of maleic acid and alkyl vinyl ether. All these examples indicate that the occurrence of the two different conformations is a well established fact. As it is unlikely to assume a reduction in coil size upon further charging of the polyelectrolyte molecules, it seems more likely that the observed reduction of $[\eta]$ is under these conditions no longer a simple measure for the coil dimensions.

With the theory of FLORY and OSTERHELD (1954) $\overline{M}_n$ for PMA-pe, at various values of α, was calculated at about 40.000 i.e. a factor of 2.5 lower than the value given by the manufacturer. This factor is of the same order as the correction factor found by FLORY and OSTERHELD. Therefore we assumed $\overline{M}_n = 10^5$.

The chain dimensions of polymer molecules can be deduced from viscosity measurements. The relevant relations (FLORY, 1953, chapter 14) are only valid for randomly coiled polymers. If one assumes their validity also for linear polyelectrolytes (e.g. NODA et al., 1970), we are able to calculate the radius of

gyration R_G for PMA-pe as a function of the degree of neutralization. At $\alpha = 0.1$ R_G was found to be about 12 nm; at $\alpha = 1.0$ it amounts to about 38 nm at 0.02 M NaCl and to about 28 nm at 0.20 M NaCl.

2.5. SUMMARY

Conformational properties of the polyelectrolytes have been studied by means of potentiometric titrations and viscosimetry. These properties have to be known since it is reasonable to assume a correlation between solution properties and the behaviour upon adsorption out of these solutions. Important variables are ionic strength and degree of neutralization.

For PMA and PMA-pe a compact, hypercoiled conformation has been found at low α values ($\alpha \leqslant 0.3$), passing into a more open conformation upon increasing α. For PAA and PAA-pe no such transformation is found. These polyelectrolytes are only present in the open conformation. These findings are in general agreement with the literature. For PMA-pe the conformational transition is also affirmed by viscosimetry.

3. INTERFACIAL TENSION AND ADSORPTION
AT THE INTERFACE BETWEEN PARAFFIN OIL
AND POLYELECTROLYTE SOLUTION

3.1. INTRODUCTION

As already mentioned, polymer adsorption is normally an irreversible process. Desorption is only possible, if all adsorbed segments of one molecule would desorb simultaneously and this is statistically very unlikely. However, desorption is sometimes possible by changing the conditions after adsorption or if biopolymers have been used. Some biopolymers, for example, desorb on dilution (BULL, 1957; MACRITCHIE, 1972). Desorption of synthetic polymers by changing the solvent has been found by e.g. HOWARD and MCCONNELL (1967). The possibility of polyelectrolyte desorption upon charging up the adsorbed molecules has been demonstrated by e.g. PEYSER and ULLMANN (1965) and COLE and HOWARD (1972).

Another aspect of polymer adsorption is its time dependence. After adsorption of a molecule, exchange of segments occurs and the ensuing reconformation gives rise to a growing amount of polymer at the interface and to a higher occupation of the first layer.

Quantitative experiments at the L/S interface show that the following factors influence the adsorption:

1. *polymer concentration.* The amount of adsorbed polymer increases with increasing c_p, finally reaching a plateau value or sometimes a semi-plateau value. In general the fraction of segments of one molecule adsorbed in the first layer p is lower at higher c_p.

2. *solvent-polymer, solvent-adsorbent and polymer-adsorbent interactions.* Adsorption from a poor solvent (i.e. having low solvent-polymer interaction as compared to polymer-polymer interaction) generally means that the adsorbed amount is high and that there are relatively long loops. Adsorption from a good solvent results in a lower adsorbed amount with small loops and long trains. If long loops would be present the polymer chain would be desorbed by strong osmotic pressures (HOEVE, 1970, 1971).

3. *molecular weight of the polymer.* An increasing molecular weight results in a higher adsorbed amount, tending to a limiting value at high molecular weight. Adsorption on porous adsorbents shows the opposite effect (SCHMIDT and EIRICH, 1962).

The final situation of an adsorbed polymer can be expressed by the following parameters:

1. total amount of adsorbed polymer Γ, usually in mg m^{-2}
2. fraction of polymer segments of one molecule adsorbed in the first layer p.
3. occupation of the first layer by polymer segments θ.
4. the segment density as a function of the distance from the interface $\rho_p(x)$.

Of the three quantities Γ, p and θ only two are independent. Examples of attempts to determine two out of these three quantities are known in the literature. FONTANA and THOMAS (1961) used infrared adsorption analysis and KILLMANN and ECKHART (1971) used a calorimetric method to measure θ on silica surfaces. These and similar measurements do not allow an unambiguous conclusion concerning the relationship between Γ, p and θ and the three adsorption parameters mentioned above (c_p, M and solvent power).

A more quantitative description of the adsorption in terms of segment density as a function of the distance of the interface is only possible if information can be obtained about $\rho_p(x)$. FLEER et al. (1972) were able to estimate the viscosimetric thickness Δ from which $\rho_p(\Delta)$ was obtained after assuming a certain analogy with the statistics of free-random coils.

At undisturbed L/L interfaces Γ cannot be obtained by a depletion method, because the total interfacial area is too small. It would therefore be convenient if it would be possible to extract Γ from $\gamma(c_p)$ measurements, just as in the case of low-molecular weight substances. However, due to the irreversible nature of polymer adsorption this relation is ambiguous. Neither may GIBBS law be applied, although this has been done very often in the literature (ELEY and HEDGE, 1957; GLASS, 1968; FROMMER and MILLER, 1968).

Direct determination of the adsorbed amount is possible by a surface radioactivity technique (QUINN and DAWSON, 1970; ADAMS et al., 1971). The use of spread monolayers or emulsification of the interface are only of limited value for the understanding of the conformation of adsorbed polymer layers, because the conformation in spread monolayers as well as that in an emulsified (i.e. disturbed) interface differ much from that in an adsorbed layer.

The time dependence of the adsorption and interfacial tension limits the number of suitable methods of measurements of γ. As described by LANKVELD and LYKLEMA (1972) it is not allowed to obtain the static interfacial tension from dynamic methods i.e. methods in which the interface changes during the measurements and where equilibrium is not attained. If, contrary to better judgement, dynamic γ measurements are applied, results obtained by different authors differ, even when working with the same polymer at the same interface (GLASS, 1968; KUHLMAN et al., 1968, 1969).

In this study the effect of the molecular weight of the polyelectrolyte samples will not be investigated in detail. Of the several other interesting variables, special attention has been paid to the charge of the polyelectrolyte, the ionic strength, nature of the counterion and the chemical constitution of the different polyelectrolytes. LANKVELD and LYKLEMA (1972) found that the molecular weight of PVA, adsorbed at the paraffin oil – water interface, is a rather insensitive parameter and that the origin of the PVA samples is at least of comparable importance.

3.2. Time Dependence and Steady-State Value of the Interfacial Tension

The term 'steady state' of interfacial tension or interfacial pressure will be used to indicate that the final values are independent of time without implying that equilibrium has been attained.

3.2.1. Mechanism of adsorption

The rate of reduction of interfacial tension $d\gamma/dt$ is determined by three processes of which at least two are consecutive, viz. diffusion from the polymer solution to the interface, spreading of the arrived molecule and reconformation of the molecule (during which more segments adsorb over a given area). In special cases $d\gamma/dt$ reflects only one of these three factors. However, generally all three processes occur simultaneously and cannot be separated solely by $\gamma(t)$ measurements. At low c_p, supply by diffusion is slow and the adsorbed molecules can spread fully. Only if a just adsorbed molecule can reconform and spread to its full extent, before the next molecule arrives at the interface one can state that $d\gamma/dt$ is fully diffusion controlled. However, adsorption from a highly concentrated solution means that in a very short time the interface has been completely occupied, so that no spreading can occur. Reconformation remains possible and is in fact the rate-determining step.

In the case of polyelectrolyte adsorption it is interesting to consider the influence of the charge on these three steps. The charge of the polyelectrolytes leads to an additional contribution in the free energy gain upon adsorption, but on the other hand the hydrophilic nature of the polyelectrolyte molecule in the charged state will give rise to a lower interfacial activity of the polyelectrolyte (JAFFÉ and RUYSSCHAERT, 1964; KATCHALSKY, 1951). Moreover, the charge on the polyelectrolyte molecule affects the flexibility of the chain. As the rate of reconformation and spreading is related to the flexibility of the chain, $d\gamma/dt$ will depend on the charge density.

3.2.2. Measurements of interfacial tension

The interfacial tension between paraffin oil and the polyelectrolyte solution has been measured by the static Wilhelmy-plate method. A Prolabo tensiometer of Dognon-Abribat was used (HEERTJES et al., 1971). PADDAY (1957) described the operational principle of this apparatus. A small roughened platinum plate, which had been tempered and wetted with the aqueous phase, was passed through the paraffin layer down to the interface between the paraffin and the polyelectrolyte solution underneath it. Upon contact with the interface the plate is pulled into the aqueous solution as a result of the interfacial tension. The plate, which is suspended from an electromagnetic balance, is brought into balance by an extra force. After correction for the buoyancy, the interfacial tension can be calculated, when the length of the platinum plate is known. This length was measured to an accuracy of 0.005 cm and varied between 1.95 and 1.97 cm for the different plates. The reproducibility of the interfacial tension

measurements was within 0.4 mN m^{-1}. It is important that the plate is well wetted with the aqueous phase, which can be seen from its reflectivity.

3.2.3. *Procedure*

All glassware used for the interfacial tension measurements, was cleaned with chromic acid, dilute nitric acid and finally with distilled water.

Solutions of different concentrations between 1 and 1000 ppm were prepared by dilution of a stock solution. Stock solutions were never older than a week to avoid possible ageing effects. 100 ml of polyelectrolyte solution was brought into a 250 ml vessel, the pH was adjusted by injection of NaOH or HCl and controlled during the experiment. Paraffin was added as quickly as possible after rigorous sucking off the liquid – air interface. This operation is very important to obtain a clean interface and reproducible measurements. The wetted plate was put in the interface as described in section 3.2.2. The first measurement was made after exactly 1 minute, whereas the timing of further readings depended on the rate of lowering in interfacial tension. For the steady-state value $\gamma(\infty)$, the interfacial tension after 24 hours was taken. This is a safe measure since the final value is always attained more rapidly. The vessel was thermostatted during the experiments at $20.0 \pm 0.2°C$. Irreproducible results are obtained when the Wilhelmy plate was taken out of the interface during the experiments. Reintroducing the plate did then disturb the interface. LANKVELD and LYKLEMA (1972) did not find such an effect for the polyvinyl alcohol solutions at the same interface.

The time dependence for PMA-pe at pH = 4.0, 5.0, 6.0, 7.0 and 9.0 has been measured in solutions of 0.01 M, 0.20 M NaCl and 0.01 N CaCl$_2$. Steady-state values have also been measured for the other polyelectrolytes in 100 and 1000 ppm solutions, containing 0.01 M NaCl.

3.2.4. *Results and discussion of time dependence measurements for PMA-pe*

Data on the interfacial tension as a function of time after the formation of the interface are given in figs. 3.1.–3.3. In fig. 3.1. the time dependence is given as a function of polymer concentration at pH = 6.0 in 0.01 M NaCl. Results at other pH and ionic strengths are analogous. It is concluded that the drop in interfacial tension is faster as the polymer concentration is higher. The steepest drop in the tension takes place during the first few minutes. The rate of decay is minimal in the more dilute solutions. The initial drop at higher concentrations proceeds so fast that the first measurement (after exactly 1 minute) is not yet accurate. Similar trends have been found by KATCHALSKY and MILLER (1951) for PMA, by HAUSER and SWEARINGEN (1941) and JAMES and RAY (1972) for proteins at air – liquid and liquid – liquid interfaces.

Fig. 3.2. gives the interfacial tension as a function of time at different pH at c_p = 100 ppm and an ionic strength of 0.01 M NaCl. The curves of fig. 3.2. are a representative selection from a large number of similar graphs that have been measured but not reported here. The decay is faster at lower pH, i.e. at lower α value in bulk. Fig. 3.3. shows the time dependence as a function of

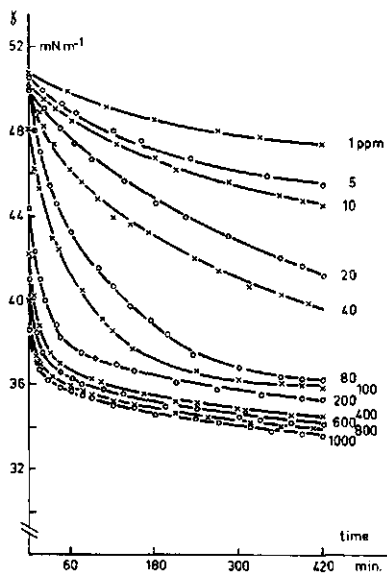FIG. 3.1. Time dependence of the interfacial tension of solutions of PMA-pe at different concentrations and at pH = 6.0 in 0.01 M NaCl.
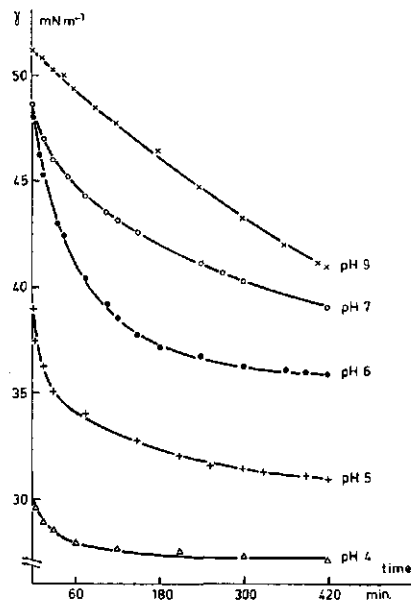

FIG. 3.2. Time dependence of the interfacial tension of solutions of PMA-pe of c_p = 100 ppm at different pH in 0.01 M NaCl.
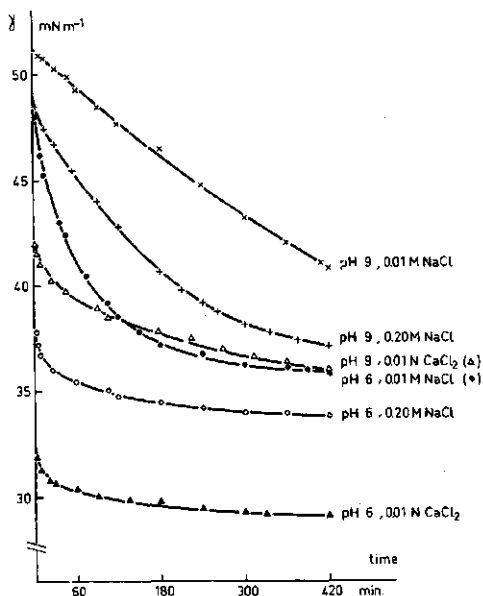

FIG. 3.3. Time dependence of the interfacial tension of solutions of PMA-pe of c_p = 100 ppm at pH = 9 and pH = 6 in 0.01, 0.20 M NaCl and in 0.01 N CaCl₂.

ionic strength and the nature of the counterion (Na^+, Ca^{2+}) at pH = 6 and 9.

From figs. 3.2. and 3.3. in combination with the viscosimetric results presented in section 2.4., it is concluded that the time dependence is related to the molecular dimensions in bulk: the more compact the molecule, the faster the stationary state is attained. These results agree with other observations. For proteins it has been found that $d\gamma/dt$ is higher at the isoelectric point than at lower or higher pH (CUMPER and ALEXANDER, 1951; JAMES and RAY, 1972). Similar effects for proteins at the air – water and paraffin – water interfaces have been found by GHOSH and BULL (1963) and ISHII and MURAMATSU (1970). Hence it is concluded that the adsorption behaviour of PMA-pe at the paraffin – water interface fits into a general experience scheme. At given supply of polyelectrolyte these results imply that for a compact molecule (low pH, high ionic strength and Ca^{2+} counterions) diffusion to the interface is relatively fast and that the influence on $\gamma(t)$ of spreading and reconformation is of a smaller extent. However, if the polyelectrolyte molecule is charged, the coil is expanded and the flexibility of the chain is reduced. At that condition the supply by diffusion is much smaller and $\gamma(t)$ becomes reconformation controlled. Due to the stiffness of the polymer chain $d\gamma/dt$ is now a slow process.

Finally a remark has to be made in relation to the conformational transition of PMA-pe in solution. At low pH the coils of PMA-pe molecules in bulk are compact, at higher pH they are expanded. In the very first moments of the adsorption process, it is diffusion controlled. At low pH diffusion will lead to a rapid accumulation of segments at the interface, which is reflected in the sharp initial drop of γ. It is likely that then the molecule adsorbs pretty much in the same conformation as it has in bulk, i.e. with both CH_2, COOH and $COOCH_3$ groups in the interface. At high pH the molecule is expanded and diffuses slowly. The supply of segments by diffusion is small in the first part of the curve, in agreement with the small decrease of γ. However, upon long standing γ continues to decrease, apparently mainly through reconformation, leading to longer and more strongly bound trains. Our experiments do not allow us to locate a specific transition region between the two conformations. However, an analogy to this transition can be extracted from another set of experiments to be reported in chapter 4.

3.2.5. *Results and discussion of steady-state measurements*

The steady-state interfacial tension values are obtained from the time dependence experiments. After 24 hours – often already before this time – no change in $\gamma(t)$ was observed any more, so that $\gamma(\infty)$ equals $\gamma(24$ hours). The results are summarized in figs. 3.4.–3.9. In figs. 3.4. and 3.5. $\gamma(\infty)$ is shown as a function of polymer concentration. In these figures the measuring points have been omitted for the sake of clearness. From these figures it can be concluded, that:

1. $\gamma(\infty)$ decreases with increasing c_p.
2. increasing the ionic strength results in a decrease of $\gamma(\infty)$, except at pH = 9.

It is noted that even at pH = 4, where the polyelectrolyte is almost un-
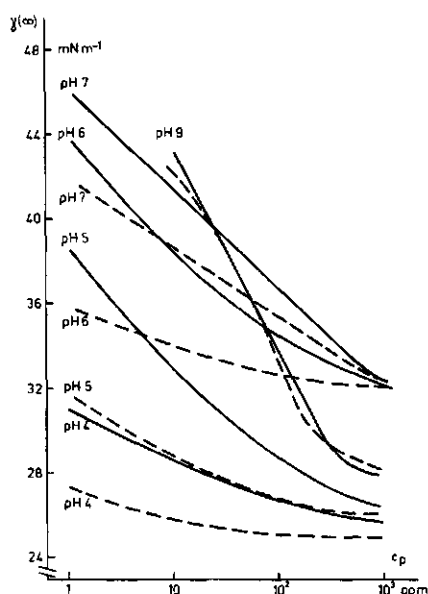
FIG. 3.4. The steady-state value of the interfacial tension of solutions of PMA-pe at different pH in 0.01 M NaCl (—) and in 0.20 M NaCl (– – –).
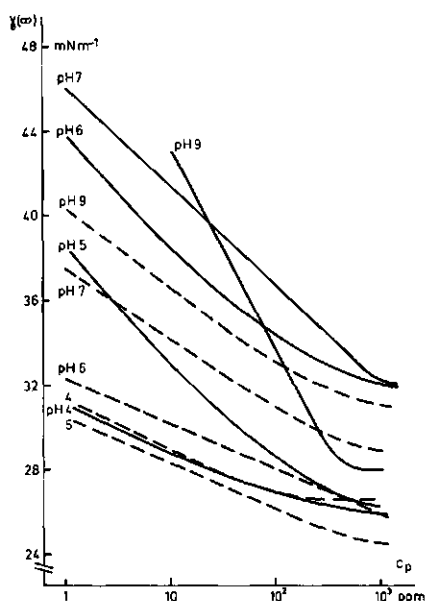
FIG. 3.5. The steady-state value of the interfacial tension of solutions of PMA-pe at different pH in 0.01 M NaCl (—) and in 0.01 N CaCl₂ (– – –).

charged, a marked effect of ionic strength has still been found. At pH = 9 the coil dimensions in bulk depend strongly on ionic strength. This is reflected in the *rate* of decrease (fig. 3.3.) but not in the stationary value. It means that $\gamma(\infty)$ is not simply correlated with the molecular dimensions in the bulk phase. Similar results have been found previously by MILLER and KATCHALSKY (1957). They reported on work with copolymers of 2-vinyl pyridine and methacrylic acid. At a positive net charge of this molecule, i.e. at low pH, the ionic strength hardly affected $\gamma(\infty)$, whereas at a negative net charge the ionic strength had an important effect. As will be shown later, there are more similarities between PMA-pe and the copolymer of 2-vinyl pyridine and methacrylic acid. The ester segments of PMA-pe show similarity with the vinyl pyridine segments in their adsorption behaviour. All this indicates that the mode of adsorption at low pH is different from that at high pH, a conclusion at which we also arrived in the preceding section.

3. in the presence of Ca²⁺ ions the interfacial activity is generally higher than with Na⁺ ions. At pH = 4 there is no difference between $\gamma(\infty)$ in the presence of Ca²⁺ and Na⁺ ions, indicating that for almost uncharged polymers the nature of the counterion is not important. The adsorption behaviour at high pH is very complicated. Ionic strength had only little or no effect (compare figs. 3.6. and 3.7.), whereas the valency of the counterion exerts a considerable influence

(compare figs. 3.6. and 3.9.). This is probably related to the strong bonding of divalent counterions with polyelectrolytes (LEYTE et al., 1968). At pH = 9 Ca^{2+} counterions cause a higher interfacial activity at c_p < 100 ppm, whereas at higher c_p, Na^+ ions cause a higher interfacial activity.

4. for pH ⩽ 7 there is a direct relationship between the rate of decay of γ and its steady-state value. However, for pH = 9 this is not always the case. At c_p > 100 ppm $\gamma(t)$ decreases more slowly than at lower pH, whereas $\gamma(\infty)$ reaches a lower value at pH = 9 than at lower pH. The variation in adsorption mechanism as a function of pH has already been mentioned in conclusion 2.

The same results are replotted as a function of pH in figs. 3.6.–3.8. In view of the increasing charge a general upward trend of $\gamma(\infty)$ with pH is anticipated. In certain literature references this trend has indeed been found, e.g. CUMPER and ALEXANDER (1950), MILLER and KATCHALSKY (1957) and JAFFÉ and RUYSSCHAERT (1964). For the L/S interface the same trend has been observed by MICHAELS and MORELOS (1955) and by COLE and HOWARD (1972) for Γ with pH. Our figures agree with this trend, except at c_p > 100 ppm in 0.01 and 0.20 M NaCl.

Since the fully dissociated carboxylic groups are interfacially inactive it is likely that adsorption of hydrophobic groups at pH = 9 is responsible for the fact that $\gamma(\infty)$ is below the blank value of 51.25 $mN\,m^{-1}$. In order to study which groups are responsible for the adsorption at different pH values, it is expedient to compare the interfacial activity of different polyelectrolytes. Results of this comparative study, using the four polyelectrolytes described in section 2.2., are shown in fig. 3.9., from which the following is concluded:

1. PAA and PMA are not interfacially active when adsorption takes place at pH > 6. The mutual difference between PMA and PAA is very small and may be caused by the differences in the acidity between these two polyelectrolytes. Moreover, for PMA the molecular weight is a factor of 10 smaller than for PAA (see table 2.1.). It is concluded from these results, that the presence of ester groups is necessary to make the polyelectrolyte interfacially active at high charge density. The presence of the methyl group in the main chain does not significantly alter the interfacial activity.

2. At low pH, PMA-pe and PAA-pe are more interfacially active than the corresponding polyacids. This shows that also at low pH the presence of the hydrophobic ester groups is required to obtain good interfacial activity. The difference between PAA-pe and PMA-pe is negligible at low pH.

3. PMA-pe and PAA-pe are both interfacially active at pH > 6, although the difference between them is that in the case of PAA-pe the bulk concentration must be sufficiently high. In a 100 ppm solution, PAA-pe is not markedly interfacially active, whereas at 1000 ppm the supply is sufficient to decrease γ. It is concluded that the presence of the methyl group in the main chain causes the difference, because the difference in the molecular weight between both polyelectrolytes is small (see table 2.1.).

Adsorption at high pH must be caused by the presence of the ester groups. By the adsorption of these polyelectrolytes at high pH, $\gamma(\infty)$ can reach a relatively

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FIG. 3.6. The steady-state value of the interfacial tension of solutions of PMA-pe as a function of pH at different c_p in 0.01 M NaCl.
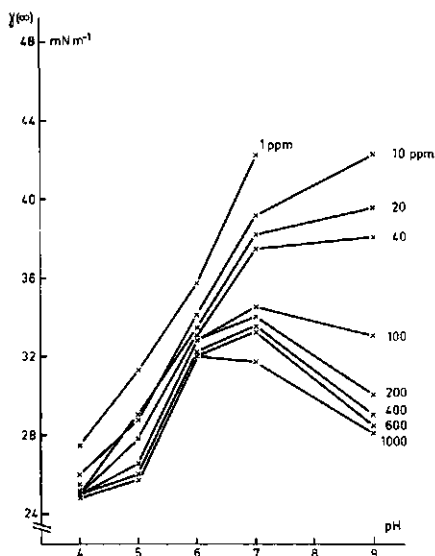
FIG. 3.7. The steady-state value of the interfacial tension of solutions of PMA-pe as a function of pH at different c_p in 0.20 M NaCl.
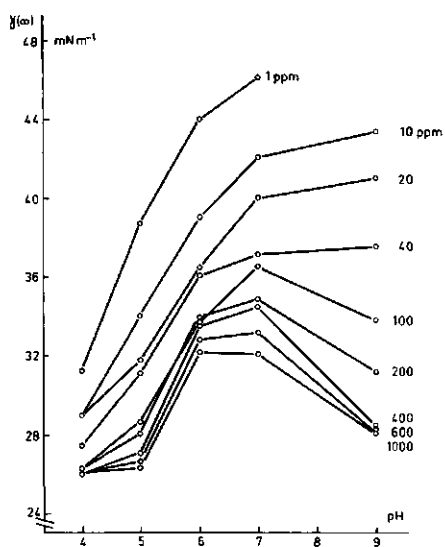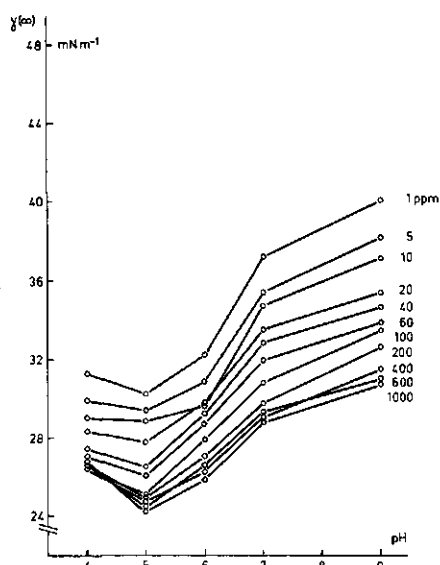

FIG. 3.8. The steady-state value of the interfacial tension of solutions of PMA-pe as a function of pH at different c_p in 0.01 N CaCl$_2$.
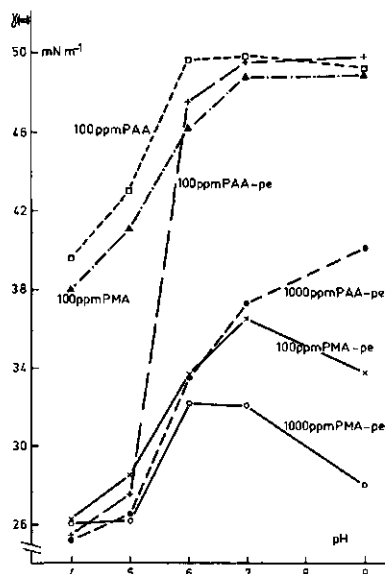
FIG. 3.9. The steady-state value of the interfacial tension of solutions of the 4 polyelectrolytes as a function of pH at $c_p =$ 1000 and/or 100 ppm in 0.01 M NaCl.

low value, which means that the interfacial free energy is considerably reduced upon adsorption. It may be expected that the charged groups contribute to this free energy decrease. However, from the absence of an electrolyte influence on $\gamma(\infty)$ we conclude that this is presumably a minor contribution (see also fig. 3.4.). As the amount of adsorbed polyelectrolyte is generally increased by increasing ionic strength (PEYSER and ULLMANN, 1965; emulsion experiments, chapter 5; adsorption on polystyrene latices, section 3.4.) it is concluded that $\gamma(\infty)$ is not a good measure of the adsorbed amount of polyelectrolyte.

For polyelectrolytes without hydrophobic groups adsorption is impossible if the molecules are charged. This has been demonstrated by the investigators already mentioned in this section. However, JAFFÉ and RUYSSCHAERT (1964) mentioned the difference between polyvinyl pyridine (PVP) and PMA, both at liquid – liquid and liquid – air interfaces. Studying spread, uncharged monolayers of PMA and PVP, they observed that charging the polyelectrolytes by changing the pH of the supporting phase resulted in a desorption of PMA, whereas PVP did not desorb. The vinyl pyridine groups cause adsorption in such a way that desorption is not possible. A similar picture has been proposed by us to explain the difference in adsorption behaviour of PMA-pe at high and low pH. The ester groups can in this sense be compared with the vinyl pyridine groups. In chapter 4 this picture will be worked out.

This picture also explains why the adsorption behaviour of proteins compares better with that of PMA-pe than with that of polyelectrolytes without hydrophobic groups. NORDE (1973) investigated the adsorption behaviour of human serum albumin (HSA) on polystyrene latices. It is likely, that hydrophobic groups in the HSA are responsible for adsorption, so that even above the isoelectric point the protein adsorbs on negatively charged latex.

Finally it can be noted that neither the time dependence measurements (section 3.2.4.) nor the static measurements are suggestive of the occurrence of a sudden transition in the properties of the PMA-pe at a given pH. We shall revert to this point in chapter 4.

3.3. SPREAD MONOLAYERS OF PMA-PE AT THE PARAFFIN OIL – WATER INTERFACE

3.3.1. *Introduction*

For the determination of the structure of proteins and synthetic polymers at liquid – liquid and air – liquid interfaces, monolayer techniques are often used. In general they are only suitable for qualitative and comparative purposes, but quantitative interpretation of the results using theoretical treatments (SINGER, 1948; MOTOMURA and MATUURA, 1963: FOWKES, 1964) is hardly possible (GAINES, 1972). Conformational transitions during compression and/or expansion of the monolayer often appear, whereas the theories do not account for this. Some examples of interesting studies are the following:

1. Orientation of polymers at interfaces.

BLOCK and LAMY (1968) examined the rate of drug transport through a L/L interface, when CMC was adsorbed. There was a rate reduction only at low pH and with a polar oil phase. HWA and RIES (1964) demonstrated how differences in stereoregularity on polymethyl methacrylate were reflected in interfacial pressure-area $(\Pi - A)$ isotherms. LOEB and BAIER (1968) used spectroscopic techniques after transfer of the monolayer to study the polypeptide conformation as a function of the spreading solvent. WILLIOT et al. (1972) investigated the surface structure of a branched poly(α-amino acid) in relation to the spreading solvent and the length of the side chain. They concluded that a quantitative investigation into the structure of the polypeptides requires more specific methods than $\Pi - A$ isotherms.

2. Mixed polymer layers.

LABBAUF and ZACK (1971) investigated the difference in surface orientation between mixtures of homopolymers of styrene and methyl methacrylate and their copolymers in the same ratio of monomers. On account of $\Pi - A$ isotherms they concluded that the copolymer is adsorbed with all segments on the same side of the backbone as in an isotactic structure. Copolymers occupy greater areas per unit mass than the mixtures of equivalent composition. This is due to the fact that polystyrene does not form a monolayer, but exists in the nonspread state.

3. Interaction of polymers with detergents.

RIES et al. (1959) have used $\Pi - A$ isotherms to obtain information on the interaction between polyvinyl acetate and stearic acid. PEARSON and ALEXANDER (1968) paid extensive attention to the interaction of several proteins with cationic and anionic soaps. Surface pressure and surface viscosity are considerably affected by the presence of the soap molecules. STRENGE et al. (1972) investigated the interaction between polyvinyl acetate and ionic detergents. The results are explained by assuming these mixed monolayers to consist of polyelectrolytes.

4. Interaction between different proteins at interfaces.

ELEY and HEDGE (1956) measured the change in pressure after injection of a second protein underneath a monolayer already occupied by a spread protein. The $\Delta\Pi$ due to this injection depends on the spread amount of protein already in the monolayer. The ensuing decay of Π after injection is slow at low ionic strength or high pH of the supporting aqueous phase, which is in general agreement with our findings in section 3.2.4. Analogous experiments have been performed by MUSSELLWHITE (1964) who found that the adsorption behaviour from a solution of casein and gelatin corresponds with the adsorption behaviour of casein solution without gelatin. Adsorption of casein is possible when the interface is already occupied by gelatin molecules. The reverse does not occur. Casein adsorbs preferently and is able to expel the gelatin molecules from the interface.

5. Enzymatic activity at interfaces.

JAMES and AUGENSTINE (1966) reviewed this field. No general rule about the variation of activity can be given. Adsorption of hydrophobic groups is impor-

tant and loss of activity upon adsorption will occur if the active centre is screened. GHOSH and BULL (1962) investigated the loss of enzymatic activity of chymotrypsin at an oil – water interface. Adsorption from concentrated solutions resulted in a lower loss of activity. They explained their results by the assumption that reconformation of the molecules takes place to a smaller extent when adsorbed from concentrated solutions.

As the application of monolayer theories is open to doubt no attempts have been made in this thesis to check them for PMA-pe monolayers. The main purpose of our monolayer experiments was to obtain interesting results with respect to the conformational transition of PMA-pe. Moreover, the monolayer experiments may give us some information about the relation $\gamma - \Gamma$, although spread and adsorbed monolayers cannot be compared unconditionally.

3.3.2. *Experimental*

Spreading of PMA-pe has been performed in the same way as by LANKVELD and LYKLEMA (1972). The PMA-pe was spread from a 500 ppm solution. pH and ionic strength of the water phase and spreading solution were equal. Using a micrometer screw the solution was dispensed from an Agla micropipette. A small glass rod was placed on the bottom of the measuring trough, just under the interface, with its roughened, tapered top just penetrating the paraffin layer. This technique was first applied by TRURNIT (1960) and gave better reproducible results than spreading directly into the interface. At an air – liquid interface spreading can also be realized by dissolving the polymer in a volatile solvent, which evaporates during spreading. At L/L interfaces this method is unsuitable. Compression and expansion was carried out by the method of ZILVERSMIT (1963). Fig. 3.10. illustrates the principle of this method. A teflon tape is placed in the interface and by rolling-up this tape the area surrounded by the band is reduced. The teflon tape (2 cm wide, 0.15 mm thick) was type A 15 ex Huth, Bietigheim, BRD, and was specially reinforced to avoid stretching. The Langmuir trough was a glass trough, measuring $60 \times 20 \times 8$ cm. The area enclosed can be readily calculated from the known distance between the fixed and the movable bridge. Corrections were made for the cross-sectional area of the four glass rods and the rotating teflon rod. A combined pH electrode was placed in the water phase and by means of a small tube the pH could be changed by injection of NaOH or HCl. The water phase could be stirred with magnetic stirrers.
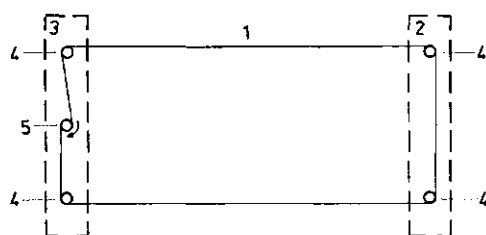
FIG. 3.10. Method of compressing monolayers at the paraffin oil–water interface.
1 = teflon tape; 2 = fixed bridge; 3 = movable bridge; 4 = glass rods; 5 = teflon rod.

The interfacial tension was always measured at a distance of about 3 cm from the teflon tape near the fixed bridge by the Wilhelmy-plate method described in section 3.2.2. On the other side of the teflon tape a second tensiometer was placed to check the interfacial tension alterations caused by possible desorbed PMA-pe.

Compression and expansion were carried out only when Π after the previous reading changed by less than 0.1 mN m^{-1} in 3 minutes. This arbitrary criterion was chosen to exlude the time dependence effect just after the compression or expansion. In fact it will be shown that this criterion is not sufficient to exclude the time dependence completely. Likewise, new PMA-pe was added only when the interfacial tension altered by less than 0.1 mN m^{-1} in 3 minutes after the previous injection.

The interface was cleaned, both inside and outside the tape, by sucking off with a capillary tube in the compressed state. This was repeated several times, till an interfacial tension was obtained of at least 51.0 mN m^{-1}. When an old interface is sucked off in this way an entirely fresh interface can be obtained. Addition of salt solution through a small tube followed by changing the pH for the next experiment is then possible. The reproducibility of the results indicated that the thus attained cleaning was complete.

It has been observed, for spread and adsorbed monolayers, that compression above about 28 mN m^{-1} leads to irreproducible values. Immediately after compression above about 28 mN m^{-1} Π increased considerably after which upon standing a continuous decrease followed till about 28 mN m^{-1} was reached again. At pH = 4 and 5 this collapse gave a visible skin, whereas at higher pH this was not the case. As this collapse is irreversible, as a rule no experiments have been done above this collapse pressure.

3.3.3. *Results and discussion*

It was first verified whether desorption occurred upon compression. GONZALEZ and MACRITCHIE (1970) observed desorption of BSA monolayers by compression. However, in our case no desorption could be detected, judging from the absence of any reduction of γ on the other side of the barrier. In the literature it has often been mentioned that spreading of polymers can give $\Pi - A$ relations depending on the amount of polymer spread before compression starts. LANKVELD and LYKLEMA (1972) working with PVA, performed two kinds of experiments, viz.:

1. spreading of polymer on an interface of constant area ($\Pi - C$ isotherm)
2. spreading of polymer in a trough with subsequent compression and expansion ($\Pi - A$ isotherm).

These two approaches did not lead to different Π values. However, AUGENSTINE et al. (1958) found a difference between $\Pi - C$ and $\Pi - A$ isotherms for trypsin films at the air – water interface. For a given amount of polymer per unit area they found that Π was lower for $\Pi - C$ than for $\Pi - A$ isotherms. In view of all this it was necessary to check whether the two different techniques led to different results in the case of PMA-pe. In figs. 3.11. and 3.12b. results are shown for pH = 4, 5 and 9. PMA-pe was spread to a level of 3.12, 1.56 or
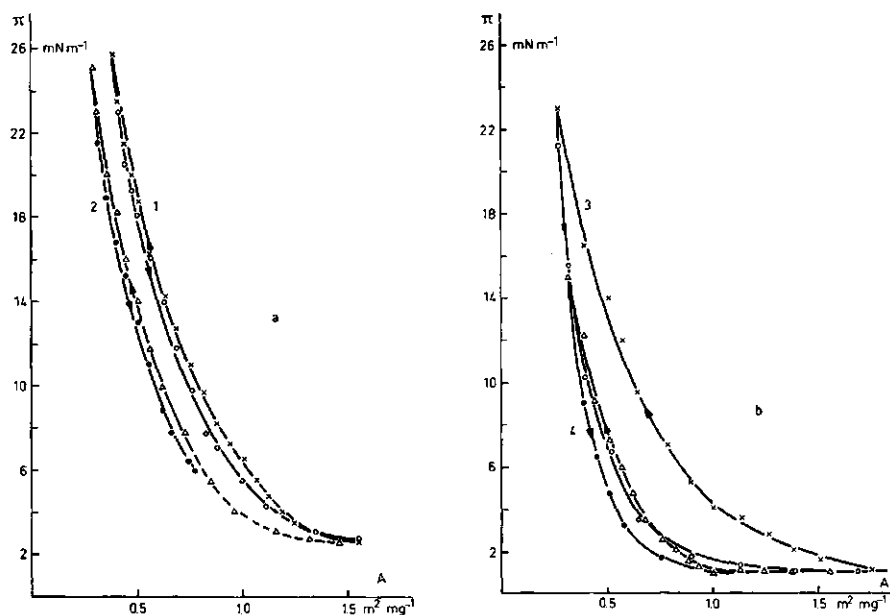
FIG. 3.11. Effect of starting concentration upon interfacial pressure – area (Π–A) isotherms of PMA-pe.
The interface is subjected to compression and expansion.
a. pH = 4.0, 0.01 M NaCl; injection till $A = 1.56$ m² mg⁻¹, directly followed by compression (curve 1); do. till $A = 0.78$ m² mg⁻¹ (curve 2).
b. pH = 5.0, 0.01 M NaCl; injection till $A = 3.12$ m² mg⁻¹, directly followed by compression (curve 3); do. till $A = 1.56$ m² mg⁻¹ (curve 4).

0.78 m²mg⁻¹. By subsequent compression till the same A a combination of the $\Pi - C$ and $\Pi - A$ isotherms is involved and comparison of the thus obtained Π values gives us information about the difference between them.

In fig. 3.11. it is shown that for PMA-pe indeed the way of reaching a given area per unit mass affects the interfacial pressure. At pH = 5 the mutual difference between both isotherms is more significant than at pH = 4. In reference to the difference between $\Pi - C$ and $\Pi - A$ isotherms BLIGHT et al. (1965), MUSSELLWHITE and PALMER (1968) and YAMASHITA and BULL (1967) arrived at similar conclusions. Following AUGENSTINE et al. (1958) it was supposed that the observed features originate from the fact that the spread layer is not uniform. The first molecules spread completely, whereas those arriving later on retain longer loops. They could confirm this supposition with activity tests of trypsin at the surface. For the results presented in fig. 3.11. the effects can be explained in the same way. Decrease of the area per unit mass by injection of PMA-pe at a constant interface increases the non-uniformity of the spread layer. Hence the non-uniformity is greater for isotherms 2 and 4 than for isotherms 1 and 3 in fig. 3.11.

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Also hysteresis is observed between compression and expansion. At pH = 4 this hysteresis is very small, but it is more pronounced at pH = 5. However, as will be shown later, this is not a real hysteresis but a relaxation. The relaxation is more pronounced at lower starting concentrations.

Further experiments were carried out starting the compression at an area per unit mass of 1.56 m^2 mg^{-1}. Compression was performed till about 25 mN m^{-1}, because further compression leads to irreproducible values.

In figs. 3.12.–3.14. $\Pi - A$ isotherms of PMA-pe under different conditions are represented. The compression results measured directly after spreading are shown in figs. 3.12a.–3.14a., whereas the results 24 hours after spreading are shown in the figs. 3.12b.–3.14b. It is clear from these figures that there is a marked time dependence, especially at high pH. In fact it means that our measuring criterion (0.1 mN m^{-1} in 3 minutes) has been insufficient. Spreading followed by immediate compression clearly differs from the same operation after a waiting time of 24 hours. Actually ageing goes on for 8–15 hours, so that 24 hours is a safe upper limit. For Ca^{2+}PMA-pe at pH = 4 the time dependence is practically absent, whereas for Na$^+$PMA-pe at high pH it is most pronounced. Although it is not possible to quantify the time effects as a function of pH, ionic strength and nature of the counterion, these results show a relationship to the interfacial tension measurements as a function of time (see
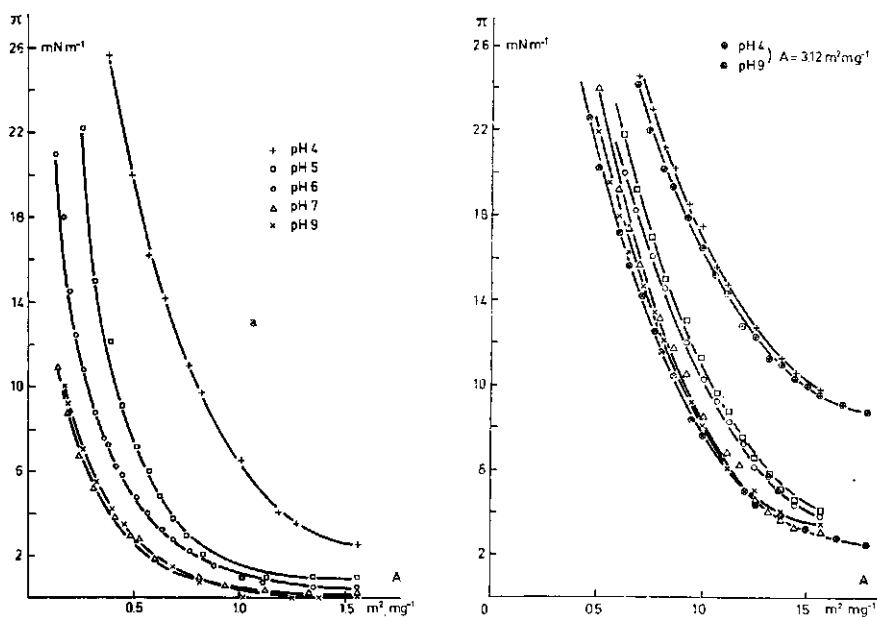
FIG. 3.12. Interfacial pressure – area isotherms of PMA-pe at different pH in 0.01 M NaCl.
a. injection till A = 1.56 m^2 mg^{-1}, directly followed by compression.
b. injection till A = 1.56 m^2 mg^{-1} or A = 3.12 m^2 mg^{-1}, followed by compression after 24 hours.
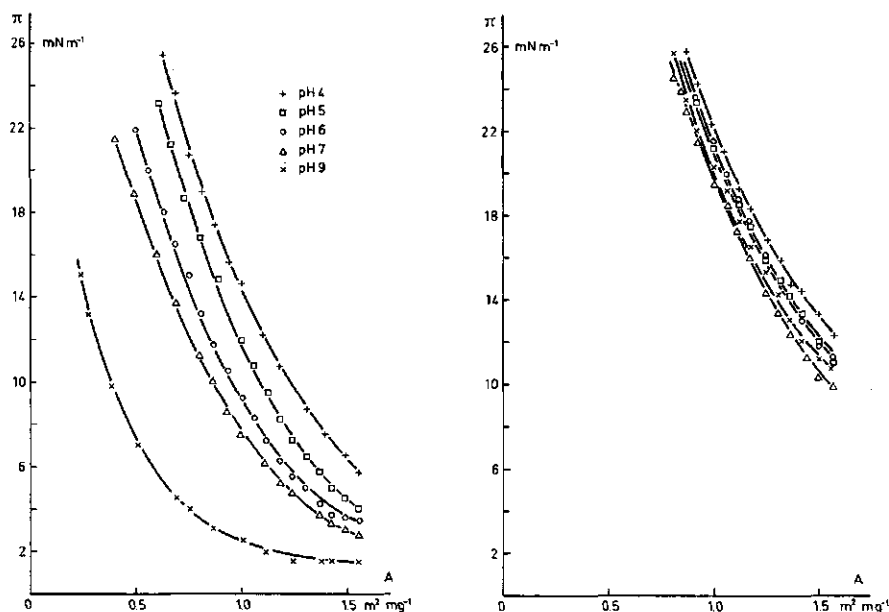
FIG. 3.13. Interfacial pressure – area isotherms of PMA-pe at different pH in 0.20 M NaCl.
a. injection till $A = 1.56$ m^2 mg^{-1}, directly followed by compression.
b. injection till $A = 1.56$ m^2 mg^{-1}, followed by compression after 24 hours.
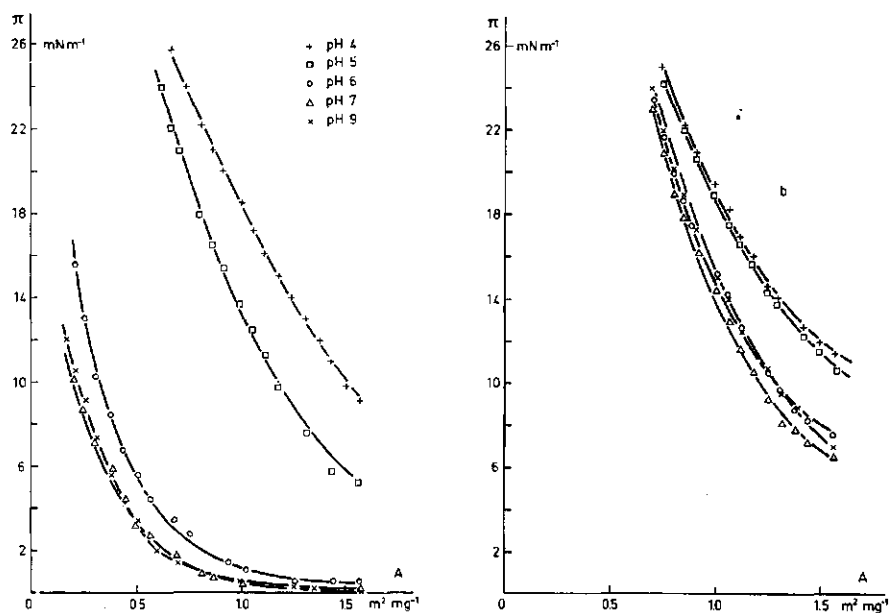
FIG. 3.14. Interfacial pressure – area isotherms of PMA-pe at different pH in 0.01 N CaCl$_2$.
a. injection till $A = 1.56$ m^2 mg^{-1}, directly followed by compression.
b. injection till $A = 1.56$ m^2 mg^{-1}, followed by compression after 24 hours.

section 3.2.4.). The more compact the molecular dimensions the less time is necessary to obtain the steady state in the monolayer. Spreading and reconformation proceed faster at low pH, high ionic strength and in the presence of Ca^{2+} ions.

Some more conclusions can be drawn from the results presented in figs. 3.12.–3.14:

1. The difference in the starting area per unit mass at compression of the monolayer has disappeared for the $\Pi - A$ isotherms, taken after 24 hours. This is demonstrated in fig. 3.12b. for pH = 4 and 9. The results obtained at 3.12 m^2 mg^{-1} do not deviate any more from those at 1.56 m^2 mg^{-1}. In fig. 3.11. it was shown that if compressed directly after spreading, definite differences were observed. The larger the starting area per unit mass, the smaller the discrepancy between direct measurements and the measurements after 24 hours. This means, that after spreading the deviation from the uniformity of the monolayer is more significant for lower area per unit mass.

2. The $\Pi - A$ isotherms after 24 hours show only a slight dependence on pH especially if the ionic strength is high (compare figs. 3.12b. and 3.13b.). The interfacial pressure always increases with decreasing pH as has also been found for adsorbed layers, except at $c_p > 100$ ppm (figs. 3.6.–3.7.).

3. Although a slight pH dependence of the $\Pi - A$ isotherms is shown, it cannot be concluded that spread monolayers give information about the existence of two different conformations in the monolayer.

SUTHERLAND and MILLER (1970) investigated monolayers of polymethyl methacrylate at the air–water interface. Their findings are similar to ours. The $\Pi - A$ isotherms of these monolayers vary with the rate of compression. This effect is more pronounced at higher molecular weight. Moreover they found a different behaviour for iso- and atactic polymer samples. One of their conclusions is that the relatively stiff molecules of polymethyl methacrylate need much time after compression to obtain the most favourable conformation. ISEMURA and HAMAGUCHI (1952) investigated monolayers of synthetic polypeptides at the air–water interface. They also found a dependence of $\Pi - A$ isotherms on the time elapsed after spreading of the monolayer. Moreover, they found their isotherms dependent on the pH of the supporting aqueous phase. At a low charge density of the chain Π is high, which agrees with our experimental findings. However, it should be mentioned that their results for these synthetic polypeptides depend strongly on the nature of the polypeptide. This indicates that interactions between the loops of these polypeptides cannot be neglected.

The relaxation observed in the compression–expansion cycles (fig. 3.11.) also fits in the picture presented in this section. For PMA-pe the stiffness of the chain increases with pH and hence it is conceivable that the disturbance of the monolayer due to compression needs more time to relax upon expansion at high pH.

3.4. Adsorption of PMA-pe on polystyrene latices

3.4.1. *Introduction*

In order to obtain information on a comparable system, some adsorption measurements of PMA-pe have been carried out on polystyrene latices. In such measurements it is possible to obtain the amount of polymer adsorbed per unit area by a depletion method. Comparison of these results with the adsorption at the paraffin oil–water interface is allowed, when we assume that specific polymer–adsorbent and/or solvent–adsorbent interactions need not be accounted for. Although the adsorbed amount of polymer per unit area is not necessarily equal at both interfaces it is reasonable to assume that at least the trends of the adsorption behaviour as a function of polymer charge, ionic strength and nature of the counterion (Ca^{2+}, Na^+) are similar for the two systems.

3.4.2. *Experimental*

The polystyrene latices were prepared in our laboratory by a modification of the method of KOTERA et al. (1970) and characterized as described by FURUSAWA et al. (1972). They were kindly supplied by Mr. W. NORDE. Two samples were used, designated as A and B. Some properties of these latices are collected in table 3.1. The surface charge of the latices is entirely due to SO_3H groups. The surface charge has been determined after ion exchange. Due to this procedure the total sulfer content of the latex was reduced, probably due to desorption of oligomers (FURUSAWA et al., 1972).

The adsorption experiments were performed in glass tubes into which first 45 ml of a 500 ppm PMA-pe solution was brought. Next 5 ml of the latex solution was carefully added to this solution in such a way that a sharp boundary between the latex and the polymer solution was obtained. Then the tubes were closed, shaken by hand and rotated vertically for 24–30 hours. The purpose of this mixing procedure is to prevent any flocculation of the latex particles due to bridging by the adsorbed PMA-pe molecules. This bridging may take place in the case of an unequal distribution of PMA-pe over the latex particles and the mixing procedure used here reduces the extent of irregularity in the polyelectrolyte distribution. Thus it is also possible to reduce the coagulation of the latex with low negative surface charge in 0.20 M NaCl almost completely.

After adsorption the latex was removed by centrifuging for 30 minutes at 15.000 rev./min. in a Sorvall RC 2–B centrifuge. The polyelectrolyte concen-

TABLE 3.1. Some properties of the polystyrene latex samples, used for adsorption of PMA-pe

	sample A	sample B
surface charge [1] (σ_o)	$- 1.4 \; \mu C \; cm^{-2}$	$- 8.2 \; \mu C \; cm^{-2}$
specific surface area	$15.6 \; m^2 g^{-1}$	$9.6 \; m^2 g^{-1}$
concentration	7.7 % w/w	6.8 % w/w

note: 1. adsorption experiments have been performed with non-ion exchanged latices.

tration in the water phase has been determined by potentiometric titration as described in section 2.3.3. To facilitate the detection of the neutralization point of the titrations, they have been performed in about 1.0 M NaCl. This makes the titrations less time dependent (GREGOR and FREDERICK, 1957) and improves the inflection point. The adsorbed amount is then found from the material balance. The results can be expressed in mg m^{-2} because the specific surface areas of the latices are known from electronmicroscopy.

The polyelectrolyte titrations were performed in duplicate. The polymer concentration has been taken at 500 ppm to ensure attainment of the plateau value in the adsorption isotherm, although this has not been checked. At this supply the amount of adsorbed PMA-pe is still accurately determinable. As the analytical technique is much less reliable at $\alpha = 0.9$ than at lower α values, the experiments at $\alpha = 0.9$ have been repeated with 10 ml latex A or B and 40 ml 1000 ppm PMA-pe solution.

3.4.3. *Results and discussion*

In contrast with the adsorption of uncharged polymers, the adsorption of polyelectrolytes on charged adsorbents will be affected by electrostatic forces. A theoretical treatment, for low surface potentials, has been given by HESSELINK (1972). A lower adsorption at higher pH is anticipated because of the increasing electrostatic repulsion between PMA-pe and the latex. High ionic strength and high valency of the counterions will reduce this repulsion. Moreover, Ca^{2+} ions can cause bridging and thus influence the adsorption more drastically. However, theory cannot yet give a quantitative answer about the extent to which the electrostatic forces affect the adsorption. It depends on the way in which and the extent to which the charge changes the segment distribution and with that the free energy gain of adsorption. For the system used here it should be realized that a surface charge of -1.4 μC cm^{-2} corresponds to one electrostatic unit of charge per 10 nm^2, which is very low. Assuming that one RSO_3^- group occupies about 0.5 nm^2 it means that about 5 % of the surface is charged. Hence it seems reasonable to assume that this latex behaves as if it is virtually uncharged and that it can be compared with the paraffin oil surface. Against this background the adsorption of PMA-pe on the latex particles has been investigated as a function of pH, ionic strength and nature of the counterion. The results are summarized in table 3.2. In this table the pH value of every adsorption condition is included. The following conclusions can be drawn:
1. The adsorbed amount Γ_i as a function of α gives the same overall picture as is normally found for polyelectrolytes. (e.g. COLE and HOWARD, 1972), viz. the adsorbed amount of polyelectrolyte decreases as α increases. COLE and HOWARD did not measure any adsorption of PAA on nylon powder at $\alpha >$ 0.25. However, for PMA-pe on latices adsorption occurred at higher α. In this respect their results are in agreement with fig. 3.9., where we found that PMA-pe is interfacially active at pH > 6, whereas PAA and PMA are not.
2. The adsorption increases with increasing ionic strength and is higher in CaCl$_2$ than in NaCl. This is in agreement with the expectations.

Table 3.2. Adsorption of PMA-pe on polystyrene latices (Γ_i)

| α | surface charge $\sigma_0 = -8.2\ \mu C\ cm^{-2}$ | | | | | | Surface charge $\sigma_0 = -1.4\ \mu C\ cm^{-2}$ | | | | | |
| | 0.02 M NaCl | | 0.20 M NaCl | | 0.02 N CaCl$_2$ | | 0.02 M NaCl | | 0.20 M NaCl | | 0.02 N CaCl$_2$ | |
	Γ_i mg m^{-2}	pH	Γ_i mg m^{-2}	pH	Γ_i mg m^{-2}	pH	Γ_i mg m^{-2}	pH	Γ_i mg m^{-2}	pH	Γ_i mg m^{-2}	pH
0.90	0 (0)[a]	7.8	0.52 (0.64)	7.0	0.61 (0.40)	6.2	0.20 (0.27)	7.8	0.92 (0.68)	7.0	0.78 (0.70)	6.2
0.70	0.40	6.8	1.25	6.2	1.72	5.7	1.08	6.8	1.74	6.2	1.94	5.7
0.50	0.64	6.2	1.44	5.8	1.66	5.4	1.34	6.2	1.84	5.8	1.94	5.4
0.30	0.70	5.8	1.50	5.3	1.84	5.0	1.22	5.8	1.74	5.3	2.14	5.0
0.10	0.95	4.7	2.18	4.3	1.97	4.4	1.50	4.7	2.54	4.3	2.38	4.4
0.0	1.87	4.0	-	-	2.54	3.9	1.92	4.0	-	-	3.36	3.9

note: a. results in brackets are duplicate values, determined using 10 ml latex and 40 ml 1000 ppm PMA-pe solution.

3. The adsorption is higher at lower negative surface charge. This is more pronounced at lower ionic strength of Na^+ ions. At $\alpha = 0.90$ in 0.01 M NaCl there was no measurable adsorption on a latex with high negative surface charge.
4. The adsorption at $\alpha = 0.90$ deviates considerably from that at lower degree of neutralization. The pH at $\alpha = 0.90$ varies between 6.2 and 7.8 and hence in this respect it is not possible to make an exact comparison with the results of the steady-state values of the interfacial tension (see section 3.2.5.).

Although a complete comparison between steady-state interfacial tension and these adsorption data is not permitted, it can be concluded that polymer–adsorbent or solvent–adsorbent interactions do not cause specific effects in one or both systems. The surface charge of the latex does not affect the results drastically and hence it appears feasible to use the results presented in this section for the description of the polyelectrolyte distribution in the adsorbed layer at the paraffin oil–water interface. The steady-state interfacial tension can perhaps help us in obtaining the adsorbed amount in the first layer and the adsorption on the latex gives us the total amount of polyelectrolyte per unit area. In the next section an attempt will be made to quantify this information. In chapters 5 and 6 attention will be paid to the comparison of adsorption on latex particles and that on emulsified oil droplets.

3.5. CALCULATIONS ON SPREAD AND ADSORBED MONOLAYERS OF PMA-PE

3.5.1. *Introduction*

As already mentioned in section 3.2.1. one of the characteristic properties of polymer adsorption is that a relatively high fraction of segments per molecule is bound in the first layer when the molecule can spread and reconform, whereas the opposite effect – a low p value – occurs when the supply of polymer by diffusion is so fast that no reconformation or spreading takes place. Below an attempt has been made to confirm this trend by semiquantitative interpretation of the results. For this purpose we need the time dependence experiments (section 3.2.4.), the steady-state values (section 3.2.5.), the monolayer experiments (section 3.3.3.) and the results of the adsorption experiments on latices (section 3.4.3.). The following assumptions have been made:
1. The maximum surface coverage θ_{max} of the first layer is 0.70. This value is chosen as a result of calculations by FLEER et al. (1972) for PVA on AgI particles.
2. θ_{max} is reached at the collapse pressure of the monolayer. The collapse takes place at about 28 mN m^{-1}, independent of pH, ionic strength and the nature of the counterion. This has been concluded on account of the spread monolayer experiments (section 3.3.).
3. The interfacial pressure is primarily related to the number of segments adsorbed in the first layer and not to the total amount of adsorbed polymer. LANKVELD and LYKLEMA (1972) concluded this already on account of the ad-

sorption of PVA at the paraffin oil–water interface. As the number of segments in the first layer is proportional to the fraction of the interface occupied by polymer one can also state that Π is related to θ. For $5 < \Pi < 28$ mN m^{-1} it has be assumed that this relation is linear:

$$\Pi = q \cdot \theta \tag{3.1.}$$

in which, $q = 28$ mN m$^{-1}/\theta_{max} = 40$ mN m^{-1}.

This linear relation can be considered as the first term of a virial expansion $\Pi = q\theta + r\,\theta^2 + s\,\theta^3 + \ldots$ Some arguments for this relation are derived from $\Pi-A$ isotherms, presented in figs. 3.12.–3.14. From these curves it can be concluded, that for $5 < \Pi < 28$ mN m^{-1} the amount of polymer spread in a monolayer Γ_{sp} increases linearly with Π. Some of these curves, taken from $\Pi-A$ isotherms after 24 hours, are presented in fig. 3.15. If it is assumed that upon compression of the monolayer the fraction of segments in the first layer p_{sp} remains constant i.e. that only water molecules are squeezed out, it can be concluded that $d\theta/d\Pi$ is constant over the region $5 < \Pi < 28$ mN m^{-1}. For $\Pi < 5$ mN m^{-1} the following relation between θ and Π exists: (see also section 3.6.)

$$\varepsilon = a_1\Pi = -\,d\Pi/d\ln A = d\Pi/d\ln\theta \tag{3.2.}$$

in which ε = surface dilational modulus, mN m^{-1}
a_1 = proportionality constant
$d\ln A$ = relative change in area

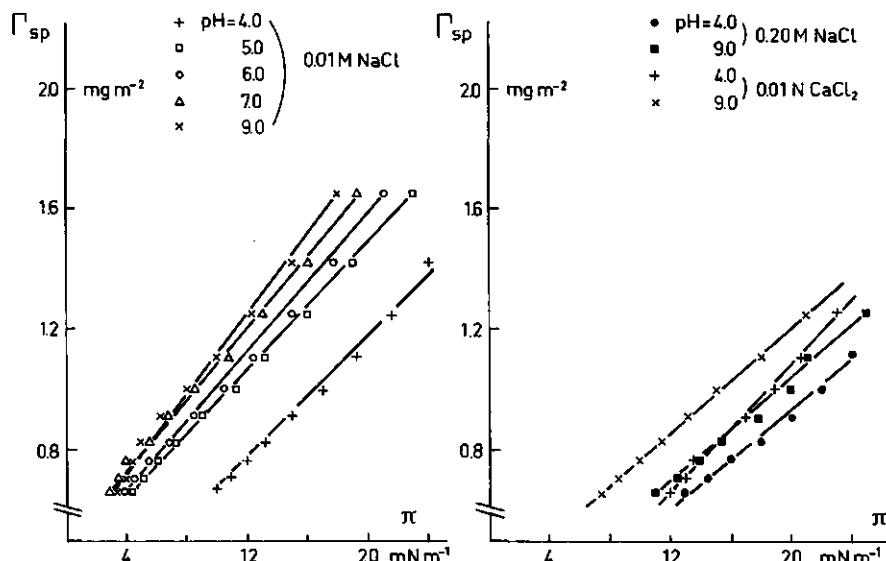Eq. (3.2.) applies only if the rate of unfolding of the polymer is low as compared

FIG. 3.15. Adsorbed amount of PMA-pe in a spread monolayer as a function of interfacial pressure (compression 24 hours after injection).

with the rate of change in area, otherwise $- \, \mathrm{d}\ln A \neq \mathrm{d}\ln \theta$. Eq. (3.2.) implies that there is an exponential relationship between θ and Π, viz. $\theta = c \, \Pi^{a_1}$ in which c is a constant value. The overall picture of the relation between θ and Π is then exponential for $\Pi < 5$ mN m^{-1} and linear for $5 < \Pi < 28$ mN m^{-1}. It implies that the contributions to Π of the lateral interactions between loops and trains, both electrostatic and non-electrostatic ones are taken up in q, c and a_1. As q is independent of pH it can be concluded that electrostatic interactions form a minor contribution.

4. The interfacial area per polymer segment A_0 is taken to be 0.20 nm^2. In the literature several values have been reported for polymethyl methacrylate spread at different interfaces. LABBAUF and ZACK (1971) summarized these values of A_0 found by different authors. Most of these segmental areas have been obtained from $\Pi - A$ isotherms by extrapolation of linear parts of these curves. However, often more than one linear region has been reported and it has not been clarified why a particular linear region has been used for the calculation of A_0. This makes comparison between the different data rather complicated. LABBAUF and ZACK (1971) found an experimental value of 0.184 nm^2 and they calculated a value of 0.228 nm^2 for the cis – form and 0.196 nm^2 for the trans – form by using a molecular model of polymethyl methacrylate. On the basis of these calculations it seems acceptable to take $A_0 = 0.20$ nm^2 for a copolymer of methyl methacrylate and methacrylic acid.

As stated before, the total adsorbed amount Γ will be derived from the adsorption experiments on the low charge latex.

3.5.2. *Polymer distribution in adsorbed and spread monolayers of PMA-pe*

Equation 3.1. will now be used for the determination of the segment distribution of PMA-pe at L/L interfaces. In order to estimate the amount of PMA-pe adsorbed in the first layer it is necessary to know θ and A_0. The results of this analysis are summarized in table 3.3. In column 3 the $\Pi(\infty)$ values at a supply of about 500 ppm are given. This supply has been chosen because the adsorption on latex has been performed at 500 ppm. Column 4 gives the interfacial occupation θ_{ad} (with the subscript *ad* indicating adsorption from solution), calculated from $\Pi(\infty)$ using equation 3.1. In column 5 is recorded the adsorbed amount of polymer in the first layer Γ_f from θ_{ad} and A_0. In column 6 the total amount of polymer adsorbed on the polystyrene latex of low surface charge Γ_t, is given. These data have been obtained from table 3.2. by interpolation. Dividing Γ_f by Γ_t gives the fraction of segments adsorbed in the first layer p_{ad}. The results summarized in columns 8 till 10 deal with spread monolayers. In column 8 the interfacial pressure for an area per unit mass of 1.00 m^{2}mg^{-1} is given for the $\Pi - A$ isotherms after 24 hours. From these pressures θ_{sp} (with the subscript *sp* indicating spread monolayers) is obtained using equation 3.1. As the total adsorption per unit area is known for spread monolayers p_{sp} is calculated from θ_{sp}, $A_0 = 0.20$ nm^2 and $\Gamma_{sp} = 1.00$ mg m^{-2}.

Although these results have been obtained only by virtue of a number of approximations it appears possible to discern some trends:

TABLE 3.3. Adsorption data of PMA-pe derived from interfacial tension measurements and adsorption on polystyrene latex. $A_0 = 0.20$ nm^2

1 pH	2 ionic strength Na$^+$/ Ca^{2+}	3 $\Pi(\infty)$ mN m^{-1}	4 θ_{ad}	5 Γ_f mg m^{-2}	6 Γ_i^a mg m^{-2}	7 p_{ad}	8 $\Pi(1.0$ m^{2}mg$^{-1})^b$ mN m^{-1}	9 θ_{sp}	10 p_{sp}
4.0		25.2	0.63	0.51	1.92	0.27	17.0	0.43	0.34
5.0	0.01 M	24.7	0.62	0.49	1.40	0.35	11.2	0.38	0.28
6.0	NaCl	18.0	0.45	0.36	1.28	0.28	10.4	0.26	0.20
7.0		17.5	0.44	0.35	0.90	0.39	8.4	0.21	0.16
9.0		23.0	0.58	0.46	–	–	8.0	0.20	0.15
4.0		26.2	0.66	0.53	2.8	0.19	22.0	0.55	0.41
5.0	0.20 M	25.5	0.64	0.51	2.0	0.25	21.6	0.54	0.40
6.0	NaCl	19.2	0.48	0.39	1.8	0.23	21.0	0.53	0.40
7.0		18.0	0.45	0.36	0.8	0.45	20.0	0.50	0.38
9.0		22.8	0.57	0.45	–	–	19.6	0.49	0.37
4.0		25.0	0.63	0.51	3.16	0.16	19.6	0.49	0.37
5.0	0.01 N	26.5	0.66	0.53	2.14	0.25	19.0	0.48	0.36
6.0	CaCl$_2$	25.0	0.63	0.51	1.50	0.34	15.4	0.39	0.29
7.0		22.0	0.55	0.45	–	–	15.0	0.38	0.28
9.0		20.0	0.50	0.41	–	–	14.5	0.36	0.27

notes: a. data obtained by interpolation from adsorption experiments with latex sample of low surface charge
b. from Π-A isotherms 24 hours after spreading

1. p_{ad} increases with pH. This is in agreement with the model proposed in section 3.2.1. It is due to extensive but slow reconformation at higher pH.
2. p_{ad} decreases with ionic strength. Although this trend can only be observed at rather low pH ($\leqslant 6$) one can state that this is again in agreement with the picture outlined before.
3. As a trend $p_{sp} > p_{ad}$. One would expect this trend, because for a spread monolayer there is no competition for the supply by diffusion.

From the results presented here it is concluded that the relation $\Pi - \Gamma$ depends strongly on the way in which the polymer is brought into the interface. Therefore, surface or interfacial tension measurements as such are inadequate for determining the total amount of adsorbed polymer per unit area. Nevertheless, it appears that these calculations corroborate the mechanism of adsorption of polyelectrolytes as a function of their flexibility (or charge density on the chain).

3.6. Dynamic measurements of surface and interfacial tension

3.6.1. Introduction

Hitherto we have investigated the adsorption behaviour of polyelectrolytes at undisturbed interfaces. As we intend to study also the emulsifying behaviour

of these polyelectrolytes it is important to use dynamic techniques, since dynamic interfacial properties are related to the behaviour during emulsification. KENNING (1968) has pointed out the importance of surface and interfacial tension gradients in processes like extraction, distillation, foaming and emulsification. Such gradients are caused by local compression and expansion of the interface. The response of the interfacial tension on this interfacial change is called the interfacial dilational modulus (see also equation 3.2.):

$$\varepsilon = d\gamma/d\ln A \tag{3.3.}$$

At L/L interfaces this modulus is probably reflected in the behaviour during emulsification.

The dynamic technique used here is a direct outgrowth of the theory of LUCASSEN (1968). The principle of the method is a direct determination of surface tension changes $\Delta\gamma$, caused by a local, periodic area variation. The area variation propagates over the surface at the velocity of a longitudinal wave. The wave is characterized by the damping coefficient β and the wavelength λ. If the wavelength is much greater than the vessel length L the area change is uniform over the whole vessel. The modulus can now be obtained by measuring at any convenient location in the vessel. LUCASSEN and V. D. TEMPEL (1972a) gave an extensive description of the method. If $\lambda \ll L$ the damping of the wave plays an important role, so that ε has to be obtained from $\Delta\gamma$ measurements at several locations in the vessel. In this case the area change is no longer uniform over the whole vessel. The application of this short wave technique has been described by LUCASSEN and V. D. TEMPEL (1972b). In a separate study LUCASSEN and BARNES (1972) have worked out the theory for the transition region between these two limiting cases. In that region the interference of the waves cannot be neglected. The surface deformation and the phase angle difference between barrier motion and surface tension τ at distance y from the moving barrier cannot be predicted by analytical calculations. A numerical calculation has to be used. However, it appears that there is an optimal location ($y = 0.42L$) at which the deformation gives the modulus and the phase angle difference, provided the surface deformation is nearly uniform.

From these dynamic measurements it is possible to obtain information about the visco-elastic behaviour of the interface. A phase difference between the oscillating surface tension and the movable barrier – after correction for wave propagation effects – indicates a relaxation process. This process has a characteristic time, which can be assessed by varying the time scale during the experiment. The theory for the relaxation mechanism has been worked out for the case when it is due to diffusion (LUCASSEN and V. D. TEMPEL, 1972a, 1972b). In view of the irreversible nature of polymer adsorption it would also in our system be interesting to pay attention to the occurrence of a relaxation mechanism. Such a mechanism could be expected e.g. due to reversible segment ad- and desorption.

Dynamic measurements of polymers and proteins at surfaces or interfaces

are scarce. BLANK et al. (1970) measured the dilaitonal modulus of spread monolayers of some proteins under the condition of low frequency (< 0.420 rad.sec^{-1}). It has been found that at low Π there exists a linear relationship between ε and Π with a proportionality constant a_1 of about 8 (see equation 3.2.). However, at $\Pi > 5$ mN m^{-1} this relation between ε and Π is no longer valid and the results for ε as a function of Π then become very erratic. It has been concluded by BLANK et al. (1970) that at about $\Pi = 5$ mN m^{-1} a partial collapse takes place. Later it has been found that protein adsorption at the air–liquid interface does not satisfy the classical LUCASSEN theory (V. D. TEMPEL 1972), at least at $\Pi > 5$ mN m^{-1}. It will be shown in this section that the same is also true for simpler polyelectrolytes than proteins.

3.6.2. *Experimental*[2]

A teflon tray of 34×10 cm with a teflon barrier was used to vary the area. The surface tension was measured using a roughened glass plate, attached to a Cahn Electrobalance. The relative change of the area was always 0.88%. At angular frequencies $\omega = 0.105$ rad.sec^{-1} and $\omega = 0.420$ rad.sec^{-1} $\Delta\gamma$ is measured as a function of the distance from the movable barrier y. Moreover, at $y = 15$ cm ($\sim 0.42L$) $\Delta\gamma$ is measured as a function of ω ($0.0105 \leqslant \omega \leqslant 0.420$ rad.sec^{-1}). The phase angle difference τ was always measured.

3.6.3. *Results and discussion*

Although both at air–water and paraffin oil–water interfaces have been measured, only the results for the air–water interface are discussed here. All experiments performed at the oil–water interface disagreed with the theory. As for experiments at the air–water interface conditions have been found which agree and disagree with the theory, we prefer to discuss the measurements at the air–water interface.

For an extensive description of the theory we refer to the literature (see section 3.6.1.). Only the parameters relevant to interpret the results will be mentioned here. For long waves ε and τ can be obtained at any convenient distance y. It appeared that for long waves τ was always zero and ε was independent of the frequency. For short waves it is possible to check if the measured β, λ and τ satisfy the theory and to calculate ε from these quantities. However, for polymers as soon as a measurable β was found, it is no longer possible to obtain agreement between the theory and the experimental results. At the measured λ, the damping is much faster than predicted by the theory.

In table 3.4. the results of these experiments are collected. They are numbered from 1–19 differing from each other in pH value, nature of the polyelectrolyte (PMA or PMA-pe), nature of the counterion (Ca^{2+}, Na^{+}) and polyelectrolyte concentration in the bulk ($c_p = 10$ or 100 ppm). The Π values obtained from these wave measurements are collected in column 5. The $\Delta\gamma$ values at $y = 15$ cm.

TABLE 3.4. Survey of dynamic measurements at the air – water interface.

	pH	poly-electrolyte	Na^+/Ca^{2+}	c_p	Π	$\triangle\gamma$ ($\gamma = $ 15 cm)	'ε' ($\gamma = $ 15 cm)	applicability to theory
				ppm	mN m^{-1}	mN m^{-1}	mN m^{-1}	
1.	4.0	PMA-pe	Na^+	10	7–8	0.20	23	–
2.	4.0	PMA-pe	Na^+	100	7–9	0.25	30	–
3.	4.0	PMA-pe	Ca^{2+}	100	10–12	0.40	45	–
4.	4.0	PMA	Na^+	100	4	0.12	13.6	+
5.	4.0	PMA	Ca^{2+}	100	6	0.16	18.2	+
6.	5.0	PMA-pe	Na^+	10	4	0.16	18.2	+
7.	5.0	PMA-pe	Na^+	100	4–5	0.18	21.5	+
8.	5.0	PMA-pe	Ca^{2+}	100	10–12	0.15	17	–
9.	5.0	PMA	Na^+	100	1	0	0	
10.	5.0	PMA	Ca^{2+}	100	2	0.06	7.0	+
11.	6.0	PMA-pe	Na^+	100	4–6	0.12	14	+
12.	6.0	PMA-pe	Ca^{2+}	100	7–8	0.08	9	–
13.	6.0	PMA	Na^+	100	0	0	0	
14.	6.0	PMA	Ca^{2+}	100	0	0	0	
15.	7.0	PMA-pe	Na^+	100	2	0	0	
16.	7.0	PMA-pe	Ca^{2+}	100	3–4	0.03	3.5	±
17.	7.0	PMA	Na^+	100	0	0	0	
18.	7.0	PMA	Ca^{2+}	100	0	0	0	
19.	9.0	at any condition			0	0	0	

note: 1. $\triangle\gamma$ is the difference between maximum and equilibrium value.

are summarized in column 6. From this $\Delta\gamma$ value the 'dilational modulus' has been calculated with equation 3.3. for d ln $A = 0.88\%$. In fact this is only a real dilational modulus as defined in equation 3.3. if the results are in agreement with the theory. This has been checked as discussed previously. From table 3.4. it is concluded that:

1. at $\Pi > 6$ mN m^{-1} the theory is not applicable to polymers. This agrees with the previously mentioned results for proteins (BLANK et al., 1970).
2. the proportionality constant a_1, at $\Pi < 6$ mN m^{-1}, is about 2 to 3 and deviates considerably from that for proteins.
3. it may not be concluded from these results that the mutual differences in elasticity are due to the nature of the polyelectrolyte or counterion. In the case studied the elasticity is directly affected by the Π value and hence differences in experimental conditions influence ε only through their Π value.
4. PMA-pe is not surface active at high pH, whereas at the paraffin oil–water interface a considerable activity has been measured for the same polymer concentration.

The disagreement between theory and experiment at $\Pi > 6$ mN m^{-1} is the more pronounced the higher Π and ω. It indicates that the assumptions made by LUCASSEN (1968) to elaborate the hydrodynamic equation of motion are no

longer completely satisfied. At $\Pi = 6$ mN m^{-1} perhaps a kind of collapse of the adsorbed layer occurs, leading to a gel layer of finite thickness at the interface. (V. D. TEMPEL, 1973). The contribution of this gel layer leads to a deviating dispersion equation in which the visco-elastic behaviour of the gel layer has to be accounted for. If the dynamic loss modulus of the gel layer is small compared with the dynamic storage modulus the wave properties do not differ from those of the classical theory (V. D. TEMPEL, 1973). It seems acceptable to assume that upon increasing Π the viscous behaviour of the adsorbed layer increases by adsorption of train segments. As a consequence of the presence of such a gel layer it is not possible to determine ε and to relate it with the emulsifying properties of the polyelectrolytes, without adapting the theory to the behaviour of polymers at interfaces. The main conclusion is that the deviation from the classical theory is not limited to proteins but applies to polymers in general.

3.7. SUMMARY

Interfacial tension measurements on adsorbed and spread monolayers of PMA-pe, PAA-pe, PAA and PMA are useful to investigate qualitatively the influences of c_p, pH, ionic strength and nature of the counterion on the adsorption behaviour. It has been argued that the decrease of γ by adsorption of polymer molecules from solution is primarily related to the number of train segments per unit area. The rate-determining factors of the decay of γ with time are diffusion, spreading and reconformation. It has been found that the polymer concentration and the dimensions of the molecules in bulk determine the relative influence of these three factors. When the supply by diffusion is high the interfacial tension reaches its steady-state value relatively fast. When reconformation and spreading occur extensively the decay of γ is very slow. The higher c_p and the smaller the molecular dimensions in bulk (i.e. low pH, high ionic strength and the presence of Ca^{2+} ions) the less extensive the occurrence of reconformation and spreading. As a consequence of this picture the fraction of adsorbed segments per molecule p_{ad} is higher at high pH, low ionic strength and low c_p.

Moreover, it has been shown that $\Pi - A$ isotherms for spread monolayers of polyelectrolytes (PMA-pe) are also time dependent. As this time dependence is also related to the molecular dimensions of the molecules in bulk it has been concluded that reconformation and spreading are again responsible for this time dependence. At a higher charge density on the polyelectrolyte molecule (i.e. at higher pH) the molecule is less flexible and reconformation and spreading take much time. From the compression of spread monolayers – after reaching the steady state – it has been concluded that ionic strength and charge density on the chain hardly affect the interfacial pressure of the monolayer.

The relation between Π and the number of train segments also implies that Π is related to the occupation of the interface θ. From $\Pi(\infty)$, θ_{ad} has been calculated. As a rule it can be stated that $\Pi(\infty)$ – and hence θ_{ad} – increase when the molecular dimensions are smaller. As θ_{ad} increases and p_{ad} decreases when

these dimensions are smaller it means that the total amount of adsorbed polymer per unit area Γ_{ad} must be considerably higher at low pH than at high pH. By adsorption of PMA-pe at the liquid–solid interface (polystyrene latex) this conclusion is underlined.

Although the picture outlined above can serve as a general picture for the adsorption of polyelectrolytes, significant differences have been found between the partly esterified and the non-esterified polyelectrolytes. PMA and PAA do not adsorb at the liquid–liquid interface at pH > 6. Their hydrophilic character prevents any adsorption. PMA-pe and PAA-pe adsorb at any pH. Moreover, it has been found that the esterified segments increase the interfacial activity even in the absence of any charge. Another remarkable finding of the adsorption behaviour of PMA-pe is the effect of ionic strength on the steady-state interfacial tension $\Pi(\infty)$. In general θ_{ad} and $\Pi(\infty)$ increase with ionic strength. However, $\Pi(\infty)$ does not depend on the ionic strength for the adsorption of PMA-pe at high charge density of the chain. It underlines the fact that the adsorption behaviour of PMA-pe is different at low and high pH.

It was hoped that interfacial tension measurements would give information about a possible existence of the a- and the b-conformation of PMA-pe in the adsorbed state. No such indications have been found. However, with the described types of experiments the possibility of the existence of two (or more) conformations in the adsorbed state is still open.

Investigations with PMA-pe at a dynamic air–water interface have shown that its behaviour is similar to that of proteins at the same interface. The determination of the dilational modulus – a significant parameter for the interpretation of the behaviour during emulsification – at $\Pi > 5$ mN m^{-1} is not possible with the theory of longitudinal waves as described by LUCASSEN (1968). An extension of this theory has to be developed to make it possible to determine the elasticity modulus under conditions comparable with emulsification.

4. INFERENCE ON ADSORPTION FROM
INTERFACIAL TENSION – pH CYCLES

4.1. INTRODUCTION

In chapter 3 some information has been obtained on the conformation of the adsorbed layer as a function of bulk conditions. In this chapter additional information about the conformation in the adsorbed layer will be gathered, especially in connection with the reversible transition between the a- and b-conformation in bulk (see chapter 2). The nature of the experiments described in chapter 3 did not allow the detection of the possible existence of two different conformations in the interfacial layer, because this relatively subtle effect has been overshadowed by the more drastic effects of dissociation and polymer concentration. It will be shown that a study of the reaction of γ upon changing the conditions in the bulk phase *after* adsorption gives significant information related to the existence of two different conformations. JAFFÉ and RUYS-SCHAERT (1964) used this method to study the adsorption behaviour of a random polyampholyte of 2-vinyl pyridine and methacrylic acid, spread at the air–water interface. A complete desorption of the spread monolayer could be obtained by increasing the pH of the supporting bulk phase, provided spreading has been realized below the isoelectric point. However, spreading at high pH, followed by a decrease of pH did not lead to a complete desorption. Supposing that adsorption is essentially realized through the uncharged groups, they concluded that the desorption energy of a methacrylic acid segment is less than that of a vinyl pyridine segment. In addition they concluded from a simplified calculation that the desorption of the methacrylic acid segments occurred under exactly the same condition where intermolecular bonds of these methacrylic acid derivatives at low pH, broke down.

It will be concluded from the experiments to be described in this chapter that the irriversible adsorption of the 2-vinyl pyridine segments is not due to the high desorption energy of one single segment, but to their ability to allow for adsorption of relatively long trains. Desorption of these long trains at increasing charge density of the chain is improbable because of their high desorption energy.

4.2. EXPERIMENTAL

Fig. 4.1. shows the way in which the cycles have been measured. The interfacial tension has been measured as described in section 3.2.2. A combined pH electrode (A) was used and by injection of NaOH or HCl through a glass tube (B) it was possible to change the pH of the solution. Stirring with the magnetic stirrer (D) led to homogenization of the water phase. Tap C was used for dilution and substitution experiments. The total volume of the water phase was always 300 ml. The amount of liquid injected through B was very small in
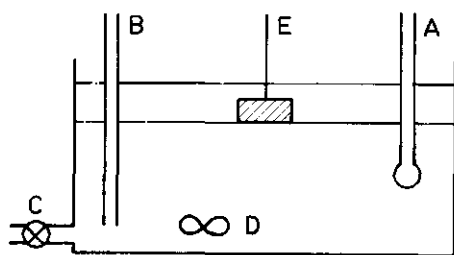
FIG. 4.1. Equipment for interfacial tension – pH cycles.
A = combined glass electrode; B = glass tube for injections in the bulk phase; C = tap to remove the supporting water phase; D = stirrer; E = Wilhelmy plate.

comparison with the total volume and the increase in the meniscus level could be neglected. As will be shown later it is very important that pH changes are relatively small and that the pH at the interface shows no local disturbances. All experiments have been performed at $20 \pm 0.1\,°C$.

The following types of experiments have been carried out:

1. Change in the pH of the solution after equilibration. In the majority of the experiments equilibration has been realized at pH = 4 or pH = 9. In the former case the pH was increased till 9 and subsequently reduced again to 4. Such a cycle will be designated as a '494' cycle. Analogously '949' cycles have been obtained, starting at pH = 9. Sometimes intermediate cycles or double cycles have been performed, e.g. 594 and 49494 cycles. The reason for starting most experiments at pH = 4 or pH = 9 is that at pH = 9 the polyelectrolyte is completely dissociated, whereas at pH = 4 it is almost uncharged. Moreover, in bulk it is in the a-conformation at pH = 4 and in the b-conformation at pH = 9. Between these pH values a transition in adsorption behaviour is expected for PMA-pe (see chapters 2 and 3). A complete cycle has normally been performed within about one hour. This implies that the pH was changed when the reading of the previous pH was constant within 0.03 units in 3 minutes. Some more details of the experimental conditions will be mentioned together with the discussion of the results.

2. Change in the (poly)electrolyte concentration of the solution after equilibration. The electrolyte concentration was increased by injecting a small amount of a highly concentrated NaCl solution. In this way a stepwise increase till 0.20 M NaCl could be reached. Lowering of the concentration is more complicated. Stepwise addition of 25 ml of a 0.01 M NaCl solution of the proper polymer concentration and subsequent removing of exactly 25 ml by tap C resulted in a final electrolyte concentration of 0.04 M NaCl. The same procedure has been applied for concentrating or diluting the polyelectrolyte solutions. In this case the limits were 10 and 1000 ppm.

3. Replacement of Na^+ by Ca^{2+} ions and vice versa in the solution after equilibration. If Na^+ had to be replaced by Ca^{2+}, a 0.01 N $CaCl_2$ solution containing 10 ppm polyelectrolyte was substituted for 25 ml 0.01 M NaCl solution of the same polyelectrolyte concentration. The substitution was finished at 80% replacement, so that the final solution contained 2.10^{-3} M NaCl and 8.10^{-3} N $CaCl_2$. The reverse process was performed similarly, also till 80% replacement.

4.3. Results and discussion

4.3.1. *pH 949 cycles of PMA-pe*

These γ—pH cycles have been performed at different c_p ($c_p = 10$, 100 and 1000 ppm) and ionic strength (0.01 and 0.20 M NaCl). Moreover time effects have been investigated by varying the rate at which a cycle has been done (one hour for a complete cycle versus 12 till 14 hours waiting after every pH change). Fig. 4.2. shows some characteristic results of one-hour cycles at $c_p = 100$ and 1000 ppm in 0.01 M NaCl. In these plots the dashed lines indicate the stationary γ values, as measured by direct adsorption at the given pH (see section 3.2.5.). The following conclusions can be drawn from these plots:

1. After a complete cycle γ returns to its starting value. As the same effect occurs in 0.20 M NaCl it is unlikely to expect that the electrostatic repulsion between charged groups causes the difference in interfacial tension between pH = 4 and pH = 9. It is more likely that by decreasing pH more segments adsorb in the first layer by reconformation and that these additional adsorbed segments desorb again by increasing pH. The adsorbed segments at pH = 9 are irreversibly adsorbed.

2. There is a clear discrepancy between the two branches of a cycle. From the study of time effects it has been found that this is a relaxation effect. Moreover, it has been determined that relaxation proceeds faster at higher ionic strength. Additional experiments at $c_p = 10$ ppm – at that concentration time effects are most pronounced – show that the descending branch relaxes faster than the ascending one. It means that desorption of segments is more delayed than the adsorption by changing pH. The faster relaxation at higher ionic strength is explained by the increased flexibility of the molecules.
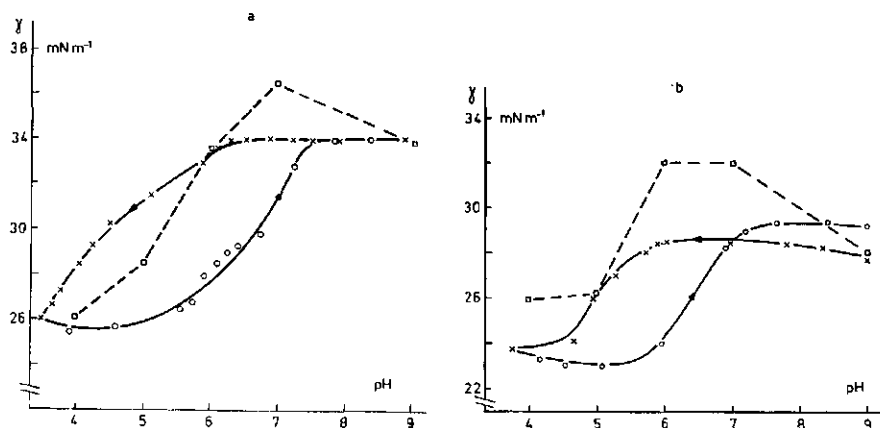

Fig. 4.2. One-hour pH 949 cycles for PMA-pe in 0.01 M NaCl.
a. $c_p = 100$ ppm
b. $c_p = 1000$ ppm
Dashed lines: $\gamma(\infty)$ at direct adsorption (see fig. 3.6.).

3. There is also a discrepancy between the $\gamma(\infty)$ values and the $\gamma-$pH cycles,
at least at $c_p = 100$ and 1000 ppm in 0.01 M NaCl. After finishing the re-
laxation process this discrepancy is still pronounced. It means that at $c_p = 100$
and 1000 ppm the conformation of the molecule at the interface depends on its
history. However, at $c_p = 10$ ppm the descending branch after finishing the
relaxation process is identical with $\gamma(\infty)$. It means that the adsorbed amount of
polymer at pH = 9 is negligible at $c_p = 10$ ppm and does not affect the inter-
facial tension after pH decrease, compared with the steady-state interfacial
tension. The higher the adsorption at pH = 9 (i.e. the higher c_p) the more pro-
nounced the discrepancy observed.
4. At pH = 4 γ gives always about the same value, even after repeating the
cycle. It means that γ itself is not very sensitive to reflect the properties of
the adsorbed layer.

4.3.2. *pH 494 cycles of PMA-pe*

In the same way as described in the previous section pH 494 cycles have been
measured. Relaxation effects could not be studied in this case, because other
time effects prevent this as will be shown below. Experiments have been perform-
ed at $c_p = 10$, 100 and 1000 ppm. Results are only discussed at 100 ppm,
because at that concentration the effects are most clearly expressed. In fig. 4.3.
a one-hour cycle at 100 ppm in 0.01 M NaCl is represented (curves 1 and 2). The
cycle has been repeated after 2 hours waiting at pH = 4 (curves 3 and 4). Fig.
4.4. shows the corresponding results in 0.20 M NaCl. From these figures the
following can be concluded:
1. Upon raising the pH from 4 to 9 an interfacial tension of 49 mN m^{-1} is
attained, which is very close to the value for paraffin oil−water. The in-
ference is that almost complete desorption has occurred. PMA-pe adsorption
at pH = 4 is completely reversible, whereas from fig. 4.2. it was concluded that
PMA-pe adsorption at pH = 9 is completely irreversible as a function of pH.
As we already concluded from fig. 3.9. the adsorption of PMA-pe at pH = 9 is
completely due to the presence of ester segments. At pH = 4 the adsorption or,
at least the interfacial activity, was strongly increased by the presence of ester
segments. It means that the effect of ester groups in PMA-pe upon the confor-
mation of the adsorbed layer is different at pH = 4 and pH = 9. The ester
groups promote the adsorption of PMA-pe to take place in such a way that it
results in a completely reversible adsorption as a function of pH at pH = 4 and
a completely irreversible one at pH = 9.
2. In 0.20 M NaCl a fast relaxation occurs. Taking into account the pH 949
cycles it appears that for 494 cycles the discrepancy between descending and
ascending branch of the cycles is less pronounced than for 949 cycles. Maybe
the extent of irreversibility in the adsorbed layer of PMA-pe is related to this
relaxation behaviour, although in this way it cannot yet be explained why for
pH 494 cycles in 0.01 M NaCl a relaxation effect has still been found.
3. The conformation of the adsorbed layer, obtained by direct adsorption at
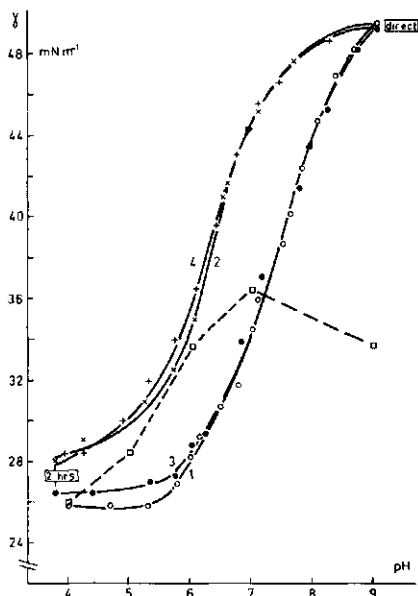pH = 4, deviates considerably from the conformation of the adsorbed

FIG. 4.3. One-hour pH 494 cycle for PMA-pe at c_p = 100 ppm in 0.01 M NaCl (curves 1 + 2).
Curves 3 + 4 represent a second cycle after 2 hours' waiting time at pH = 4.
Dashed line: γ (∞) at direct adsorption (see fig. 3.6.).
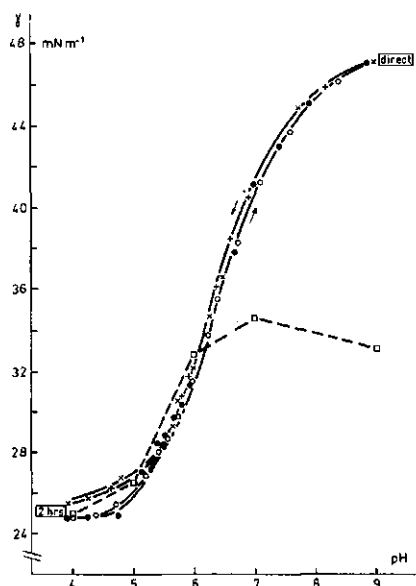
FIG. 4.4. One-hour pH 494 cycle for PMA-pe at c_p = 100 ppm in 0.20 M NaCl.
The cycle has been repeated after 2 hours' waiting time at pH = 4.
Dashed line: γ (∞) at direct adsorption (see fig. 3.7.).

layer obtained at pH = 4 after adsorption at pH = 9 (till the steady state) and subsequent reduction of pH. Nevertheless the interfacial tensions are the same for both cases. This illustrates again that γ is not too sensitive a parameter to reflect all the subtleties of the conformation of the adsorbed layer. The interfacial tension–pH cycles are more informative in this aspect.

The pH 494 cycles were repeated with PAA-pe at 100 ppm in 0.01 M NaCl. As the difference in pK between the two acids could be relatively important, the cycles have also been done, starting at pH = 3 (393 cycles). The results are given in fig. 4.5. The effect is surprising: for PAA-pe no complete desorption could be realized. The pH 393 cycle is similar to a pH 949 cycle of PMA-pe. On account of a comparison with PMA-pe one would not expect this irreversible adsorption behaviour of PAA-pe at pH = 4. It should be concluded, that the conformations of the adsorbed layers of PMA-pe and PAA-pe at pH = 4 differ considerably. It has been suggested, that the hypercoiled a-conformation of PMA-pe in bulk was reflected in its adsorption behaviour at pH = 4. As adsorption of PMA-pe and PAA-pe at pH = 4 lead to identical $\gamma(\infty)$ values (see fig. 3.9.) γ itself is not sensitive to the existence of two different conformations at pH = 4.

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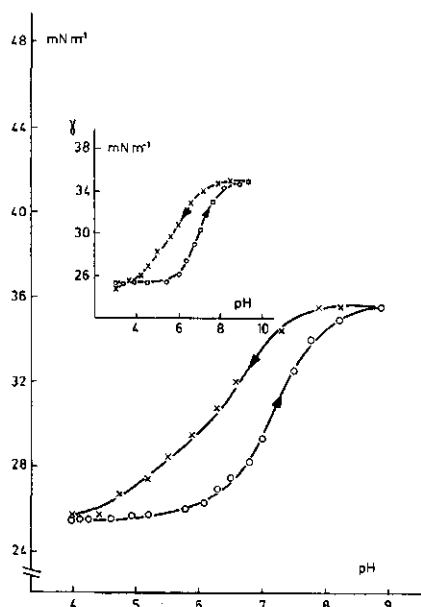
FIG. 4.5. pH 494 and 393 cycle for PAA-pe at $c_p = 100$ ppm in 0.01 M NaCl.

The results presented here plead strongly in favour of the assumption that the bulk conformation affects the number of adsorbed segments in one train. From the time dependence of the interfacial tension (section 3.2.4.) it appeared already that adsorption at high pH is characterized by a considerable reconformation, leading to longer and more strongly bound trains. Adsorption at low pH means that the supply by diffusion leads to a rapid accumulation of segments at the interface with relatively short trains and less reconformation. However, it appears that the adsorption of PAA-pe at pH = 4 gives also enough reconformation to form long trains. As long as attractive forces in the PMA-pe molecule are sufficiently strong they prevent the formation of long trains. Reversible or irreversible adsorption is not due to the differences in free energy gain of adsorption (ΔG_{ads}) of individual segments as was proposed by JAFFÉ and RUYSSCHAERT (1964). ΔG_{ads} of one segment is of the order of kT, for an esterified segment some kT higher than for an undissociated acid segment. The differences in ΔG_{ads} of single segments are too small to be responsible for the difference in desorption. However, differences in ΔG_{ads} between long and short trains are higher. For example for a train of about 5 segments $\Delta G_{ads} \sim 5$ till 10 kT and simultaneous desorption upon increasing charge density is perhaps still possible. For a train of, say 25 segments, simultaneous desorption is not possible. It depends on the bulk conformation (and probably also on other factors) how long the trains are in the adsorbed state. Adsorption at high pH gives apparently always long trains and upon pH lowering only additional adsorption of short trains seems possible, because these trains are always reversibly adsorbed.

More information about the adsorption mechanism has been obtained by some additional experiments. The cycles illustrated in figs. 4.3. and 4.4. have been repeated including waiting times at pH = 9. As already mentioned γ decreases as a function of time for PMA-pe at high pH. The results are represented in figs. 4.6. and 4.7. The consequence of the waiting time at pH = 9, is a reduction of γ. After 5 hours waiting the pH was reduced to pH = 4 again (curve 2 in figs. 4.6. and 4.7.). Then, at pH = 4 two hours have elapsed before the cycle was completed (curve 3). Thus, at pH = 9 γ reached values of 42 and 40 mN m^{-1} respectively for 0.01 and 0.20 M NaCl, which is, within the experimental error, identical with the interfacial tension at pH = 9 before the reduction of pH was started. Consequently, during the adsorption time of 5 hours at pH = 9 a number of segments have been irreversibly adsorbed. The reversible part of the pH 949 cycle (curves 2 and 3) must be attributed to adsorption of segments in short trains. If after completion of the experiment just described, another waiting time of 15 hours is allowed for at pH = 9, γ obtains its

FIG. 4.6. pH 494 cycles for PMA-pe at c_p = 100 ppm in 0.01 M NaCl with waiting times at pH = 4 and pH = 9.
curve 1: pH increase; curve 2: pH decrease after 5 hours at pH = 9; curve 3: pH increase after 2 hours at pH = 4; curve 4: pH decrease after 15 hours at pH = 9; curve 5: pH increase after 2 hours at pH = 4.
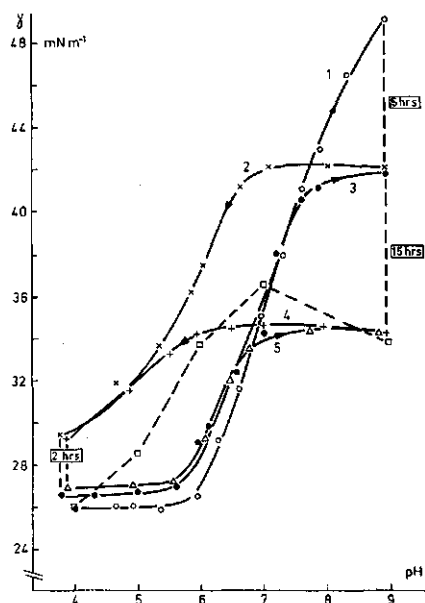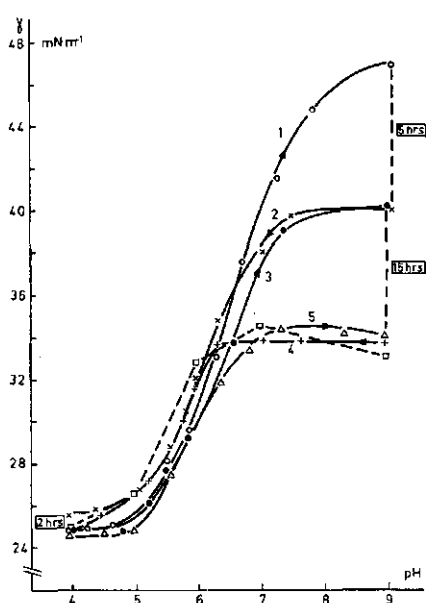Dashed line: γ (∞) at direct adsorption (see fig. 3.6.).

FIG. 4.7. pH 494 cycles for PMA-pe at c_p = 100 ppm in 0.20 M NaCl with waiting times at pH = 4 and pH = 9.
Curves 1-5: see fig. 4.6.
Dashed line: γ (∞) at direct adsorption (see fig. 3.7.).

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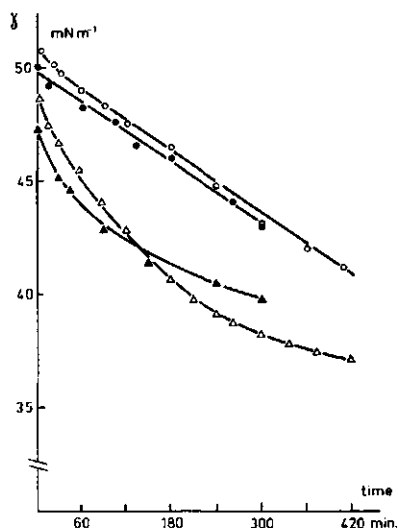
FIG. 4.8. Time dependence of the interfacial tension of solutions of PMA-pe at $c_p = 100$ ppm at pH $= 9$.
Directly, 0.01 M NaCl (○); after pH increase from pH $= 4$ to pH $= 9$, 0.01 M NaCl (●); directly, 0.20 M NaCl (△); after pH increase from pH $= 4$ to pH $= 9$, 0.20 M NaCl (▲).

steady-state value at that pH. A subsequent pH 949 cycle (curves 4 and 5) agrees now rather well with the 949 cycle reported in fig. 4.2a. In 0.20 M NaCl both pH cycles are the same, but a 949 cycle at $c_p = 100$ ppm in 0.20 M NaCl has not been shown in section 4.3.1. Apparently during these 15 hours still more segments are irreversibly adsorbed. In fig. 4.8. it is shown that the rate of decrease of γ at pH $= 9$ does not significantly depend on the way of adsorption, i.e. whether adsorption takes place directly from the solution at pH $= 9$ or from the solution after adsorption at pH $= 4$, followed by pH increase to 9. This indicates that upon increasing pH, after adsorption at pH $= 4$, the blank value of the interfacial tension indeed reflects a complete desorption of the PMA-pe molecules. Moreover, it underlines that at pH $= 9$ the rate of reduction of interfacial tension is mainly caused by reconformation and spreading and that diffusion is only a minor factor.

4.3.3. pH cycles of PMA-pe in the presence of Ca^{2+} ions

Hitherto the adsorption behaviour has been examined in the presence of Na^+ ions. Ca^{2+} ions can behave differently, because of bivalent bonding of Ca^{2+} ions with dissociated carboxylic groups. Therefore the pH cycles have been repeated at 10, 100 and 1000 ppm in the presence of Ca^{2+} ions. Some results, both for a pH 949 and a 494 cycle at $c_p = 100$ ppm are given in fig. 4.9.

For a pH 949 cycle the results are in agreement with those for Na^+ ions (fig. 4.2.) except for some slight differences viz. there is hardly any discrepancy between $\gamma(\infty)$ and the pH cycle values of γ. For a pH 494 cycle it can be seen that on pH increase the blank value at pH $= 9$ has not been reached, although a definite increase was found. If at pH $= 9$ the pH decrease was delayed the γ was lowered till the corresponding $\gamma(\infty)$ value at pH $= 9$ had been reached.
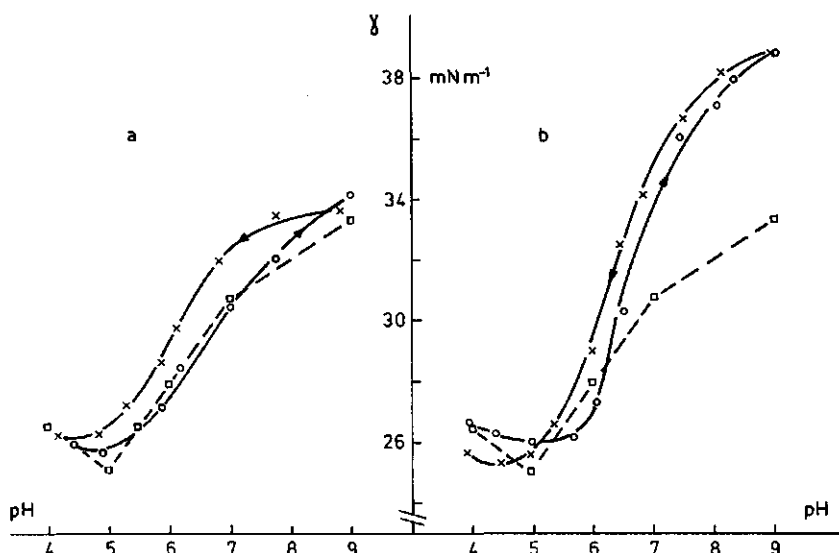
FIG. 4.9. pH cycles for PMA-pe at $c_p = 100$ ppm in 0.01 N $CaCl_2$.
a. One-hour pH 949 cycle.
b. One-hour pH 494 cycle, without waiting time at pH = 9.
Dashed lines: $\gamma\,(\infty)$ at direct adsorption (see fig. 3.8.).

Consequently at pH = 4 the amount of irreversibly adsorbed segments is smaller than at pH = 9, although a desorption of the whole molecule is not possible. Even for a pH 494 cycle at $c_p = 10$ ppm it was not possible to obtain the blank value. From these results we can conclude that the binding force between Ca^{2+} ions and dissociated carboxylic acid groups is so strong that complete desorption of PMA-pe molecules is prevented. By Ca^{2+} ions some of the trains consist of a sufficiently large number of segments that desorption is mainly prevented.

4.3.4. *pH x94 and x49 cycles of PMA-pe*

If the polymer conformation behaviour in bulk is compared with that at interfaces the following picture emerges. In bulk, PMA and PMA-pe can occur in two conformations, a and b. The transition is reversible and occurs at a degree of neutralization of about 0.3, i.e. about pH = 5, depending on c_p and ionic strength. The transition pH increases with increasing intramolecular interaction (see chapter 2). On the surface a comparable situation has been found in that the mode of adsorption at low pH and high pH are different. For sake of argument these two modes can be designated as a_s and b_s. It has already been ascertained that no reversible transition $a_s \rightleftharpoons b_s$ can occur in the interface. Now the question is studied at what pH the mode of adsorption from solution leads to the a_s- and to the b_s-form. To that order we performed x94 and x49 cycles.

For the sake of comparison with the preceding cycles this effect has been studied again with 100 ppm solutions containing 0.01 or 0.20 M NaCl. Fig. 4.10. shows some results in 0.01 M NaCl (the descending branches of the cycles are not plotted). Adsorption at pH = 7, followed by pH increase to 9 did not change γ significantly. Also if the pH was first decreased to 4, and subsequently increased to pH = 9 (not shown in the figure) the same γ was obtained at pH = 9. Curve 2 of fig. 4.10. shows the results of the same experiment, after adsorption at pH = 6. Again at pH = 9 γ was obtained at 36 mN m^{-1}. Starting at pH = 5 (curve 3) does still not significantly alter the result, although the relaxation is somewhat reduced. This leads to the conclusion that, starting at pH $\geqslant$ 5 in 0.01 M NaCl already an appreciable part of the adsorbed segments is irreversibly attached. However, starting at pH = 4.7 (curve 4) the result is completely different. Upon pH increase, γ now reaches about 48 mN m^{-1} which is quite near the blank value. From fig. 2.2. it is concluded that at pH = 4.7 at c_p = 100 ppm in 0.01 M NaCl the degree of ionization is about 0.10 and that in bulk PMA-pe is present in the a-conformation. Hence adsorption takes place from a solution in which PMA-pe is in the hypercoiled structure
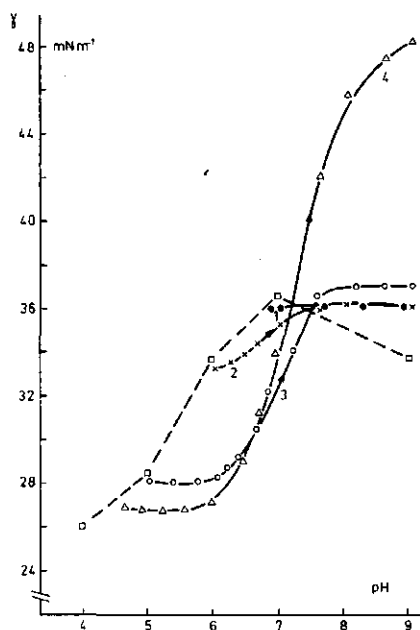
FIG. 4.10. pH x 9(4) cycles for PMA-pe at c_p = 100 ppm in 0.01 M NaCl. Only the ascending branches have been plotted.
curve 1 : x = pH 7; curve 2 : x = pH 6; curve 3 : x = pH 5; curve 4 : x = pH 4.7. Dashed line: γ (∞) at direct adsorption (see fig. 3.6.).
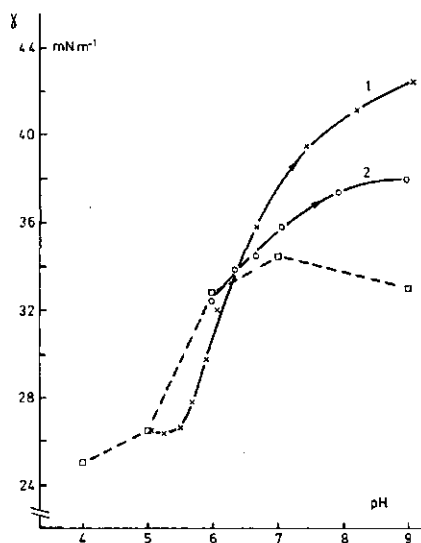
FIG. 4.11. pH x 9(4) cycles for PMA-pe at c_p = 100 ppm in 0.20 M NaCl. Only the ascending branches have been plotted.
curve 1 : x = pH 5; curve 2 : x = pH 6. Dashed line: γ (∞) at direct adsorption (see fig. 3.7.).

and it explains the reversible nature of the adsorption upon pH increase. At pH = 5, the degree of ionization (see fig. 2.2.) is about 0.15 and hence in bulk PMA-pe is still mainly in the a-conformation, whereas this is not reflected in the reversible adsorption upon pH increase. This means that at pH = 5.0 the hypercoiled bulk structure of PMA-pe is broken down after adsorption onto the interface. An analogous break-down during adsorption has been found for proteins at interfaces. The surface denaturation of proteins upon adsorption already occurs as the native structure in bulk is still stable (CUMPER and ALEXANDER, 1950).

Fig. 4.11. shows some results for x94 cycles in 0.20 M NaCl. Again the descending branches of these cycles are not plotted.). For adsorption at pH = 6 still a fraction of the segments is reversibly adsorbed. At pH = 5 this fraction is much larger. In the case of 0.20 M NaCl the conformational transition in the interfacial layer is not yet complete at a bulk degree of ionization of 0.65 (α' = 0.65 is comparable with pH = 6 at c_p = 100 ppm in 0.20 M NaCl). The shift in the conformational transition in the adsorbed layer with respect to 0.01 M NaCl agrees with the analogous shift in the bulk phase transition as found in figs. 2.2. and 2.3. In the case of 0.20 M NaCl it cannot be concluded that the hypercoiled structure in bulk breaks down during adsorption, as was found for 0.01 M NaCl.

FIG. 4.12. pH cycles for PAA at c_p = 100 ppm.
a. pH 494 cycles in 0.01 M NaCl.
   curve 1 + 2: without waiting time at pH = 9.
   curve 1 + 3: 24 hours' waiting time at pH = 9.
b. pH 949 cycle in 0.20 M NaCl with 24 hours' waiting time at pH = 9.

4.3.5. *Comparison of PMA and PAA cycles with PMA-pe and PAA-pe cycles*

In chapter 2 it was found that the existence of the hypercoiled conformation of PMA-pe and PMA was due to the presence of the methyl sidegroup in the main chain. Therefore it is interesting to investigate the adsorption mechanism from solutions containing the a-conformation and the b-conformation of the non-esterified polyelectrolytes and to compare them with the γ—pH cycles of PMA-pe and PAA-pe. For that purpose γ—pH cycles have been performed for 100 ppm solutions of PMA and PAA at different ionic strength of NaCl. Special attention has been paid to the effect of ionic strength, which is more pronounced for PMA than for the esterified polyelectrolytes.

Figs. 4.12a. and 4.12b. give the results for a pH 494 cycle in 0.01 M NaCl and a pH 949 cycle in 0.20 M NaCl respectively, both for PAA. These two cycles are a selection of many more, taken at different ionic strengths. The directly estimated $\gamma(\infty)$ values (see fig. 3.9.) are not replotted here, because they coincide with the γ values obtained with the cycles. As is shown here the effect of ionic strength (0.01 and 0.20 M NaCl) is not significant. However, for PMA the effect of ionic strength is more pronounced as is shown by comparison of figs. 4.13. and 4.14. For PMA the 494 and 949 cycles are plotted for 0.01 M NaCl in figs. 4.13a. and 4.13b. respectively. These results agree roughly with those of fig. 4.12. except for the somewhat higher deviation from the blank value at high pH. The following conclusions can be drawn:
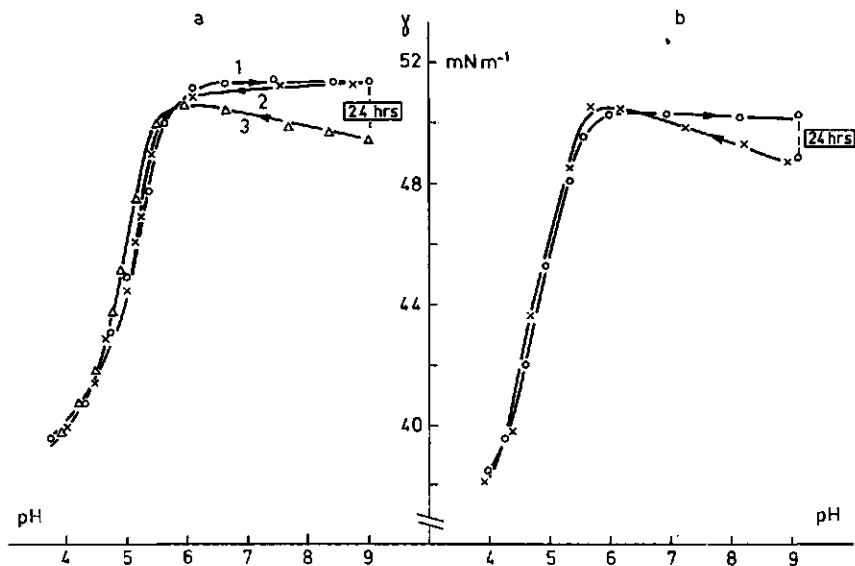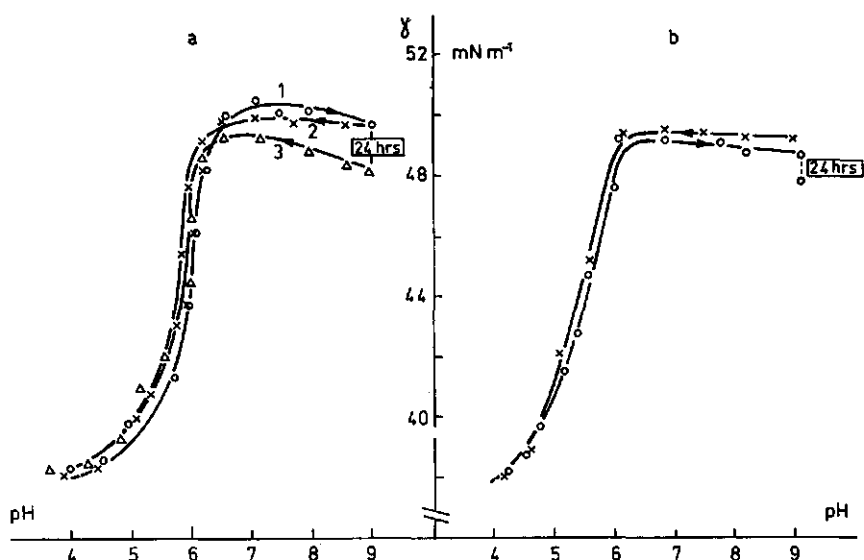

FIG. 4.13. pH cycles for PMA at $c_p = 100$ ppm in 0.01 M NaCl.
a. pH 494 cycles.
   curve 1 + 2: without waiting time at pH = 9.
   curve 1 + 3: 24 hours' waiting time at pH = 9.
b. pH 949 cycle with 24 hours' waiting time at pH = 9.

1. Relaxation after changing pH is fast. From our earlier findings with PMA-pe and PAA-pe (figs. 4.2. and 4.5.) it can be concluded that the ester groups are fully responsible for any slow relaxation that occurs. The ester groups cause long and strongly bound trains which lead to steric hindrance in the conformational changes of the adsorbed polyelectrolyte molecules due to pH changes.
2. Irrespective of whether or not the a-conformation is present in bulk complete desorption upon increasing pH always takes place. Hence in the absence of ester groups the trains are too small to give a ΔG_{ads} per train that is sufficient to prevent desorption upon pH increase. It follows that in the absence of ester groups adsorption is too weak to allow for the discrimination between a- and b-conformation.

The adsorption behaviour of PAA was not affected by the ionic strength, but for PMA this is quite different (compare fig. 4.13. with fig. 4.14.). Fig. 4.14a. shows a pH increase from 4 to 9 (curve 1) and, after 24 hours waiting at pH = 9, a complete 949 cycle has been performed (curves 2+3). This has been repeated after another 24 hours waiting at pH = 9 (curves 4+5). Waiting at pH = 9 results in an appreciable γ lowering. This γ lowering is irreversible. Fig. 4.14b. shows the corresponding pH 949 cycle and again it has been demonstrated that contrary to the situation in 0.01 M NaCl, an appreciable lowering of γ is
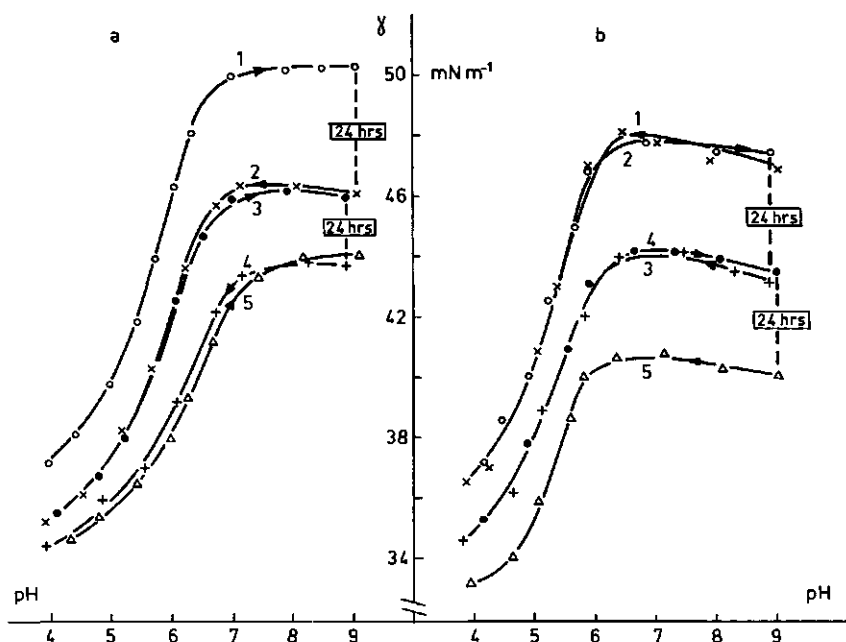

FIG. 4.14. pH cycles for PMA at c_p = 100 ppm in 0.20 M NaCl.
a. pH 494 cycles.
b. pH 949 cycles.
The curves 1–5 correspond to the subsequent pH changes after adsorption at pH = 4 (a) and pH = 9 (b).

observed. After one complete cycle (curve $1+2$) the interfacial tension reached the starting value of about 46.5 mN m^{-1}, but during the next 24 hours at pH $= 9$ γ gradually decreased to 43 mN m^{-1}. A pH 494 cycle (curves $3+4$) demonstrates the irreversible nature of this additional adsorption. Again 24 hours waiting at pH $= 9$ results in a further decrease (curve 5). The irreversibility of the additional adsorption after a pH 949 cycle is still more pronounced at higher molarity (0.5 M NaCl, not shown). Summarizing it can be stated that PMA can also adsorb at the paraffin oil–water interface at a high charge density on the chain, provided that the ionic strength is sufficiently high. Moreover this adsorption is irreversible and a disruption of the structure of the adsorbed layer by pH cycles results in an additional, irreversible adsorption. The irreversible nature of PMA adsorption at high pH indicates that ester segments are not essential for irreversible adsorption; they only make a favourable contribution to the formation of long trains, especially with charged molecules. The results of PMA adsorption at high pH plead also strongly in favour of the train length model as the determining factor for (ir)reversible adsorption behaviour.

4.3.6. *Changes in PMA-pe concentration after adsorption*

When the number of adsorbed segments per unit area in the first layer does not change when diluting or concentrating the bulk solution, interfacial tension measurements will be inadequate to detect changes in the adsorbed layer which occur after this dilution or concentration. However, pH cycles made after dilution or concentration seem to be a more suitable tool. Cycles, measured after changing the bulk conditions have to be compared with the cycles pertaining to the initial polyelectrolyte concentration.

Concentration experiments have been performed at pH $= 4$ and pH $= 9$. The initial concentration was 10 ppm and was stepwise increased till a final concentration of 1000 ppm. At pH $= 9$ the lowering of γ during concentrating was very pronounced and the final pH cycle corresponds with that of fig. 4.2b. Therefore it is safe to conclude that upon concentrating at pH $= 9$ the adsorption increases. By performing a pH cycle after concentration at pH $= 4$ the results were analogous to a pH 494 cycle at $c_p = 1000$ ppm. Hence it can be concluded that in all cases adsorption was increased upon concentrating.

Dilution experiments have also been performed at pH $= 4$ and pH $= 9$. The initial concentration was 1000 ppm and the final one about 10 ppm. After each dilution step a time lapse of one hour has been observed. No rise in γ could be observed during dilution, neither at pH $= 9$ nor at pH $= 4$. At pH $= 9$ the final cycle corresponds to that of fig. 4.2b. and it has been concluded that no desorption occurred upon diluting the bulk solution. However, at pH $= 4$ the final cycle corresponds with a pH 494 cycle at $c_p = 10$ ppm, which means that upon dilution desorption of PMA-pe can take place.

4.3.7. *Electrolyte substitution cycles*

These experiments have been performed at $c_p = 10$ ppm, since the substitu-

tion effects can be measured most clearly at this concentration (see figs. 3.3.–3.4.). After each change the pH has to be corrected. The interfacial tension is measured one hour after the change in ionic strength. From the results it can be concluded, that:

1. an increase of the NaCl concentration (from 0.01 to 0.20 M NaCl) causes a decrease of γ, except at pH $= 9$. The lowering of γ agrees roughly with the differences between the $\gamma(\infty)$ values for 0.01 M and 0.20 M NaCl (see fig. 3.4.).
2. a decrease of the NaCl concentration (from 0.20 to 0.04 M NaCl) does not result in an increase of γ.
3. substituting $CaCl_2$ up to 80% for 0.01 M NaCl decreases γ. This has been examined at pH $= 6$ and pH $= 9$. At pH $= 9$ this substitution always resulted in an instantaneous lowering of γ, whereas at pH $= 6$ the effect is much more time-dependent.
4. substituting NaCl up to 80% for 0.01 N $CaCl_2$ does not give any appreciable change of γ.

It is indicated that desorption of segments is not likely by these substitution effects. Only more rigorous disturbances e.g. charging the polyelectrolyte after adsorption can result in a desorption, provided the trains of adsorbed segments are not too long.

4.4. SUMMARY

Changing bulk conditions after equilibration of the adsorbed layer gives interesting information about the mode of adsorption. The changes in pH after equilibration (pH 494 and 949 cycles) enable us to distinguish between reversible and irreversible adsorption of the polyelectrolyte molecules upon charging. It has been put forward that (ir)reversible adsorption as a function of pH is related to the number of segments in one train rather than to differences in adsorption energies of individual segments (ester and undissociated acid segments). Long trains make desorption very unlikely upon increasing the electrostatic repulsion on the polyelectrolyte chain. In this connection, reversible adsorption upon pH increase is possible if the trains are short enough to desorb upon charging.

By measuring $\gamma-$pH cycles it has been shown that the mode of adsorption of PMA-pe depends to some extent on the conformation in the bulk phase. At low pH PMA-pe adsorbs with relatively short trains. As a consequence, after adsorption at low pH the PMA-pe molecules desorb completely upon charging. However, at high pH PMA-pe adsorbs irreversibly. The adsorption of PAA-pe is always irreversible, both at low and high pH. As only PMA-pe has been characterized by a hypercoiled a-conformation at low pH it is concluded that adsorption from solution with PMA-pe in the a-conformation gives short trains and that adsorption from solutions with PMA-pe in the b-conformation results in the formation of long, irreversibly adsorbed trains.

By comparing the $\gamma-$pH cycles with those for PMA and PAA the effect of the ester groups has been investigated. As PAA does not occur in the hyper-

coiled conformation at low pH, it would be expected to desorb irreversibly at low pH. However, PAA desorbs completely upon pH increase. It means that reversible adsorption at low pH is only prevented if the molecule is partly esterified.

The pH 494 cycles for PMA show that some adsorption of the non-esterified polyelectrolytes is possible at pH = 9, provided that the ionic strength is high enough ($\geqslant$ 0.20 M NaCl). For PAA no adsorption could be detected at pH = 9 in 0.20 M NaCl. The adsorption of PMA at pH = 9 is irreversible, indicating that the ester segments are not essential for adsorption at pH = 9, although they promote it. It is notable that a molecule with a low interfacial activity (PMA, see fig. 3.9.) can adsorb irreversibly after long periods of time by the formation of long trains.

The pH cycles of PAA-pe and PMA-pe are characterized by a relaxation effect after every pH change. The relaxation is faster at higher ionic strength, which makes the chain more flexible, and upon pH lowering. PAA and PMA in the interface relax very rapidly and the γ values for pH-increase after adsorption at pH = 4 always agree with the γ values for pH-decrease. Hence, relaxation effects are attributable to the presence of ester segments, which delay reconformation after changing the electrostatic repulsion at the polyelectrolyte chain.

Changing the polyelectrolyte concentration (PMA-pe), electrolyte concentration (NaCl) or substitution of counterions after equilibration have also been investigated. By PMA-pe concentration the adsorption always increases, whereas by PMA-pe dilution a desorption possibly occurs at low pH. By NaCl concentration the interfacial tension decreases, whereas by dilution an increase of the interfacial tension could not be detected. Substitution of Ca^{2+} ions for Na^+ ions decreases the interfacial tension, whereas the reverse substitution does not result in the opposite effect.

The time dependence and steady-state interfacial tension measurements (section 3.2.) did not allow us to locate the possible existence of the a- and b-conformation in the adsorbed layer. It is shown that the reaction of γ upon changing the conditions in the bulk phase *after* adsorption gives more information.

5. EMULSIONS STABILIZED BY POLYELECTROLYTES AND THE MECHANISM OF EMULSIFICATION

5.1. INTRODUCTION

The emulsification process and the stability of emulsions are subjects of great significance in applied as well as fundamental fields of research. This is underlined by the great number of articles published in a wide range of journals.

An emulsion is a dispersion of liquid droplets in another liquid, the two of which are immiscible. As the thermodynamically stable state of two immiscible liquids is their bulk form with a minimum of interfacial area, any emulsion is metastable. The presence of a suitable emulsifying agent is necessary to maintain the metastable state for longer periods of time. It means that the way of preparation of an emulsion and the kind of emulsifying agent can have a considerable effect upon emulsion properties, such as dispersity, stability to coalescence, flocculation and viscosity. Moreover, other physicochemical parameters affect the behaviour of the emulsion, such as the concentration of the emulsifying agent, the time and intensity of agitation, the temperature, the nature of the oil phase and the volume fractions of both phases. BECHER (1967) demonstrated that some of these parameters affect the formation of the droplets, whereas other parameters rather influence the stability to coalescence. Therefore it seems appropriate to distinguish between the emulsifying capacity and the stabilizing capacity of an emulsifying agent. The dispersity after agitation is a measure of both and the rate of coalescence after agitation a measure of the second parameter. Just one of the main differences between low molecular and macromolecular stabilizers is their ability to prevent coalescence after agitation (KITCHENER and MUSSELLWHITE, 1968). In many technological processes this property of macromolecules is a chief point of interest and therefore much applied research on emulsions has been concerned with this aspect. However, to obtain basic information about the factors that affect the stabilizing capacity of an emulsifying agent, one needs to investigate systems that are not very stable to coalescence. This explains, for example, why fundamental investigations on this subject are more concerned with low molecular weight stabilizers, allowing a stepwise variation in molecular properties, e.g. in the H.L.B. value. Proteins and synthetic polymers are much less suitable for this type of quantitative investigations. Several authors have tried to avoid the difficulties for polymers, by preparing a small number of droplets in the continuous phase and measuring their averaged life-time (BISWAS and HAYDON, 1962; EL'-SHIMI and IZMAILOVA, 1967). SHAREV et al. (1970) tried to coalesce emulsions stabilized by polymers, by increasing the temperature or by centrifugation. BOYD et al. (1972) demonstrated that the oil separation method is unsuitable to be used for comparing the stabilizing capacity of macromolecules, since significant changes in droplet size already occur before oil separation.

In this chapter the properties of oil-in-water emulsions stabilized by any of the four polyelectrolytes (see chapter 2), will be discussed in relation to their emulsifying capacity. In other words emphasis is not so much laid on the properties of the emulsions once they are formed, but on their very formation. As a measure of this, we shall use the interfacial area of the obtained emulsion (S, in m² per ml paraffin oil) and the adsorption of the polyelectrolytes after emulsification (Γ_e, in mg per m²). Therefore it is necessary to measure both factors – specific area and total adsorption – simultaneously and independently. The adsorption has been measured analytically and the specific interfacial area by using the turbidity technique as described by GOULDEN (1958) and WALSTRA (1965, 1968). The adsorption per unit area can be compared with interfacial tension measurements and with the adsorption at the liquid–solid interface (see chapter 3). Emulsification, however, considerably increases the interfacial area during the adsorption process and therefore it cannot be anticipated, that the conformation of the adsorbed layer agrees with the one on an undisturbed L/L interface.

Special attention will be paid to the effect of the degree of neutralization, the polyelectrolyte concentration, the ionic strength and the nature of the counterion on the dispersity and the adsorption. Moreover, in view of the interesting differences in the adsorption behaviour at low and high pH (chapter 4) and because of the observed conformational transition in bulk (chapter 2) it was found worth-while to verify whether these phenomena were also reflected in the emulsion behaviour. In this chapter a general description of the experiments and results will be given, followed by a more detailed discussion of the emulsification process with polyelectrolytes as emulsifiers in an Ultra-Turrax disperser.

5.2. Preparation of the emulsions

As the properties of the emulsions may strongly depend on the way of preparation a standard method has been adapted for preparing reproducible emulsions. For the sake of comparison with experiments on PVA stabilized emulsions (LANKVELD and LYKLEMA, 1972), the method was the same as used in that investigation. A 250 ml glass beaker (diameter about 7 cm) was filled with exactly 80 ml polyelectrolyte solution of known concentration. Paraffin was then added until exactly 20 ml paraffin of known density had been introduced. The contents of the beaker were emulsified with a type T45 Ultra-Turrax, ex Janke and Kunkel K.G., Germany. The time of emulsification was exactly 2 minutes. At low α values this time was long enough to obtain maximum dispersity, whereas at high α values a further increase in the dispersity could be obtained by longer emulsification.

During emulsification the temperature of the emulsion rose to about 54°C, the final value depending on the polyelectrolyte concentration. Finally the emulsions were cooled to room temperature. The specific area of the emulsion was slightly dependent on the final temperature after emulsification. By chang-

ing the starting temperature a greater variation in the final temperature was obtained. The temperature coefficient varies between 0.017 and 0.029 m² °C⁻¹ per ml oil depending on α, for a final temperature below 65°C. In the experiments, where the dispersity was studied as a function of polymer concentration, the final temperature varied between 52°C at low and 58°C at the highest concentration. Therefore the maximal correction is about 0.18 m² °C⁻¹ per ml oil, i.e. 10% of the measured dispersity. The temperature corrections have not been made in the dispersities given in this chapter.

Γ_e and S were always determined between 14 and 20 hours after preparation, unless explicitly mentioned otherwise. Before measuring S the emulsions were highly diluted with an aqueous solution of 0.1% polyoxyethelene lauryl ether (Brij 35, ex Atlas Chemicals) to keep them stabilized in this diluted form. Using this standard procedure the inaccuracy of S was within 5% for the higher specific areas. For the lower areas ($S < 1.0$ m²/ml) this was within 10%. The dispersity was not time-dependent, indicating the high stabilizing capacity of these macromolecular stabilizers once the emulsions were formed and cooled.

In view of the reproducibility of the area determination (section 5.4.) and the neglection of temperature corrections systematic trends for S and Γ_e as a function of polyelectrolyte supply will only be considered if they exceed about 10%.

5.3. DETERMINATION OF THE POLYELECTROLYTE ADSORPTION

Γ_e was calculated from the material balance and the dispersity. The remaining concentration in the aqueous phase was determined in duplicate by the titration procedure (see section 2.3.). The oil phase was removed by centrifuging the emulsion for 10–30 minutes in a Sorval RC 2-B centrifuge at 4.000 till 15.000 rev./min.; the number of revolutions was higher at increased α values and polymer concentrations. The time of centrifugation had no influence on S as was shown by redispersion. To check whether this centrifuging process causes a desorption, some experiments have also been performed by simple creaming of the emulsions for some days. No desorption could be detected. Γ_e is not dependent on the waiting time after preparation for $\alpha < 0.70$; at higher α values Γ_e was slightly time-dependent, indicating that reconformation under that condition takes much time, which agrees with the results of chapter 3. In that case, after 15 hours the adsorption is about 10% higher than immediately after agitation.

The inaccuracy of the adsorption experiments was found to be within 2% for $\alpha \leqslant 0.70$, whereas at higher α values it was as high as 10% depending on the supply of polyelectrolyte. This poorer reproducibility is caused by the relatively short titration stretch to $\alpha = 1.0$ and the relatively small amount adsorbed in comparison with the supply of polyelectrolyte.

5.4. DETERMINATION OF THE SPECIFIC AREA OF THE EMULSIONS

5.4.1. *Introduction*

The determination of the size-distribution function of a dispersed system is normally a rather time-consuming procedure. For our experiments we are primarily interested in the dispersity, i.e. the specific interfacial area of the emulsion S, expressed in m^2/ml paraffin oil. Since S depends on the supply of polymer, it has to be determined for every emulsion. It is therefore not necessary to use a technique by which fine details of the globule size distribution are accurately obtained and it is advantageous if the technique is suitable for routine analysis. The turbidity technique as extensively applied in milk research by GOULDEN (1958) and WALSTRA (1965, 1968), is very suitable for this purpose once the preliminary computations are performed. WALSTRA (1968) and LANKVELD and LYKLEMA (1972) used it already for paraffin oil-in-water emulsions. It was concluded that this method can be applied for globule volume-surface diameters $\bar{d}_{vs}$ between 0.2 and 15 µm and for any distribution. For relatively coarse emulsions $\bar{d}_{vs}$ can be obtained with accuracy, but little information about the distribution function will then be obtained.

The first step of the method is the computation of theoretical turbidity spectra for a wide scale of assumed globule-size distributions at a given ratio of the refractive indices of the continuous and dispersed phase on the basis of the MIE (1908) theory. Experimental spectra are obtained by measuring the optical density of the emulsion at several wavelengths. Both spectra are then compared after plotting the same parameters. The shift between the two of them, required to merge them then gives $\bar{d}_{vs}$. The turbidity measurements have been checked independently with a model A Coulter Counter. Thus the particle-size distribution of the emulsions was found to be an upper limit function with the width σ and maximum droplet diameter d_m depending on the emulsifying conditions. In formula:

$$f(u) = \frac{r}{u^4 (r-u)} \exp\left[-\frac{\ln^2\{ru/(r-u)\}}{2\ln^2\sigma}\right], 0 < u < r \qquad (5.1.)$$

where $u^3 f\{ru/(r-u)\}$ is a log-normal distribution and $u = d/d_1$, d being the droplet diameter and d_1 an auxiliary parameter (WALSTRA, 1968). The width is determined by σ and the truncation by $r = d_m/d_1$.

In this study, no further attention will be paid to possible differences in the width and maximum diameter in the particle-size distribution due to differences in α and c_p. Although such differences do exist, they are probably small as has also been found with PVA stabilized emulsions (LANKVELD and LYKLEMA, 1972).

5.4.2. *Turbidity measurements*

The optical density E of a dilute homodisperse system of spherical particles obeys LAMBERT-BEER'S law for light scattering:

$$E = \log I_0/I = \tfrac{1}{4}\,\pi d^2\, Q\, N\, l\, (\log e) \tag{5.2.}$$

in which for a monodisperse emulsion:

E = optical density

I_0, I = intensity of incident and transmitted light respectively

d = droplet diameter

N = number of emulsion droplets per unit volume

l = optical path length

Q = light scattering coefficient

Q depends on the droplet diameter d, the ratio of refractive indices n_d/n_c and the wavelength λ. The magnitude of Q can be related to the dimensionless parameter ρ:

$$\rho = \frac{2\,\pi\,d\,(n_d - n_c)}{\lambda} \tag{5.3.}$$

This parameter again contains the droplet size in which we are interested.

The relation between Q and ρ can in principle be derived from the MIE theory. HELLER et al. (1959) give an approximation for this highly complicated relation for $\rho < 2.5$ and WALSTRA (1964) derived an approximation for $\rho \geqslant 2.5$ and $1 < n_d/n_c < 1.25$. As our experimental conditions lie also in the latter range, it is suitable for our purpose.

It is necessary to make corrections for forward scattering. Formally this can be represented by replacing Q in equation 5.2. by a quantity Q^*. The relationship between Q and Q^* has been given by WALSTRA (1965) for an angle of acceptance of $1.5°$ and $n_d/n_c = 1.10$. LANKVELD (1970) makes a similar correction for $n_d/n_c = 1.05$.

To be able to compare theoretical and experimental spectra it is useful to introduce the reduced turbidity $Z = Q^*/\rho$ (dimensionless). Combination and simplification of equation 5.2. and 5.3. yields:

$$Z = Q^*/\rho = \frac{E\,\lambda}{1.30\,\pi\,l\,\varphi\,(n_d - n_c)} \tag{5.4.}$$

in which:

Q^* = scattering coefficient, corrected for forward scattering

φ = volume fraction of the dispersed phase in the cuvette

The right-hand side parameters of equation 5.4. are known or can be measured for each emulsion.

For polydisperse systems the relations 5.2. and 5.3. must be replaced by more complicated ones. Instead of equation 5.4. can then be derived (WALSTRA, 1965):

$$Z = \overline{Q^*/\rho_{32}} = \frac{\lambda}{2\,\pi\,(n_d - n_c)} \cdot \frac{\sum_i Q^*\, N_i\, d_i^2}{\sum_i N_i\, d_i^3} \tag{5.5}$$

As $d_i = d_1 \cdot u_i$ equation 5.5. can be modified as follows:

$$Z = \overline{Q^*/\rho_{32}} = \frac{\lambda}{2\pi d_1 (n_d - n_c)} \cdot \frac{\sum_i Q^* N_i u_i^2}{\sum_i N_i u_i^3} \tag{5.6.}$$

or:

$$Z = \overline{Q^*/\rho_{32}} = \frac{1}{\rho_1} \cdot \frac{\int_0^\infty Q^* u^2 f(u)\, du}{\int_0^\infty u^3 f(u)\, du} \tag{5.7.}$$

in which: ρ_1 is the dimensionless auxiliary parameter and ρ_{32} the dimensionless volume-surface diameter.

If Q^* is known as a function of ρ, one can calculate the theoretical turbidity spectrum for a certain droplet-size distribution function. For the paraffin-water system ($n_d/n_c = 1.10 \pm 0.01$) and a fixed angle of acceptance (1.5°) these calculations have been performed for $r = 1, 2, 3$ and 5 and for $1.4 < \sigma < 7.0$ (see equation 5.1.).

The experimentally reduced turbidity has been measured with a modified Beckman DU spectrophotometer. The standard cuvette holder is replaced by one in which several diaphragms and a lens are placed, as shown in fig. 5.1., the angle of acceptance being set at 1.5°. Before each measurement the emulsion was diluted till the optical density at 380 nm in a 0.5 cm cuvette was between 0.2 and 0.6. The optical density was measured at 380, 420, 470, 530, 615, 725, 890 and 1150 nm. The refractive indices at these wavelengths were taken from the literature (WALSTRA, 1968) and each batch of paraffin was checked by measuring the refractive index at 589 nm.

The Z value, obtained from equation 5.4. has been plotted as a function of $\log m$, where m is defined by:

$$m = \overline{\rho}_{32}/\overline{d}_{32} = 2\pi (n_d - n_c)/\lambda \tag{5.8.}$$

One can find $\overline{d}_{32}$ by shifting the experimental $Z - \log m$ curve until it coincides with the calculated theoretical $Z - \log \overline{\rho}_{32}$ curve. The shift corresponds
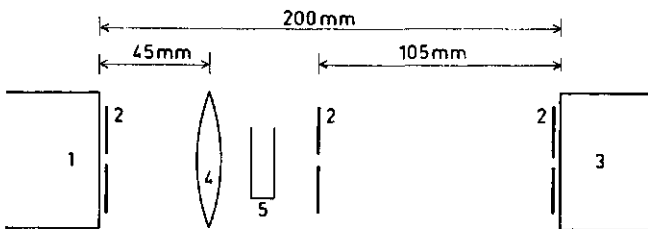

FIG. 5.1. Modification of the Beckman DU spectrophotometer for turbidimetry.
1 = monochromator; 2 = diaphragm; 3 = photocell; 4 = lens (+20d); 5 = cuvette.

with log $\bar{d}_{32}$. The specific interfacial area can then be calculated from:

$$S = 6/\bar{d}_{32} \tag{5.9.}$$

in which S is the interfacial area per ml oil phase.

5.5. Results and discussion

S and Γ_e are measured as a function of several experimental conditions. Of each emulsion both parameters have been measured in duplicate which normally differs less than a few percents.

The results have been plotted as a function of polyelectrolyte supply c_p' (expressed in mg/ml paraffin oil) and not as a function of the final concentration after finishing emulsification. In this way results are better comparable at different values of φ (see chapter 6). Moreover S and Γ_e for emulsions stabilized by polymers are not related to the final concentration. The range of c_p' normally lies between 1 and 16 mg/ml paraffin oil, although at low α and low ionic strength we are restricted to lower upper limits. At a given value of φ, c_p' is proportional to c_p.

5.5.1. *Effect of the degree of neutralization and ionic strength on the specific area*

Results are represented in fig. 5.2. as a function of c_p' at $\alpha = 0.10$–1.0 at 4 NaCl concentrations (0.02, 0.05, 0.10 and 0.20 M NaCl). Definite differences as a function of α can be observed. Roughly one can distinguish three main regions of α:

1. $\alpha = 0.10$. S increases strongly with c_p'. The effect of ionic strength reverses with increasing c_p'.
2. $0.30 \leqslant \alpha \leqslant 0.50$. S is independent of c_p' at $c_p' \geqslant 1$ mg/ml paraffin oil. S is slightly reduced with increasing ionic strength. The differences between $\alpha = 0.30$ and $\alpha = 0.50$ are negligible.
3. $\alpha \geqslant 0.70$. As a function of c_p', S passes through a maximum. At higher ionic strength and lower α this effect is more significant. The maximum in S cannot be caused by temperature effects during emulsification (see section 5.2.). If corrected for differences in the final temperature this maximum is even more pronounced. It means that counterbalancing factors during emulsification determine the final dispersity. S is slightly reduced with increasing ionic strength, although it is remarkable that at $\alpha = 1.0$ this effect is negligible for 0.02 M < NaCl < 0.20 M.

The three main regions of α agree more or less with previous results for PMA-pe. Viscosimetry (section 2.4.) showed that at $\alpha < 0.30$ the PMA-pe molecules were hypercoiled. Between $\alpha = 0.30$ and 0.70 the hypercoiled structure passes into a more open, flexible conformation. At $\alpha > 0.70$ the high charge density of the chain reduces the flexibility of the polyelectrolyte again. From steady-state interfacial tension measurements as a function of pH (see fig. 3.6. and 3.7.) it is also found that there are three regions of α (c.q. pH). This
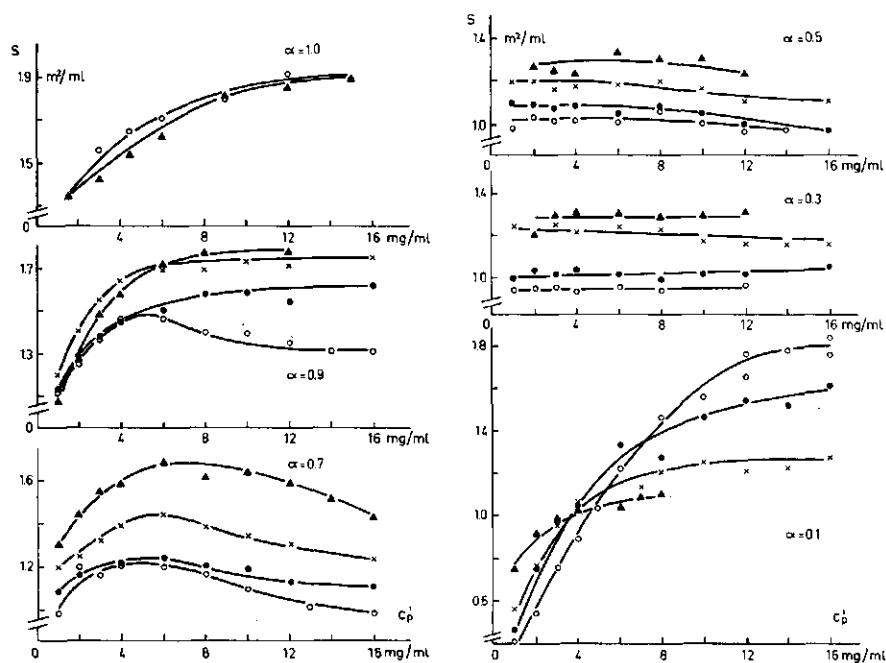
FIG. 5.2. Specific area of emulsions (m²/ml paraffin oil) stabilized by PMA-pe as a function of polyelectrolyte supply (mg/ml paraffin oil). 0.02 M NaCl (▲); 0.05 M NaCl (×); 0.10 M NaCl (●); 0.20 M NaCl (○).

indicates that the properties of PMA-pe as a function of α are reflected in bulk and at undisturbed and disturbed interfaces. However, it will be shown below that the hypercoiled a-conformation of PMA-pe is not responsible for the reduced dispersity at $\alpha = 0.10$.

Fig. 5.3. compares results for all polyelectrolytes. Here, S has been plotted as a function of α at $c_p' = 4$ mg/ml. The following information has been obtained:
1. The main differences between the polyelectrolytes are caused by ester groups and not by methyl groups. At $\alpha < 0.40$ PMA and PAA are more effective emulsifiers than PMA-pe and PAA-pe. At $\alpha > 0.50$ PMA and PAA do not give stable emulsions, whereas the emulsifying capacity of PMA-pe and PAA-pe is even higher than at $\alpha < 0.40$. It is concluded that the hydrophilic nature of the polyelectrolytes has to be reduced to make them suitable for emulsion stabilization in the dissociated form. ROE (1970) finds similar results for the stabilization of latex by copolymers of acrylonitril and acrylic acid. SHAREV et al. (1970 used a copolymer of maleic acid and styrene and found a maximum in stability as a function of α for oil-in-water emulsions, which indicates that the styrene component is not sufficient to compensate for the increasing hydrophilic nature upon dissociation. YURZHENKO and ANDOR (1970) affirmed that PMA can stabilize styrene emulsions only at low α values. Actually, for proteins it is generally found that the stabilizing effect is maximal in the
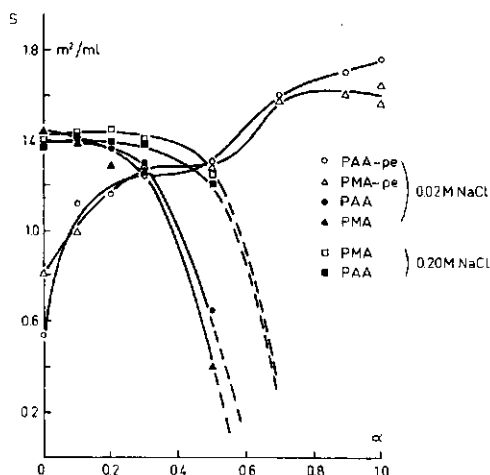
FIG. 5.3. Specific area of emulsions (m²/ml paraffin oil), stabilized by the polyelectrolytes used in this study, as a function of the degree of neutralization at $c_p' = 4$ mg/ml paraffin oil.

neighbourhood of the isoelectric point of the protein (MUKERJEE and SHUKLA, 1965; NIELSEN et al., 1958). It indicates that the presence of hydrophobic groups does not sufficiently counterbalance the increasing hydrophilicity upon dissociation. For PMA-pe and PAA-pe the counterbalancing effect is sufficiently high. In this connection it cannot be explained why the emulsifying capacity of PAA-pe and PMA-pe at $\alpha < 0.40$ is lower than for PAA and PMA.

2. The occurrence of two different conformations of PMA-pe in bulk (a- and b-conformation) and at the interface (a_s- and b_s-conformation, chapter 4) as a function of α is not reflected in their emulsifying capacities. In chapter 4 it has been concluded that this transition is found in the adsorption behaviour at undisturbed interfaces.

3. The effect of ionic strength on the emulsifying capacity of PMA and PAA is not very pronounced. At $\alpha = 0.70$ none of these emulsions is stable, independent of ionic strength. It means that the emulsifying capacity is not significantly enlarged by the electrostatic repulsion. From fig. 5.2. it appears that for PMA-pe a higher ionic strength reduces S.

4. The stepwise increase of S as a function of α for PMA-pe and PAA-pe indicates that counterbalancing trends are operative in the emulsifying process. The same can be concluded from the maximum in S as a function of c_p' at $\alpha \geqslant 0.70$ (see fig. 5.2.). The relation between c_p' and S is ambiguous and depends on the charge density on the chain. In section 5.6. we will pay further attention to the explanation of these counterbalancing trends in the emulsification process.

5.5.2. Effect of the degree of neutralization and ionic strength on the adsorption

Results are presented in fig. 5.4. as a function of c_p'. The investigated α values and ionic strengths are the same as those in section 5.5.1., except at $\alpha = 1.0$ for which no adsorption data are available. Again a definite influence
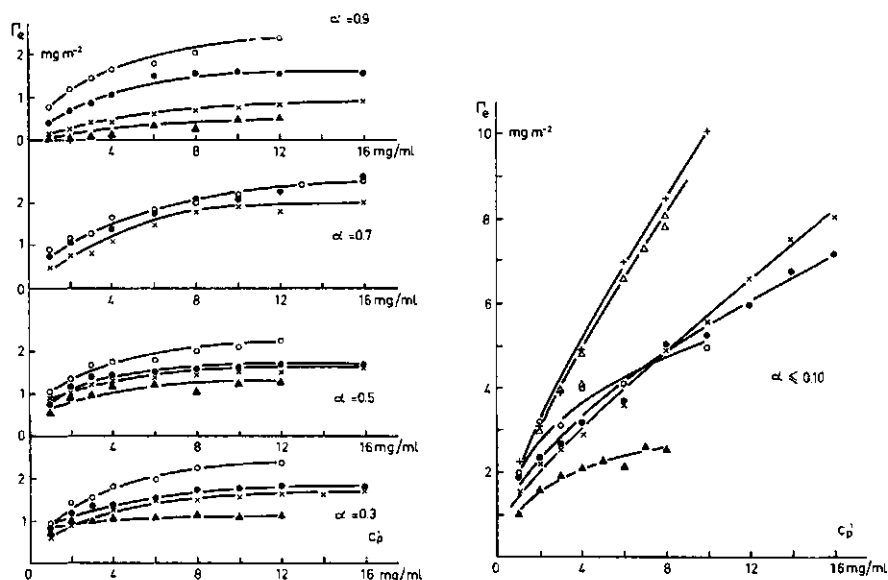
FIG. 5.4. Adsorption of PMA-pe at the emulsion interface as a function of polyelectrolyte supply (mg/ml paraffin oil). 0.02 M NaCl (▲); 0.05 M NaCl (×); 0.10 M NaCl (●); 0.20 M NaCl (○); 0.02 M NaCl, $\alpha = 0.0$ (+); 0.05 M NaCl, $\alpha = 0.03$ (△).

of α is observed. At $\alpha \geqslant 0.30$ only slight effects as a function of ionic strength and c_p' have been found. Γ_e does not exceed about 2.5 mg m^{-2}, which agrees with PMA-pe adsorption at the polystyrene–water interface (section 3.4.) and with PVA adsorption at the liquid–solid (FLEER et al., 1972) and the liquid–liquid interface (LANKVELD and LYKLEMA, 1972). At $\alpha \leqslant 0.10$ a much stronger dependence of Γ_e on c_p' has been found. Γ_e becomes even as high as 10 mg m^{-2}. At relatively low supply ($c_p' < 4$ mg/ml) all polymer molecules are quantitatively adsorbed, as can be calculated from the results presented figs. 5.2. and 5.4. At these low α values, Γ_e at this disturbed L/L interface is considerably higher than at the polystyrene–water interface (section 3.4.). It is suggested that the high adsorption at $\alpha \leqslant 0.10$ is due to coalescence of droplets without desorption during emulsification. We will return to this aspect in section 5.5.4.

As a sequel to the study of the effect of the nature of the polyelectrolyte on the emulsifying capacity we have also investigated Γ_e of these polyelectrolytes. Results are presented in fig. 5.5., at $c_p' = 4$ mg/ml. Again significant differences between esterified and non-esterified polyelectrolytes are observed. The effect of the methyl group in the main chain is hardly of any influence. The following conclusions can be drawn:

1. PMA-pe and PAA-pe adsorption is much higher than that of PAA and PMA. The slight difference between PMA-pe and PAA-pe at low α is perhaps due to the slightly higher degree of esterification of PAA-pe. The
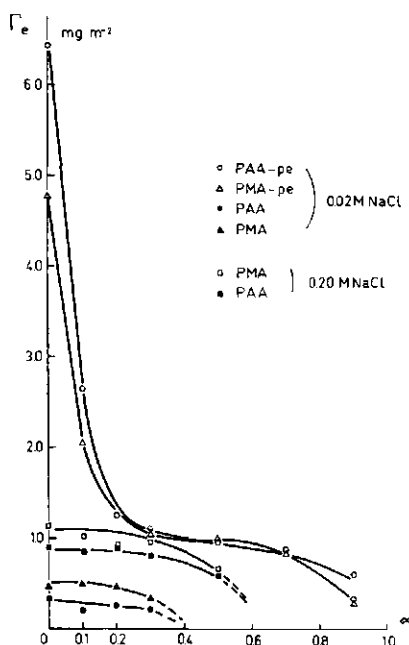
FIG. 5.5. Adsorption of the polyelectrolytes used in this study at the emulsion interface as a function of the degree of neutralization at $c_p' = 4$ mg/ml paraffin oil.

Legend in figure:
- ○ PAA-pe
- △ PMA-pe
- • PAA
- ▲ PMA
} 0.02 M NaCl

- □ PMA
- ■ PAA
} 0.20 M NaCl

difference between PMA and PAA is more pronounced, which is likely to be caused by differences in flexibility.

2. The occurrence of two different conformations of PMA-pe and PMA in bulk (a- and b-conformation) and of PMA-pe at the interface (a_s- and b_s-conformation, chapter 4) does not play any role in the adsorption of these polyelectrolytes.

3. The much higher adsorption of PMA-pe and PAA-pe at $\alpha \leqslant 0.10$ as compared to $\alpha \geqslant 0.30$ corresponds with a decrease of the dispersity (see fig. 5.3.). It indicates that coalescence of droplets takes place without desorption during emulsification. As this coalescence occurs for both PMA-pe and PAA-pe it cannot be due to the presence of the hypercoiled a-conformation of PMA-pe in bulk. Coalescence without desorption at low α values does not occur for PMA and PAA and hence it seems that the presence of ester groups is responsible for this effect.

5.5.3. *Effect of Ca^{2+} ions on the specific area and the adsorption of PMA-pe in emulsions*

By interfacial tension measurements it has been demonstrated that bivalent counterions (Ca^{2+}) influence the adsorption behaviour of polyelectrolytes. In this section an attempt has been made to examine its effect upon the emulsifying behaviour of PMA-pe. In view of the difficulty of preparing concentrated polymer solutions in the presence of Ca^{2+} ions the supply of polymer was limited to 8 mg/ml at $\alpha \geqslant 0.50$ and to 4 mg/ml at $\alpha < 0.50$ in 0.01 N $CaCl_2$. Due to the
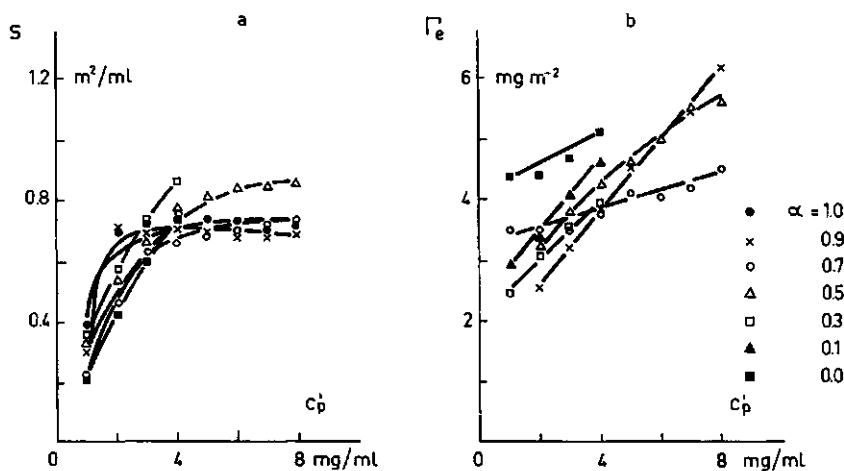
FIG. 5.6. Properties of emulsions stabilized by PMA-pe in 0.01 N CaCl$_2$ as a function of poly-electrolyte supply (mg/ml paraffin oil).
a. Specific area (m^2/ml paraffin oil).   b. Adsorbed amount of polyelectrolyte.

relatively low dispersities of these emulsions the determinations are rather inaccurate. Nevertheless the following trends have been found (fig. 5.6.):

1. The specific interfacial area is considerably lower than in the presence of Na$^+$ counterions.
2. The specific interfacial area is not dependent on α.
3. The adsorbed amount of polyelectrolyte is higher than in the presence of Na$^+$ counterions, especially at higher values of α.
4. The adsorbed amount of polyelectrolyte is not very sensitive to α.

5.5.4. *Comparison between the adsorption of PMA-pe at the liquid–solid interface and the emulsified liquid–liquid interface*

This comparison is made in fig. 5.7. The adsorption experiments at the L/S interface have been performed under conditions of a high c_p. Hence, for the sake of comparison, the maximum in Γ_e has been taken from fig. 5.4. and for Ca^{2+} emulsions Γ_e at $c_p' = 4$ mg/ml from fig. 5.6. For Na$^+$PMA-pe the results are only plotted for 0.02 M NaCl. Γ_l at the L/S interface has been taken from the latex sample with a low negative surface charge. From fig. 5.7. it is concluded, that the adsorbed amount at both interfaces compares very well for Na$^+$ PMA-pe at $\alpha \geqslant 0.30$. At $\alpha < 0.30$ and for Ca^{2+}PMA-pe at every α value the adsorbed amount at the L/L interface is considerably higher.

If the very high value of Γ_e at low α is indeed due to coalescence without desorption it must correspond with a low specific interfacial area. This has been checked for the emulsion $\varphi = 0.20$, $\alpha = 0.0$, $c_p' = 4$ mg/ml and 0.02 M NaCl. If coalescence would not take place Γ would be about 2.0 mg m^{-2} (as inferred from latex adsorption in fig. 5.7.). A specific interfacial area of about 1.65 m^2/ml is assumed (as inferred from the maximum in S for emulsions sta-
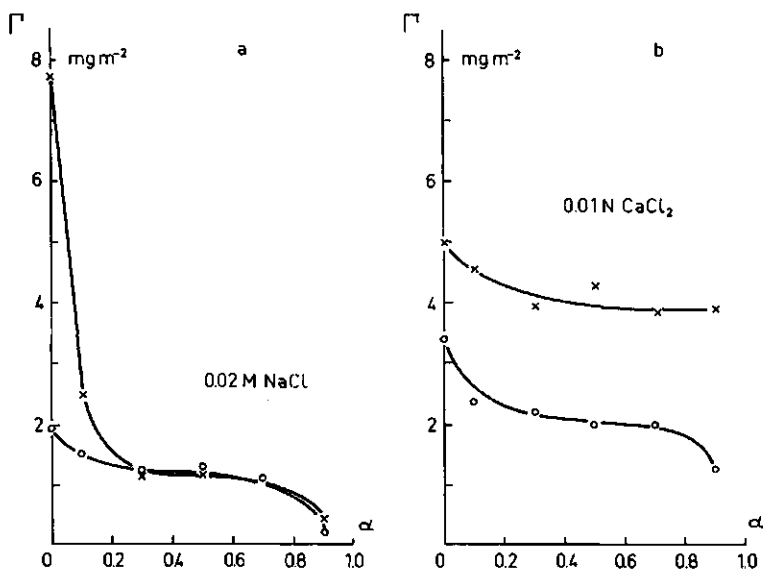
FIG. 5.7. The adsorbed amount of PMA-pe at the polystyrene latex surface ($\bigcirc$) and at the emulsion interface ($\times$).
a. Na$^+$ PMA-pe   b. Ca^{2+}PMA-pe

bilized by PMA-pe at $\alpha = 1.0$, see fig. 5.3.). The real situation gives $S = 0.81$ m^2/ml (see fig. 5.3.) and $\Gamma_e = 4.8$ mg m^{-2} (see fig. 5.5.). Hence the coalescence factor should result in an adsorption of $(1.65/0.81) \cdot 2.0 = 4.1$ mg m^{-2}. This is still considerably lower than the actually measured value. However, it is only a rough calculation with the assumptions that without enhanced coalescence S would reach the same value as at $\alpha = 1.0$ and that the coalescence occurs in one step (a continuous coalescence could very well account for this discrepancy).

For emulsions stabilized by Ca^{2+} PMA-pe, Γ_e is higher by about a factor of two. Hence it is supposed that Ca^{2+} ions also cause an enhanced coalescence over the whole range of α values. The factor of two agrees roughly with the drop in interfacial area, if it is supposed that 1.65 m^2/ml would be the maximum area without the enhanced coalescence.

For Na$^+$PMA-pe at $\alpha \geqslant 0.30$ the adsorption plateau is roughly equal for both the L/L and the L/S interface. It indicates that coalescence of newly created droplets during the emulsifying process, goes on till the adsorbed amount becomes equal to that of undisturbed interfaces, provided the supply is sufficiently high.

5.5.5. *Changes in the continuous phase after emulsion preparation*

In chapter 4 it has been demonstrated how definite differences in adsorption behaviour could be observed by changing the bulk conditions after establishment of the stationary value. Changing the conditions in the continuous phase

of the emulsion could perhaps demonstrate similar effects. In order to verify this possibility the following types of experiments were performed:
1. Preparation of emulsions at $\alpha = 0.0$ ($\varphi = 0.20$, 0.02 M NaCl, $c_p' = 4$ mg/ml). 15 hours after the preparation, α was increased to 0.1, 0.2, 0.3, 0.5, 0.7 and 0.9 respectively. Having brought about these changes the emulsions were rotated vertically under exclusion of air for 15 hours and S and Γ_e determined.
2. Preparation of emulsions at $\alpha = 1.0$ and analogously subsequent decrease of α. The decrease of α could only be brought about for PMA-pe and PAA-pe, since the non-esterified polyelectrolytes are not suitable as emulsifiers at $\alpha = 1.0$.

The results of increasing α are plotted in fig. 5.8. and the following conclusions can be drawn:
1. For PMA-pe and PAA-pe no coalescence occurs. Γ_e decreases to a level of about 2 mg m^{-2}. There is no significant difference between PAA-pe and PMA-pe. From comparison with pH 494 cycles of both polyelectrolytes (figs. 4.3.–4.5.) one would expect a difference due to the completely reversible adsorption of PMA-pe in the a-conformation. It means that by emulsification part of the adsorbed molecules of PMA-pe at low α are also irreversibly adsorbed i.e. due to γ gradients along the interface during emulsification the spreading is improved and longer trains of adsorbed segments are formed. This underlines that the findings about the behaviour of polymers at undisturbed interfaces cannot be directly compared with the behaviour at disturbed interfaces. Nevertheless it can be concluded that the rise of γ for pH increase in the pH cycles (chapter 4) can be attributed to desorption.
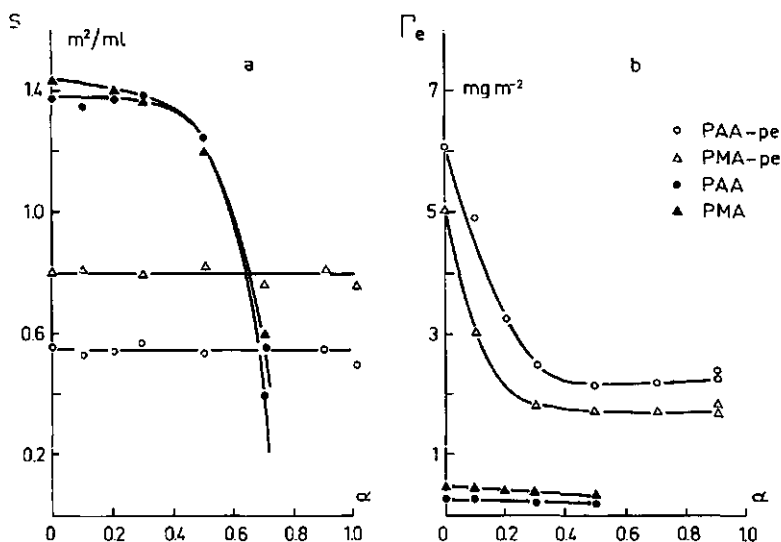
FIG. 5.8. Specific area (a) and adsorbed amount of polyelectrolyte (b) upon increasing degree of neutralization α for emulsions prepared at $\alpha = 0.0$, $c_p' = 4$ mg/ml paraffin oil and 0.02 M NaCl.

2. Emulsions stabilized by PAA and PMA coalesce upon increasing α and
$S(\alpha)$ agrees with that of the directly prepared emulsions (see fig. 5.3.). It
means that PAA and PMA desorb upon increasing α. For these polyelectrolytes
the pH cycles fit in with the behaviour of emulsions after preparation.

The results of decreasing α are plotted in fig. 5.9. and the following conclusions can be drawn:

1. S decreases upon lowering α for both PMA-pe and PAA-pe. However, the
final value of S at $\alpha = 0$ is still higher than that attained in direct measurements. The removal of dissociated groups apparently transforms the adsorbed
layer in such a way that partial coalescence must occur.
2. Γ_e increases, but to a much lower extent than by preparing the emulsion
directly at the same α (see fig. 5.5.). The increased Γ_e corresponds with the
extent of coalescence. Hence it appears that by this α decrease no additional
adsorption from solution takes place.
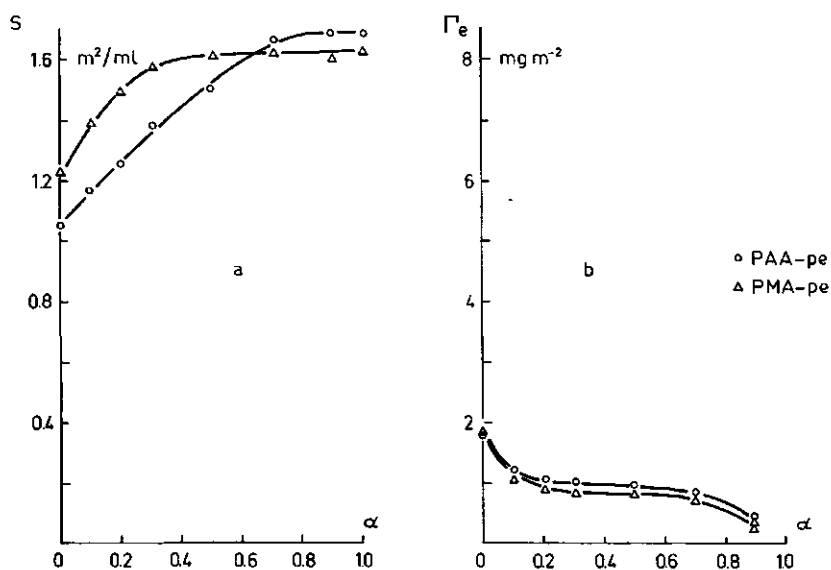
FIG. 5.9. Specific area (a) and adsorbed amount of polyelectrolyte (b) upon decreasing degree
of neutralization α for emulsions prepared at $\alpha = 0.90$, $c_p' = 4$ mg/ml paraffin oil and 0.02 M
NaCl.

5.6. THE MECHANISM OF EMULSIFICATION

If there is no coalescence after finishing emulsification, S and Γ_e reflect the
behaviour during emulsification. With the information summarized in this
chapter and with the findings of PVA's as emulsifying agents under comparable
conditions (LANKVELD and LYKLEMA, 1972) the mechanism of emulsification in
an Ultra-Turrax disperser will be worked out.

If two immiscible liquids, such as paraffin oil and water are agitated, at first long filaments of the dispersed phase are broken up into smaller units. This breakup is followed by a coalescence of droplets just formed, resulting during longer agitation time in a local dynamic balance between breakup and coalescence. Both, the degree of breakup and the coalescence depend on a great number of factors such as type of disperser, intensity of agitation, volume fraction of dispersed phase, nature and supply of the emulsifying agent. Some of these parameters (type of disperser, intensity of agitation) mainly affect the breakup, whereas other factors (type of disperser, nature and supply of the emulsifying agent, volume fraction of dispersed phase) exert their influence especially on coalescence. We will now discuss these parameters in more detail.

The type of disperser

WALSTRA (1973) investigated paraffin oil-in-water emulsions, stabilized by PVA and/or sodium laurylsulfate (NaLS) and prepared in a high-pressure homogenizer and an Ultra-Turrax disperser of the same type as the one used in our study. In such a homogenizer at sufficiently high pressure the degree of breakup of droplets is determined by the dynamic pressure fluctuations during turbulent agitation (KOLMOGOROV's theory, 1949). As the time of agitation for one droplet is very short the degree of coalescence during emulsification is very low. WALSTRA (1973) has found that addition of PVA with or without 0.3% NaLS, reduces the specific interfacial area. It is concluded that PVA suppresses turbulent agitation and hence the final dispersity after finishing emulsification.

In an Ultra-Turrax type disperser the intensity of agitation is lower than in a high-pressure homogenizer. The breakup of the droplets is less effective and not determined by dynamic pressure fluctuations but by shearing actions of large eddies surrounding a droplet. The suppression of turbulence by polymers favours the disruption. As the time during which a volume element is subjected to agitation is much longer, the degree of coalescence is higher than in a high-pressure homogenizer and the process results in a dynamic balance between breakup and coalescence during emulsification.

The intensity of agitation

SHINNAR (1961) described the behaviour of liquid dispersions in a mixing vessel, which is comparable with an Ultra-Turrax type disperser. He paid special attention to the intensity of agitation. It is found that the dispersity increases with higher agitation. By colouring the dispersed phase he was able to determine more details. At low agitation the droplet size is determined only by the degree of breakup. At higher intensity of agitation the final droplet size is determined by the prevention of further coalescence. We also found that a higher agitation gives a more dispersed emulsion.

The volume fraction of the dispersed phase φ

E.g. DAVIES (1972) stated that generally the dispersity decreases with increasing φ. If the intensity of agitation and other conditions remain constant, a

higher φ would give a greater number of droplets per unit volume after breakup. As more particles per unit volume enhance the chance of coalescence, S is more reduced at higher φ. LANKVELD and LYKLEMA (1972) have investigated the effect of φ on the dispersity of emulsions stabilized by PVA. For low amounts of PVA per ml paraffin oil, S is almost solely determined by this amount but not by φ. For higher amounts of PVA per ml paraffin S indeed decreases with increasing φ. As coalescence is responsible for this reduced dispersity it means that the decrease of S with increasing φ is probably less pronounced in a homogenizer than in an Ultra-Turrax type disperser.

Polyelectrolyte supply c_p' and the nature of the polyelectrolyte

As the parameters discussed hitherto are not varied in our study they cannot cause the differences in S and Γ_e. Hence these differences must be attributed to variations in c_p' and the nature of the polyelectrolyte. We shall now discuss both parameters in more detail and with special emphasis on the degree of neutralization of PMA-pe. Varying the degree of neutralization affects the flexibility and hence its nature.

In an analogous study LANKVELD and LYKLEMA (1972) investigated the effect of c_p' and the hydrophilic nature of PVA on S and Γ_e. A notable difference was found between the emulsifying capacity as a function of c_p' for the more hydrophobic PVA-88 and the more hydrophilic PVA-98. In the region of low c_p', S increases with c_p' for both types of PVA. At higher c_p' this results in a plateau value of S for PVA-98. However, for PVA-88 S passes through a maximum which is higher than the plateau value for PVA-98. We will first work out the way in which LANKVELD and LYKLEMA (1972) have explained their findings and afterwards extend it for polyelectrolytes as emulsifying agents.

Both supply and nature of the polymer generally determine the final dispersity. By breakup of droplets gradients in γ along the newly created interfaces arise and by adsorption of polymer from the bulk (i.e. diffusion) and/or spreading of the adsorbed molecules these gradients relax again. The chance of surviving the breakup depends on the time the newly created interfaces have to become covered by sufficient polymer in a proper conformation to prevent coalescence. This time is determined by the chance of encounter between the droplets (i.e. φ and the droplet size) and by the rate of diffusion and the rate of spreading. The longer the gradients in γ persist the more time is available for separation of the newly created droplets.

In the region of low c_p' the rate of supply by diffusion during emulsification is the important factor and the final dispersity is determined by the deficiency of polymer. Increasing c_p' therefore leads to higher dispersities for both types of PVA. For PVA-98, the more flexible of the two PVA's used in the cited study, the rate of spreading is higher than for PVA-88. This means that, at a given c_p', the gradients in γ relax faster for PVA-98 than for PVA-88 and explains why the dispersity is lower for PVA-98 than for PVA-88 in the region of low c_p'. The increase of S with higher c_p' will not go on indefinitely because the rate

of coalescence also increases owing to the increased number of droplets per unit volume. For PVA-98 this results in a levelling of the dispersity, whereas for PVA-88 a maximum is observed.

In this region of high supply, c_p' is no longer the determining factor for S. Both factors, c_p' and the flexibility, now determine the final dispersity. Generally it depends on the flexibility to what degree the relaxation of γ gradients is caused by either one of the relaxation mechanisms (i.e. diffusion or spreading). If spreading of the adsorbed molecules is a relatively fast process (i.e. fast in comparison with the rate of breakup of droplets) the γ gradients relax mainly by spreading and diffusion with concomitant introduction of liquid between the droplets cannot take place. As this sucking-in of the polymer solution is a factor favouring high dispersity, it means that relaxation of gradients by spreading results in relatively low dispersities. Moreover, the rate of spreading is probably independent of c_p' and the supply will therefore not affect the final dispersity. For PVA-98 the plateau value for S with increasing c_p' and the low dispersity, compared with PVA-88, indicate that the relaxation of gradients is determined by spreading of adsorbed molecules.

If spreading takes a longer time, i.e. a lower flexibility of the molecule, the sucking-in of solution between the new interfaces takes place and also supply by diffusion keeps on relaxing the gradients in γ. The higher c_p' the less solution has to be sucked in before the gradients are relaxed and the resistance to coalescence upon encounter between the droplets is decreased. Hence it depends on c_p' how fast gradients in γ are reduced by diffusion. As during diffusion at the same time the driving force for further suction is reduced, it follows that the relaxation of gradients through diffusion has a double-edged influence on the final dispersity. For PVA-88 the lower S with higher c_p' is caused by this diffusion procedure.

From these results it is concluded that both the rate of spreading (i.e. the flexibility of the chain) and the rate of diffusion are important parameters in the mechanism of emulsification. For PVA the rate of diffusion has been investigated by varying the molecular weight of the PVA's. The higher the molecular weight, the slower the diffusion, the longer the γ gradients can persist and the higher the final dispersity.

For polyelectrolytes the rate of spreading and the rate of diffusion are affected by the degree of neutralization as has been shown from the time dependence measurements of the interfacial tension (section 3.2.), though in the absence of a shear field. On account of these results and the results of viscosimetry of PMA-pe in bulk (section 2.4.) three regions of α can be distinguished, viz.:

1. $\alpha \leqslant 0.10$; PMA-pe in bulk is characterized by a compact structure. The charge density is low. From $\gamma(t)$ experiments it is deduced that the rate of supply by diffusion is high (γ decreases very fast during the first few minutes of the adsorption process, see figs. 3.2.–3.3.). The flexibility of the molecules is relatively low and the spreading of adsorbed molecules hardly takes place.

2. $0.30 \leqslant \alpha \leqslant 0.50$; PMA-pe is more flexible. The rate of supply by diffusion is lower than at $\alpha \leqslant 0.10$ as the bulk dimensions are increased.

3. $\alpha \geqslant 0.70$; Due to the very high charge density with increasing α the flexibility of the chain gradually diminishes. Moreover, the rate of supply by diffusion is again reduced compared with $\alpha < 0.70$. Summarizing these results it is concluded that the rate of supply by diffusion decreases with increasing α and that the rate of spreading passes through a maximum with increasing α. Moreover, for PMA-pe the following additional factors have to be taken into account:
1. the reduction of coalescence by electrostatic repulsion between droplets adsorbed by polyelectrolytes.
2. the enhanced coalescence without desorption at $\alpha \leqslant 0.10$.

With the results of the investigations with PVA and with these additional factors for PMA-pe it is tried to explain the dispersity of emulsions stabilized by PMA-pe as a function of α and c_p'. With respect to the flexibility it is likely that PVA-98 is comparable with PMA-pe at $0.30 \leqslant \alpha \leqslant 0.50$ and PVA-88 with PMA-pe at $\alpha \leqslant 0.10$ and $\alpha \geqslant 0.70$. From fig. 5.2. it is concluded that in the region of low c_p' S increases with c_p'. This is expected because of the results with PVA in this region of c_p'. Moreover, S increases with α in this region of c_p' (see also fig. 5.3.). As diffusion is the determining factor in this region of c_p' and as diffusion is faster at lower α, one would expect this trend. The faster the diffusion the faster the gradients in γ have disappeared and the smaller the final area that can be created (compare molecular weight effect for PVA). In the region of high c_p' it is indeed found at $0.30 \leqslant \alpha \leqslant 0.50$ that spreading determines the relaxation of the gradients. S is independent of c_p' and low compared with $\alpha \geqslant 0.70$ and $\alpha \leqslant 0.10$. The effect of ionic strength in this region of α can also be explained in this connection. The electrostatic repulsion between droplets is considerably reduced with increasing ionic strength leading to an enhanced coalescence. At $\alpha \geqslant 0.70$ S passes trough a maximum, although less pronounced than for PVA-88. Moreover, one would expect this trend to become more pronounced with increasing α and lower ionic strength, because of a further reduction of the flexibility. However, there are some counterbalancing factors viz. the reduction of the rate of diffusion and the increase in electrostatic repulsion with higher α and lower ionic strength. By these counterbalancing factors coalescence is reduced the higher α and the lower the ionic strength. To find a maximum in S as a function of c_p' one needs to investigate higher ionic strength.

Hitherto the mechanisms of emulsification have been discussed for PMA-pe at $\alpha \geqslant 0.30$, solely by interpretation of the dispersity of the emulsions. At $\alpha < 0.30$ the rate of supply by diffusion is high and the flexibility is low. One would expect a relaxation of the γ gradients by diffusion with a very pronounced maximum in S. As shown in fig. 5.2. this maximum is not found at $c_p' \leqslant 16$ mg/ml. From the comparison with the L/S interface (section 5.5.4.) it is known that Γ_e also gives information about the mechanism of emulsification. When the gradients in γ have disappeared coalescence can be prevented by the adsorbed molecules. On account of the results presented in fig. 5.7. it is stated that for Na^+PMA-pe at $\alpha \geqslant 0.30$ coalescence goes on till Γ_e equals Γ_t. For Na^+PMA-pe at $\alpha < 0.30$ and for Ca^{2+}PMA-pe over the whole region of α coalescence

proceeds much further, the final dispersity reduces and Γ_e reaches very high values. At last it should be mentioned that neither the reduced dispersity nor the increased adsorption at $\alpha < 0.30$ for Na^+PMA-pe is due to the existence of the hypercoiled a-conformation, but to the presence of the ester segments, since Na^+PAA-pe behaves in the same way. As for $Ca^{2+}PMA$-pe this enhanced coalescence occurs over the whole region of α, it is concluded that bivalent Ca^{2+} binding with dissociated acid groups are related to it.

5.7. SUMMARY

The properties of oil-in-water emulsions, stabilized by PMA-pe, PAA-pe, PMA and PAA have been studied by determination of the specific area S (in m^2/ml paraffin oil) and the adsorbed amount of polyelectrolyte Γ_e (in mg m^{-2}). Emulsions stabilized by PMA-pe are studied as a function of the supply of polyelectrolyte c_p' (1–16 mg/ml paraffin oil), degree of neutralization ($0.0 \leqslant \alpha \leqslant 1.0$), ionic strength (0.02–0.20 M NaCl) and the nature of the counterion (Na^+, Ca^{2+}). The effect of the chemical constitution has been investigated at $c_p' = 4$ mg/ml and in 0.02 M NaCl.

Three regions of α could be distinguished with respect to the properties of PMA-pe stabilized emulsions, viz. $\alpha \leqslant 0.10$, $0.30 \leqslant \alpha \leqslant 0.50$ and $\alpha \geqslant 0.70$. At $\alpha \leqslant 0.10$ S and Γ_e increase with c_p', at $0.30 \leqslant \alpha \leqslant 0.50$ S and Γ_e are independent of c_p' and at $\alpha \geqslant 0.70$ S passes through a maximum and Γ_e levels out to a plateau value. The maximum of S indicates that the relationship between S and c_p' is not unequivocal.

The effect of ionic strength is relatively small. In general, S decreases and Γ_e increases with increasing ionic strength. The nature of the counterion has a much more drastic effect. Due to the presence of Ca^{2+} ions S is reduced and Γ_e increased over the whole region of α.

By comparison of Γ_e with the adsorbed amount at the polystyrene latex surface Γ_t it could be confirmed that the emulsions stabilized by Na^+PMA-pe at $\alpha < 0.30$ and by $Ca^{2+}PMA$-pe over the whole region of α, are characterized by an enhanced coalescence of the covered droplets without desorption during emulsification.

Additional information about the emulsifying capacity was obtained from a comparison with PAA, PMA and PAA-pe. Important differences in S and Γ_e show up between the esterified and non-esterified polyelectrolytes. It means that the presence of the hydrophobic ester groups is responsible for differences in emulsifying capacity and not the methyl group in the main chain. It also means that the occurrence of the so-called a-conformation in bulk at low pH does not reflect itself in emulsion properties such as S and Γ_e. The most striking difference between esterified and non-esterified polyelectrolytes is their emulsifying capacity at $\alpha > 0.5$. PMA and PAA are not able to stabilize emulsions at $\alpha > 0.5$, whereas PMA-pe and PAA-pe give more dispersed emulsions at $\alpha > 0.5$ than at $\alpha < 0.5$.

As neither S nor Γ_e are affected by the time after emulsification, the findings of these experiments can be used for explaining the mechanism of emulsification by polyelectrolytes. The results fit very well into an extended picture of the mechanism of emulsification as worked out by LANKVELD and LYKLEMA (1972). Both the supply and nature of the polymer generally determine the final dispersity. The nature of the polyelectrolyte is modified by the degree of neutralization. The rate of supply by diffusion and the rate of spreading of adsorbed molecules are determined by α and both factors relax the gradients in γ that arise during the breakup of droplets. It depends on the flexibility of the chain to what extent the relaxation of these gradients is caused by either one of these relaxation mechanisms. For polyelectrolytes the additional factor of the stability to coalescence by electrostatic repulsion has to be accounted for.

6. CHARACTERIZATION OF THE ADSORBED
LAYER OF EMULSIONS BY RHEOLOGY

6.1. INTRODUCTION

There are a great number of factors that generally influence the rheological behaviour of emulsions (SHERMAN, 1968, p. 286). One of the most important variables is the nature of the stabilizer. Also in this study the stabilizer is expected to play an important role.

Polymers are able to bring about aggregation (flocculation) of emulsion droplets in different ways. One can distinguish between flocculation by real bridging of the molecules and by loop interaction. A real bridging mechanism means that the polymer molecule is anchored with part of its segments on two or more droplets. A loop interaction mechanism means that attractions between the molecules adsorbed on different droplets lead to a flocculated system. In the case of higher volume fractions of the dispersed phase, agitation of the flocculated system enables us to verify which mechanism is responsible for flocculation. Under imposed shear of moderately high shear rate both real bridging and loop interactions are disrupted and the viscosity is reduced. However, on cessation of shear reflocculation can only occur for the loop interaction mechanism. The breakdown of the structure is usually irreversible in the case of a real bridging mechanism. By the shear forces the bridges are broken down and rearrangement of other molecules in the adsorbed layer replaces the lost molecules. SHOTTON and DAVIS (1968) and DAVIS (1971a) found such a real bridging mechanism for emulsions stabilized by acacia gum. Other investigators found completely reversible systems i.e. emulsions in which on cessation of shear forces the viscosity built up again, e.g. IZMAILOVA et al. (1972) with benzene-in-water emulsions stabilized by PVA. Also DAVIS (1971b) investigated a system in which the occurrence of real bridges could not be confirmed. It was shown that a mixture of anionic surfactant and anionic polyelectrolyte sometimes gives a high viscosity, depending on the way of preparation of the emulsion. It is likely that in these cases a real bridging is absent.

In this rheological study it will be confirmed that the high viscosity of PMA-pe stabilized emulsions is not caused by a real bridging mechanism, but by attractive forces between the interfacial layers of different droplets.

6.2. EXPERIMENTAL

The viscosity has been measured with a Haake-rotovisko at a shear rate $D_s = 7.05$ sec^{-1} for 5 minutes shearing time. This shearing time has been chosen because after 5 minutes shearing time the decrease in viscosity became insignificant under all experimental conditions. Moreover, the viscosity has also

been measured as a function of D_s ($7.05 < D_s < 64$ sec^{-1}). By increasing and subsequent decreasing of D_s information could be obtained about any hysteresis or relaxation effects. The temperature was kept at $20.0 \pm 0.2\,°C$.

A volume fraction of $\varphi = 0.50$ has been chosen to achieve a complete network in the emulsified system. The ionic strength was 0.05 or 0.10 M of NaCl, the time of emulsification 2 minutes or, in some experiments, only 1 minute.

6.3. RESULTS AND DISCUSSION

One of the difficulties in these experiments is the poor reproducibility because the viscosity depends on the way in which the emulsion is brought into the apparatus. By this action some breakdown of the network structure cannot be prevented. Although a standardized procedure was adopted to minimize the poor reproducibility, great differences in viscosity were usually encountered between experiments in duplicate. However, if after bringing the emulsion into the viscometer, the viscosity was measured as a function of D_s relative to the viscosity at $D_s = 7.05$ sec^{-1}, the results were highly reproducible (see inset fig. 6.2.). It implies that the extent of shear destruction brought about, once the emulsion was in the viscometer cup was independent of the initial extent of breakdown.

6.3.1. *The high viscosity of emulsions stabilized by PMA-pe for a degree of neutralization smaller than 0.30*

In section 6.1. it is shown that the high viscosity of emulsions stabilized by macromolecules can be caused by two different mechanisms, viz. real bridging and loop attractions. Starting from these two possibilities it will be argued that in our case the latter is more likely.

The results of some experiments are given in fig. 6.1. from which the following can be concluded:

1. The viscosity of all types of emulsions, except those stabilized by PMA-pe at $\alpha \leqslant 0.30$ is rather low ($\eta < \sim 300$ cP). For the apparatus used this is about the lower limit of measurability.

2. As S and Γ_e for PMA-pe and PAA-pe stabilized emulsions are equal (see fig. 5.3. and 5.5.), it appears that the high viscosity of PMA-pe stabilized emulsions is not caused by a difference in S and/or Γ_e. As the region of the high viscosity coincide with the occurrence of the a-conformation of PMA-pe in bulk it is more likely that the high viscosity is due to the presence of this hypercoiled conformation. This means that the attractive forces, responsible for this hypercoiled conformation, are also effective in the adsorbed layer. More arguments in favour of this suggestion will be put forward in this section.

3. If the continuous phase of PMA-pe stabilized eumlsions contains 50% methanol the viscosity will be considerably lower. It should be noted that the origin of the attractive forces in the a-conformation is hydrophobic bonding or/and V. D. WAALS forces of attraction between -CH$_3$ groups. MANDEL et al.
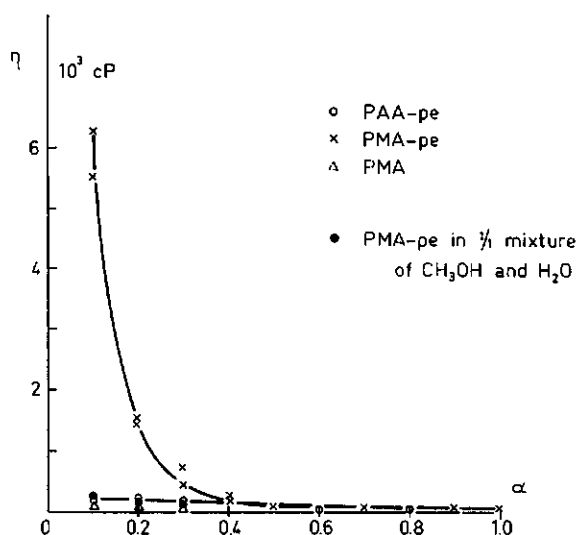
86

FiG. 6.1. Viscosity of emulsions stabilized by polyelectrolytes as a function of the degree of neutralization.
$D_s = 7.05$ sec^{-1}, time of shear: 5 minutes.
$\varphi = 0.50$, $c_p' = 2$ mg/ml paraffin oil, 0.05 M NaCl, time of agitation: 2 minutes.

(1967) concluded that v. d. WAALS forces of attraction are the major factor, because the a-conformation still exists in the water-methanol mixture with 40% methanol. If hydrophobic bonding would be the main factor, the presence of methanol would reduce the forces of attraction. From these rheological experiments it is concluded that hydrophobic bonding is the main factor and hence our conclusion disagrees with that of MANDEL et al. (1967).

The breakdown of the network structure has been investigated by varying D_s, as shown in fig. 6.2. The viscosity decreases with D_s and after returning to $D_s = 7.05$ sec^{-1} the final viscosity depends on the highest shear rate $D_{s, max}$. The higher $D_{s, max}$ the lower η $(D_s = 7.05$ sec$^{-1})$. This phenomenon is interpreted as due to the breakdown of attractive forces between the droplets upon intensive shearing. Fig. 6.2b. demonstrates that the breakdown is reversible. After varying D_s $\eta(D_s = 7.05$ sec$^{-1})$ increases with waiting time and increasing temperature. It is even possible to attain a viscosity higher than the starting value at $D_s = 7.05$ sec^{-1} (i.e. $> 3.10^3$ cP). It indicates a restoration of the network proceeding faster at higher temperature. Restoration can even repair any destruction caused by the deposition of the emulsion in the viscometer. These relaxation effects mean that real bridging between the droplets is improbable.

Mixtures of PAA-pe and PMA-pe have also been used as emulsifying agents. All emulsions have been prepared under the same condition: $\varphi = 0.50$, 1 minute agitation, $\alpha = 0.10$, $c_p' = 2$ mg/ml paraffin oil and 0.10 M NaCl. The control experiments had a c_p' equal to the PMA-pe part of the mixtures. From com-
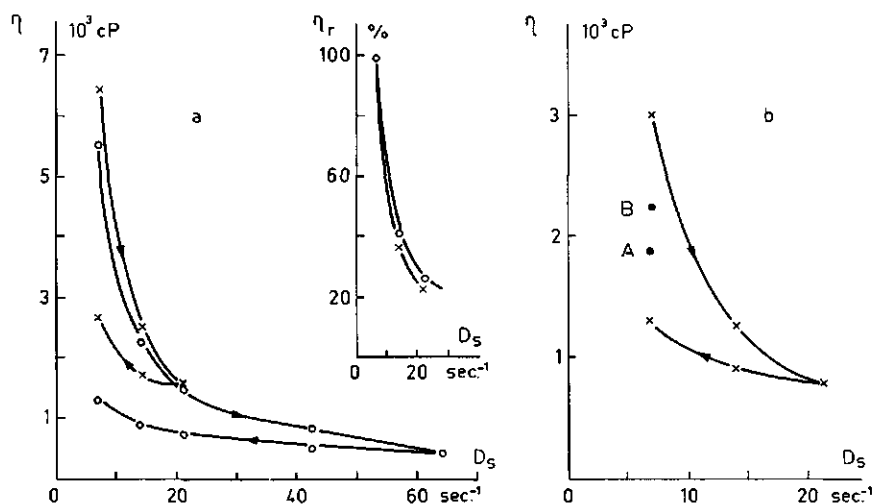
FIG. 6.2. Viscosity of emulsions stabilized by PMA-pe at $\alpha = 0.10$ as a function of the shear rate D_s.
$D_{s,max} = 64 \text{ sec}^{-1}$ (○), $D_{s,max} = 21 \text{ sec}^{-1}$ (×).
$\varphi = 0.50$, $c_p' = 2 \text{ mg/ml}$ paraffin oil, 0.05 M NaCl.
a. 2 minutes agitation.
b. 1 minute agitation.
   A: after shearing, increase of temperature from 20° to 45°C in 40 minutes.
   B: after temperature increase to 45°C and 60 minutes' waiting time at 45°C.

parison with the results given in figs. 5.2. and 5.4. it is deduced that at $\alpha = 0.10$ at $c_p' = 2 \text{ mg/ml}$ paraffin oil all polyelectrolyte is quantitatively adsorbed. The viscosity is measured at $D_s = 7.05 \text{ sec}^{-1}$. The results are collected in table 6.1. From these experiments it is concluded that the high viscosity is dominated by the amount of PMA-pe in the adsorbed layer and that the presence of PAA-pe does not have any effect upon the viscosity. If real bridging would be responsible for the high viscosity of PMA-pe stabilized emulsions, the presence of PAA-pe would reduce the viscosity the higher the amount of PAA-pe in the adsorbed layer. However, since this is not the case real bridging is improbable.

TABLE 6.1. Viscosity of oil-in-water emulsions, stabilized by (mixtures of) PMA-pe and PAA-pe.
$\varphi = 0.50$, $\alpha = 0.10$, 0.10 M NaCl, 1 minute agitation; time of shear: 5 minutes

c_p' (mixture) mg/ml paraffin		$\eta(D_s = 7.05 \text{ sec}^{-1})$ P	c_p' (control) mg/ml paraffin		$\eta(D_s = 7.05 \text{ sec}^{-1})$ P
PMA-pe	PAA-pe		PMA-pe	PAA-pe	
0.50	1.50	8.0 ± 0.5	0.50	–	6.7 ± 0.2
0.75	1.25	9.5 ± 1.5	0.75	–	11.5 ± 1.5
1.00	1.00	17.5 ± 2.0	1.00	–	24.5 ± 2.0
			–	0.50	1.5 ± 0.5
			–	1.00	1.5 ± 0.5

A PMA-pe stabilized emulsion, prepared at $\alpha = 0.60$ under conditions otherwise the same as those of fig. 6.1. gives a significant rise in viscosity if the degree of neutralization is reduced by addition of HCl under constant stirring. For the reduction in the volume phase of the paraffin oil by this addition has been corrected. An analogous experiment has been performed with PAA-pe. In this case no rise in viscosity has been measured after decreasing α to 0.10. Quantitatively the results are:

$$\text{PAA-pe } \alpha = 0.70 \rightarrow 0.10 \qquad \eta\ (D_s = 7.05\ \text{sec}^{-1}) = \ 1.8 \pm 0.5\ \text{P}$$
$$\text{PMA-pe } \alpha = 0.60 \rightarrow 0.10 \qquad \eta\ (D_s = 7.05\ \text{sec}^{-1}) = 23.0 \pm 2.5\ \text{P}$$

As real bridging due to simple decreasing α is highly improbable, attractive forces between the adsorbed layers of different droplets cause the high viscosity.

The high viscosity of PMA-pe stabilized emulsions is obtained if the molecules are adsorbed in the hypercoiled a-conformation. As shown this is due to intermolecular attractive forces between molecules adsorbed at different droplets. From viscosity measurements of PMA-pe in bulk (chapter 2) it has been concluded that the attractive forces of the a-conformation are intramolecular forces.

6.3.2. *Quantitative comparison with adsorption experiments*

In the previous section it has been concluded that the high viscosity of the emulsions is dominated by the amount of PMA-pe adsorbed in the a-conformation at low degree of neutralization. As PMA assumes also the a-conformation at low degree of neutralization (see chapter 2) one would expect the high viscosity also for PMA stabilized emulsions. However, both emulsions differ considerably with respect to their adsorbed amount of polyelectrolyte (see fig. 5.5.). Hence it is reasonable to state that for PMA stabilized emulsions Γ_e is too small for effective intermolecular attractive forces to occur between different droplets. Therefore an attempt has been made to correlate the amount of polyelectrolyte adsorbed in loops Γ_{lp} with the viscosity. Some results are collected in table 6.2. All emulsions have been prepared under the same conditions

TABLE 6.2. Relation between Γ_{lp} and η for emulsions stabilized by PMA-pe.
$\alpha = 0.10$, $\varphi = 0.50$, 0.10 M NaCl, 1 minute agitation.
time of shear: 5 minutes

c_p' mg PMA-pe ml paraffin	$\eta(D_s = 7.05\ \text{sec}^{-1})$ P	Γ_e^1 mg m^{-2}	Γ_{lp} mg m^{-2}
0.50	6.7 $\pm$ 0.2	1.1 $\pm$ 0.1	0.54 $\pm$ 0.1
0.75	11.5 $\pm$ 1.5	1.4 $\pm$ 0.1	0.84 $\pm$ 0.1
1.00	24.5 $\pm$ 2.0	1.90	1.34
2.00	38.6 $\pm$ 4.2	2.35	1.79
3.00	129 $\pm$ 30	2.70	2.14
4.00	300 $\pm$ 100	3.20	2.64
5.00	480 $\pm$ 150	3.60	3.04

note: 1. taken from fig. 5.4.

($\varphi = 0.50$, 0.10 M NaCl, $\alpha = 0.10$, 1 minute agitation and $c_p' = 0.5$–5.0 mg/ml paraffin oil). The viscosity has been measured at $D_s = 7.05$ sec^{-1}. To obtain Γ_{lp} it has been assumed that at $\alpha = 0.10$ S and Γ_e are equal for $\varphi = 0.20$ and $\varphi = 0.50$. Γ_e can then be calculated from previous results (figs. 5.2. and 5.4.). As Γ_f has been taken to be 0.56 mg m^{-2} (see section 3.5.) the difference between column 3 and 4 is always 0.56 mg m^{-2}.

It is seen that $\eta(D_s = 7.05$ sec$^{-1})$ increases roughly linearly with Γ_{lp} till about $c_p' = 2$ mg/ml paraffin oil. Although at higher c_p' the viscosity measurements are inaccurate it is nevertheless possible to state that η increases more than proportionally with Γ_{lp}. As only interparticle forces of attractions – i.e. forces of attraction between segments of molecules adsorbed at different droplets – contribute to the rigidity of the network, it means that these forces increase with the length of the loops.

In table 6.3. analogous calculations have been performed for PMA-pe stabilized emulsions with $c_p' = 2$ mg/ml paraffin oil and different degrees of neutralization. Although a quantitative interpretation is thwarted, because at high degree of neutralization the concentration in the a-conformation is reduced it is found again that η increases with Γ_{lp}.

Comparison of table 6.2. with 6.3. and fig. 6.2a. with fig. 6.2b. shows at $\alpha = 0.10$ and $c_p' = 2$ mg/ml paraffin oil that the time of agitation has also a considerable effect on η. This is due to the difference in dispersity. At a higher dispersity (i.e. a longer agitation) the number of droplets per unit volume increases and this enhances the rigidity of the network.

Finally, some attention has been paid to the modification of α ($\alpha = 0.60 \rightarrow 0.10$) and the ensuing increase in viscosity. The viscosity rose till about 23 P (section 6.3.1.). In the case of direct preparation at $\alpha = 0.10$ and otherwise the same conditions, η becomes 60 P (see table 6.2.). In section 5.5.5. it has been shown that the adsorbed amount at decreasing α to 0.10 does not increase to the value obtained by direct preparation at $\alpha = 0.10$ (see section 5.5.4.). At $c_p' = 4$ mg/ml paraffin oil and $\varphi = 0.20$ the difference in the total amount of adsorbed PMA-pe is about a factor of two and for the adsorbed amount in loops about a factor of three. This factor is roughly reflected in the viscosity ratio of both emulsions. However, one should realize that these results have

TABLE 6.3. Relation between Γ_{lp} and η for emulsions stabilized by PMA-pe. $c_p' = 2$ mg/ml paraffin oil, $\varphi = 0.50$, 0.05 M NaCl, 2 minutes agitation. time of shear: 5 minutes.

α	$\eta(D_s = 7.05$ sec$^{-1})$ P	Γ_e^1 mg m^{-2}	Γ_{lp} mg m^{-2}
0.10	60 $\pm$ 2.0	2.20	1.64
0.20	15.0 $\pm$ 1.5	1.20	0.64
0.30	5.0 $\pm$ 0.5	0.85	0.29
0.50	2.0 $\pm$ 0.5	–	–

note: 1. taken from fig. 5.4.

been compared at two different values of c_p' and φ. Nevertheless all these data enable us to describe the origin of the high viscosity of PMA-pe stabilized emulsions very well.

6.4. SUMMARY

The rheology of concentrated emulsions ($\varphi = 0.50$) stabilized by PMA-PMA-pe, PAA-pe and mixtures of PMA-pe and PAA-pe has been studied. It is found that the high viscosity of emulsions stabilized by PMA-pe at $\alpha \leqslant 0.30$ is related to the occurrence of the a-conformation. From a quantitative comparison with adsorption experiments (chapter 5) it could be confirmed that the viscosity under this condition is related to the amount of PMA-pe adsorbed in loops.

The network for PMA-pe stabilized emulsions at $\alpha \leqslant 0.30$ is not obtained by a real bridging mechanism between the droplets (i.e. one molecule is anchored on at least two different droplets) but by attractive interparticle forces in the adsorbed layers. This is also concluded from a number of additional experiments.

In the literature there appears to be some doubt as to whether the forces responsible for the stabilization of the a-conformation are hydrophobic bonding and/or V. D. WAALS forces of attraction between the CH_3 groups of the main chain. Some authors arrived at the conclusion that V. D. WAALS forces of attraction are the major factor, because in a water-methanol mixture the attractive forces still exist. From the rheological study presented here it is concluded that hydrophobic bonding is the main factor.

SUMMARY

In this study we have investigated the adsorption behaviour of a number of synthetic polyelectrolytes at the paraffin oil–water interface and the properties of paraffin oil-in-water emulsions stabilized by these polyelectrolytes.

Polyacrylic acid (PAA), polymethacrylic acid (PMA) and the copolymers of the monomeric acids with their methyl esters (resp. PAA-pe and PMA-pe) are used. Most of the experiments have been performed with PMA-pe, whereas the other polyelectrolytes are mainly used for the sake of comparison. In chapter 2 the synthesis and some relevant bulk properties are described. These properties are determined by potentiometric titrations and by viscosimetry. In agreement with the literature it is found that PMA and PMA-pe undergo a reversible conformational transition as a function of pH. At low charge density these polyelectrolytes are characterized by a compact hypercoiled conformation (a-conformation) and by increasing the charge density they unfold, resulting finally in an expanded conformation (b-conformation). This conformational transition is not observed for PAA and PAA-pe.

Several techniques are used to obtain information about the mode of adsorption of these polyelectrolytes at the paraffin oil–water interface and about the properties of emulsions stabilized by them. At undisturbed interfaces the interfacial tension as a function of time $\gamma(t)$ has been determined from interfacial tension measurements with the Wilhelmy-plate technique. Adsorbed (section 3.2.) as well as spread (section 3.3.) monolayers are investigated. It is found that the attainment of the steady state of the interfacial tension $\gamma(\infty)$ is faster the more compact the molecules are (i.e. lower charge density, higher ionic strength, Ca^{2+} counterions) and the higher the polyelectrolyte concentration. These findings agree with the fact that the rate of reduction of the interfacial tension $d\gamma/dt$ is determined by three processes, viz. diffusion of the polymer molecule to the interface with adsorption in its bulk conformation, reconformation and spreading of the arrived molecules. As all three processes usually occur simultaneously, the adsorption behaviour of polymers is very complex. For compact molecules diffusion leads to a rapid accumulation of segments at the interface and reconformation and spreading hardly take place. For more expanded molecules diffusion is slow and the rate of reduction of γ takes place mainly through reconformation. As at higher c_p the supply by diffusion is faster, it is understandable that the steady state is attained faster according as c_p is higher and reconformation and spreading are reduced.

If spreading can take place to a high degree, the fraction of segments per molecule adsorbed in the first layer p, becomes relatively high. From a semi-quantitative interpretation of the interfacial tension measurements it is indeed found that p increases the less compact the molecules are (section 3.5.). To be able to do these calculations also adsorption experiments at an undisturbed liquid–solid (L/S) interface have been performed (section 3.4.). The amount

of adsorbed PMA-pe at the polystyrene latex of low surface charge has been determined and it is assumed that Γ at the oil–water interface and the latex surface does not differ.

Additional information about the mode of adsorption has been obtained from experiments in which the conditions in the water phase were changed after adsorption (chapter 4). Especially changes in pH produced interesting results (so-called γ–pH cycles). It was found that the mode of adsorption determines the degree of (ir)reversibility of the adsorbed layer by increasing pH. The longer the average train length of the adsorbed molecule, the higher the degree of irreversibility. These findings agree with the mode of adsorption as described already in chapter 3. If reconformation and spreading can take place to a high degree (i.e. at high pH) the average train length is large and the molecules are irreversibly adsorbed. If diffusion is the main factor (i.e. at low pH) the average train length is small and desorption is possible.

The properties of emulsions stabilized by these polyelectrolytes have been investigated by the specific interfacial area S (expressed in m² per ml paraffin oil), the amount of adsorbed polyelectrolyte at the emulsified interface Γ_e (expressed in mg per m²) and the viscosity of the emulsions. Γ_e has been obtained by a depletion method (section 5.3.) and S by turbidity measurements (section 5.4.). As these properties did not change with time after finishing emulsification, they enable us to characterize the adsorbed layer at an emulsified interface and they reflect the interesting but complex dynamic processes occurring during emulsification with polyelectrolytes as stabilizers. The results of these investigations are summarized in chapter 5 (S, Γ_e and the mechanism of emulsification) and in chapter 6 (rheology of emulsions and characterization of the adsorbed layer at an emulsified interface).

The interfacial tension at undisturbed interfaces and the emulsion properties have been investigated as a function of a number of parameters. These parameters are polyelectrolyte concentration c_p or polyelectrolyte supply $c_p{}'$, degree of neutralization α (charge density) or pH, ionic strength, nature of the counterion (Na^+, Ca^{2+}) and chemical constitution of the polyelectrolytes. Moreover, it was investigated whether the a- and b-conformation in bulk was reflected in the adsorbed layer, the emulsion properties and the behaviour during emulsification. We will here summarize the effects of these parameters on the interfacial tension (undisturbed interface) and on the emulsion properties (disturbed interface). The comparison between both conditions of the interface is not meant to predict emulsion properties from the adsorption behaviour at an undisturbed interface. We intend to find out which of the investigated parameters play a major role in the interfacial activity at undisturbed interfaces, the emulsification process and the properties of the emulsions once they are formed. To predict the emulsifying behaviour of a polyelectrolyte it is necessary to investigate its interfacial behaviour under dynamic conditions. Such measurements are available (section 3.6.). However, it appears that the theory for the

interpretation of these results is not yet applicable to polymers.

In the course of this study the parameters mentioned before have been investigated seperately for each emulsion property or for each technique to determine the interfacial properties at undisturbed interfaces. Therefore it seems worth while to summarize the results here systematically for each parameter.

Polyelectrolyte concentration c_p or polyelectrolyte supply c_p'

The steady-state value of the interfacial pressure for *adsorbed* layers always increases with c_p, d $\Pi(\infty)/$d $c_p > 0$ (see figs. 3.4. and 3.5.). For *spread* monolayers it is always found that d $\Pi(\infty)/$d $\Gamma_{sp} > 0$ (see figs. 3.11.–3.14.). From the literature it is known that at L/S interfaces d $\Gamma/$d $c_p \geqslant 0$. Hence it is acceptable to assume d$\Gamma_{ad}/$d $c_p \geqslant 0$ for the adsorption of polyelectrolytes onto undisturbed L/L interfaces. However, for adsorbed polymer layers an unambiguous relation between c_p, Π and Γ_{ad} cannot be given. In this study it is argued that Π is primarily related to the occupation of the first layer θ_{ad} (see section 3.5.).

At emulsified interfaces it is always found that d$\Gamma_e/$d$c_p' \geqslant 0$ (see section 5.5.2.). S as a function of c_p' is not univocal and depends on both c_p' and the flexibility of the polyelectrolyte (see below: degree of neutralization). In the region of low c_p' it is always found that S increases with c_p' and that the flexibility only affects the value of S. Above a given c_p' the relation $S(c_p')$ depends on the flexibility of the polyelectrolyte molecule (see section 5.6.). As the flexibility depends strongly on the degree of neutralization the relation between S and c_p' is a function of α.

The viscosity of emulsions – restricted to the highly viscous emulsions with PMA-pe at $\alpha \leqslant 0.30$ as the stabilizer – increases with c_p'. It is found that the viscosity is a function of the amount of PMA-pe adsorbed in loops in the a-conformation (see chapter 6).

Degree of neutralization α (or pH)

As shown in chapter 2 an increase of α gives an expansion of the coil in bulk. At an oil–water interface a higher charge density will reduce the interfacial activity and if adsorption takes place it will result in a thin layer. Moreover, a higher charge density of the adsorbed molecules will give and increased stability of the emulsion droplets by electrostatic repulsion.

To summarize our findings for this parameter it is necessary to distinguish between esterified (PAA-pe and PMA-pe) and non-esterified (PAA and PMA) polyelectrolytes.

In general the steady-state interfacial pressure is reduced at higher pH or α (see figs. 3.6.–3.9.). PAA and PMA are even not interfacially active at pH > 6. From the $\Pi(\infty)$ values of PMA-pe it is deduced that the adsorption mechanism at high pH differs from that at low pH. The $\gamma-$pH cycles underline this conclusion (chapter 4). It appears that adsorption of PMA-pe at pH $= 4$ enables desorption upon pH increase. However, adsorption at pH $= 9$, followed by a

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reduction of the pH to 4, gives an adsorbed layer that is *not* desorbable upon pH increase. Adsorption at pH = 4 takes place with short sequences of segments in trains, whereas at pH = 9 these sequences are longer. Desorption of the long sequences is unlikely.

Spread monolayers of PMA-pe do not confirm the important differences in the interfacial properties as a function of pH. The $\Pi - A$ isotherms of PMA-pe are hardly dependent on the pH (figs. 3.12–3.14.).

The differences between esterified and non-esterified polyelectrolytes are also reflected in the emulsifying and stabilizing capacity of these polyelectrolytes as a function of α. At $\alpha < 0.5$ emulsions stabilized by any of the polyelectrolytes are stable to coalescence, whereas at $\alpha > 0.5$ emulsions prepared with PMA and PAA coalesce directly but emulsions prepared with PMA-pe and PAA-pe remain stable to coalescence (see fig. 5.3.). The obtained area of emulsions stabilized by PMA-pe and PAA-pe as a function of α reflects again the difference in adsorption mechanism between low and high pH.

As the emulsions have been prepared under standard conditions (time of agitation, intensity of agitation and volume fraction of dispersed phase constant) the differences in S as a function of α and c_p' reflect the mechanism of emulsification. The main factor is the way in which the gradients of γ along the interfaces of newly created droplets are reduced. The supply by diffusion to the interface and the rate of reconformation and spreading reduce these gradients and it is the ratio of their contributions that determine the mechanism of emulsification. From earlier experiments with PVA as emulsifying agent it was found that for polymers with a relatively low flexibility S passes through a maximum as a function of c_p'. For polymers with a relatively high flexibility S levels off with increasing c_p'. Analogous results are now found for PMA-pe as a function of α. Especially at $\alpha \geqslant 0.70$ the flexibility is low and a maximum in S is observed. However, the higher α the less pronounced the maximum is, because of additional factors such as the increased electrostatic repulsion and the reduced diffusion (see section 5.6.). At $0.30 \leqslant \alpha \leqslant 0.50$ S levels off with increasing c_p'. At $\alpha \leqslant 0.10$ an enhanced coalescence without desorption results in an increasing S with c_p' and the leveling-off or the maximum is not reached in the region of c_p' investigated by us.

Γ_e decreases with increasing α for all types of polyelectrolytes (see fig. 5.5.). From a comparison with the adsorption at the polystyrene latex surface it is concluded that emulsions stabilized by Na^+PMA-pe at $\alpha < 0.30$ and emulsions stabilized by $Ca^{2+}PMA$-pe over the whole region of α are characterized by a coalescence without desorption during emulsification (see section 5.5.4.).

The viscosity of emulsions stabilized by PMA-pe decreases considerably with higher α. For the explanation see below the section on the conformational transition.

Ionic strength (NaCl)

A high ionic strength reduces the electrostatic repulsion on the polyelectrolyte chain and hence increases its flexibility. Moreover, the diffusion to the

interface increases with increasing ionic strength. These effects will be more pronounced the higher the degree of neutralization. It is anticipated that Γ and $\Pi(\infty)$ will increase with increasing ionic strength. The effect on the emulsion interface is not easy to predict. It depends on the sum effect of the increased diffusion and flexibility and the reduced electrostatic repulsion.

The effect of ionic strength is only investigated for PMA-pe. In general the interfacial pressure increases with higher ionic strength (see fig. 3.4.). It is notable that the ionic strength has no effect on the interfacial pressure at pH = 9, whereas it is still measurable at pH = 4. This again indicates the differences in adsorption mechanism as a function of pH.

At the polystyrene latex surface it is indeed found that Γ increases with increasing ionic strength.

S decreases and Γ_e increases slightly with increasing ionic strength. The viscosity of PMA-pe stabilized emulsions at $\alpha < 0.30$ does not depend on ionic strength.

In general the effects of ionic strength are small compared with the more drastic effects for α and the nature of the counterion.

Nature of the counterion (Na^+, Ca^{2+})

It is anticipated that Ca^{2+} counterions considerably affect all investigated properties. The bivalent bonding of Ca^{2+} ions with dissociated carboxylic groups reduces the flexibility of the polyelectrolyte molecule.

The interfacial pressure is increased and becomes much less a function of α and c_p (see figs. 3.5. and 3.8.).

S is decreased and Γ_e considerably increased in the presence of Ca^{2+} ions. Moreover, S and Γ_e are also hardly dependent on α. It is concluded that bivalent bonding is indeed responsible for this behaviour. From a comparison with the adsorption on polystyrene latex it is deduced that emulsions stabilized by PMA-pe in the presence of Ca^{2+} ions undergo coalescence without desorption during emulsification (see section 5.5.4.). The effect of Ca^{2+} ions on the viscosity of emulsions is not investigated.

Chemical constitution of the polyelectrolytes

A number of the results are already mentioned in the summary of the effect of the degree of neutralization. On account of bulk properties a distinction between PMA(-pe) and PAA(-pe) is obvious (see chapter 2). However, it appears that in the interfacial pressure, S and Γ_e the difference between esterified and non-esterified polyelectrolytes is more pronounced. The interfacial activity of the esterified polyelectrolytes is higher than that of the non-esterified ones (see fig. 3.9.). In general S is higher for the esterified polyelectrolytes, although at $\alpha < 0.30$ the presence of the ester groups is responsible for an additional coalescence during emulsification, resulting in a lower S for emulsions stabilized by esterified polyelectrolytes (see fig. 5.3.). Γ_e is higher for the esterified polyelectrolytes than for the non-esterified ones. This effect is very obvious at $\alpha < 0.30$.

It is found that the viscosity of emulsions is strongly affected by the presence of the methyl groups in the main chain but not by the presence of esterified groups (see fig. 6.1.). It appears that the high viscosity of emulsions stabilized by PMA-pe at $\alpha < 0.30$ is related to the occurrence of a hypercoiled conformation in the molecules.

Conformational transition

The occurrence of two different conformations in bulk is partly reflected in the interfacial and emulsion properties. S and Γ_e are not affected by the presence of the hypercoiled conformation, but only by the presence of the ester groups. Moreover, the interfacial pressure as such does not depend on the conformation. However, the $\gamma-$pH cycles (chapter 4) allow us to locate a transition region in the conformation of the adsorbed layer, which is related to the occurrence of the a- and b-conformation in bulk. Adsorption of the PMA-pe molecules onto the interface from the solution in which the a-conformation exists, leads to reversibility of the adsorbed molecules upon increasing pH after adsorption. However, the molecules are irreversibly adsorbed if the b-conformation exists in solution. This difference in the conformation is only detectable for the esterified polyelectrolytes, since for PMA and PAA desorption always occurs upon increasing pH.

The reversible adsorption of PMA-pe at low pH as compared to the irreversibility at high pH is interpreted by proposing an adsorption model in which the length of the trains plays a dominant role. Adsorption of PMA-pe at pH $= 4$ gives relatively short trains which are desorbable by increasing pH. However, adsorption from solutions in which the b-conformation exists gives relatively long trains and desorption is less probable by increasing pH.

The occurrence of two different conformations in the adsorbed layer is indicated in the viscosity of emulsions stabilized by PMA-pe and/or PAA-pe. The viscosity is only very high for emulsions stabilized by PMA-pe at $\alpha \leqslant 0.30$. It appears to be caused by intermolecular forces of attraction between molecules adsorbed at different droplets and not by a bridging of the droplets by adsorption of one molecule at two or more droplets. These forces are of the same origin as those responsible for the stabilization of the hypercoiled a-conformation. From the viscosity of emulsions stabilized by PMA-pe at $\alpha = 0.10$ in a mixture of water and methanol as the continuous phase it is concluded that the main stabilizing factor for the hypercoiled structure is hydrophobic bonding. This conclusion disagrees with some literature references in which v. d. WAALS forces of attraction are held responsible.

It appears that the prediction of emulsion properties from the interfacial tension measurements at undisturbed interfaces and from the bulk properties of the polyelectrolyte is a difficult problem, because of the very complex dynamic processes occurring during emulsification. However, this study demonstrates that a number of parameters exert an influence on one or more of the investigated emulsion properties and on the interfacial properties at undisturbed

interfaces. It provides more insight into the factors which influence the behaviour of polyelectrolytes at disturbed and undistrubed liquid–liquid interfaces. It contributes to a better conception of the behaviour of proteins at interfaces in more practical systems.

ACKNOWLEDGEMENTS

SAMENVATTING

In het eerste deel van dit onderzoek is het adsorptieproces van een aantal synthetische polyelektrolyten aan het niet-verstoorde grensvlak paraffine olie–water bestudeerd; in het tweede deel zijn de eigenschappen van paraffine olie-in-water emulsies, die gestabiliseerd zijn door deze polyelektrolyten, onderzocht.

Polyacrylzuur (PAA), polymethacrylzuur (PMA) en de beide copolymeren van de monomeren van deze zuren met hun methylesters (resp. PAA-pe en PMA-pe) zijn als synthetische polyelektrolyten gebruikt. Het grootste deel van de experimenten is uitgevoerd met PMA-pe, terwijl experimenten met de andere polyelektrolyten hoofdzakelijk bedoeld zijn om een vergelijking met PMA-pe mogelijk te maken.

In hoofdstuk 2 is de bereidingswijze van de polyelektrolyten beschreven, gevolgd door een karakterisering van hun bulk eigenschappen d.m.v. potentiometrische titraties en viscosimetrie. Het blijkt, dat de beide polymethacrylaten (PMA en PMA-pe) een reversibele conformatieovergang vertonen bij verandering van de pH. Deze overgang is in de literatuur reeds uitvoerig beschreven. Bij lage pH zijn de beide polyelektrolyten opgelost in de vorm van kompakte kluwens (z.g. a-conformatie); zij gaan bij verhoging van de pH geleidelijk over in meer geexpandeerde kluwens (z.g. b-conformatie). De conformatieovergang, het zwak zure karakter van deze polyelektrolyten en de onderlinge verschillen in het hydrofiel gedrag t.g.v. de verschillen in de chemische samenstelling, maken deze polyelektrolyten geschikt als vereenvoudigde modelstoffen voor eiwitten, die in veel praktische systemen gebruikt worden als emulgator of stabilisator.

De eigenschappen van de polyelektrolyten aan het grensvlak olie–water en als emulgator zijn onderzocht als functie van een aantal parameters nl. polyelektrolytconcentratie c_p of polyelektrolytaanbod c_p', neutralisatiegraad α (d.w.z. ladingsdichtheid) of pH, ionensterkte (NaCl), soort tegenion (Na$^+$, Ca^{2+}) en de chemische samenstelling van de polyelektrolyten. Bovendien is nagegaan in hoeverre de a- en b-conformaties zijn terug te vinden in de geadsorbeerde toestand van de polyelektrolyten.

In hoofdstuk 3 is het adsorptieproces van de polyelektrolyten aan het niet-verstoorde olie–water grensvlak bestudeerd d.m.v. de grensvlakspannings-metingen met de Wilhelmy methode. Zowel de grensvlakspanning als functie van de tijd $\gamma(t)$ als de eindwaarde van de grensvlakspanning $\gamma(\infty)$ zijn onderzocht (zie sectie 3.2.). Het blijkt, dat $\gamma(\infty)$ sneller bereikt wordt naarmate de moleculaire afmetingen van het polyelektrolyt in oplossing geringer zijn (d.w.z. lagere pH, hogere ionensterkte, Ca^{2+} i.p.v. Na$^+$ tegenionen) en naarmate c_p hoger is. De resultaten zijn te verklaren uit het feit dat de snelheid waarmee de grensvlakspanning daalt $d\gamma/dt$, bepaald wordt door 3 processen nl. diffusie van polyelektrolyt naar het grensvlak en spreiding en reconformatie van de geadsorbeerde moleculen. De afzonderlijke bijdragen zijn vaak moeilijk te bepalen,

omdat de processen tegelijkertijd verlopen. In kwalitatieve zin kunnen er wel een aantal trends bepaald worden. Indien de afmetingen van de moleculen in bulk gering zijn zal een snelle bezetting van het grensvlak door diffusie optreden en zijn reconformatie en spreiding van weinig invloed. Zijn daarentegen de afmetingen van de moleculen in oplossing groot dan zal de aanvoer door diffusie veel geringer zijn en zal ook reconformatie en spreiding kunnen plaatsvinden. Juist deze beide laatste processen zijn verantwoordelijk voor een lage waarde van $d\gamma/dt$. De invloed van c_p kan eveneens op deze wijze bepaald worden.

De waarde van $\Pi(\infty)$ is in de regel hoger naarmate de pH hoger is. Dit houdt in dat de grensvlakaktiviteit van de gedissocieerde vorm geringer is dan van de niet-gedissocieerde vorm. Uit deze metingen werd aangetoond, dat het adsorptiemechanisme voor PMA-pe voor hoge en lage pH moet verschillen en dat PMA en PAA niet grensvlakaktief zijn bij hogere pH.

Uit metingen aan gespreide monolagen van PMA-pe (zie sectie 3.3.) kan niet worden aangetoond, dat het adsorptiemechanisme van PMA-pe afhankelijk is van de pH. Wel is opnieuw aangetoond, dat de tijdsafhankelijkheid van het spreidingsproces toeneemt bij hogere pH en geringere ionensterkte.

M.b.v. de $\Pi(\infty)$ metingen, de metingen aan gespreide monolagen en de adsorptie experimenten aan polystyreen latex (zie sectie 3.4.) is geprobeerd om de conformatie van de geadsorbeerde monolaag semi-kwantitatief te interpreteren. Hierbij is verondersteld, dat de grensvlakdruk hoofdzakelijk bepaald wordt door de bezettingsgraad van de eerste laag. Inderdaad blijkt, dat de fractie van het aantal segmenten, dat in de eerste laag geadsorbeerd is, stijgt bij toenemende pH en afnemende ionensterkte.

Aan het slot van hoofdstuk 3 zijn de resultaten van experimenten aan een dynamisch lucht–water grensvlak vermeld. Deze experimenten zijn uitgevoerd, omdat op deze wijze het gedrag tijdens het emulgeerproces beter benaderd wordt dan met een statisch grensvlak. Een interpretatie van de resultaten is echter niet goed mogelijk, omdat de bestaande theorie nog niet toepasbaar is op systemen met polymeren.

In hoofdstuk 4 is nagegaan hoe de grensvlakspanning verandert bij verandering van de pH van de oplossing (z.g. γ – pH cycli). Juist voor polyelektrolyten blijkt dit een mogelijkheid te zijn om extra informatie te verkrijgen over de conformatie in de geadsorbeerde laag. Op deze manier werd nog eens duidelijk aangetoond, dat de grensvlakspanning op zich slechts beperkte informatie geeft t.a.v. de conformatie van de geadsorbeerde moleculen. De adsorptie van PMA-pe bij lage pH is volledig reversibel m.b.t. pH verhoging. Daarentegen is de adsorptie van PMA-pe bij hoge pH volledig irreversibel als de pH verlaagd en vervolgens verhoogd wordt. Dit effect staat in direkt verband tot de conformatie van het PMA-pe in de oplossing waaruit adsorptie plaatsvindt. Is de a-conformatie aanwezig dan leidt dit tot reversibele adsorptie, is de b-conformatie aanwezig dan leidt dit tot irreversibele adsorptie. De mate van (ir)reversibiliteit hangt samen met de treinlengte van de geadsorbeerde moleculen. Bij relatief lange treinen (adsorptie vanuit de b-conformatie) is desorptie t.g.v. de

verhoging van de ladingsdichtheid minder waarschijnlijk dan bij relatief korte treinen (adsorptie vanuit de a-conformatie). De beide conformaties kunnen in het grensvlak niet in elkaar overgaan.

In hoofdstuk 5 worden de eigenschappen van emulsies, die gestabiliseerd zijn door deze polyelektrolyten, bestudeerd. Dit gebeurt aan de hand van het specifiek oppervlak S en de geadsorbeerde hoeveelheid polyelektrolyt Γ_e. Opnieuw worden belangrijke verschillen gevonden tussen de veresterde en de niet-veresterde polyelektrolyten. Bovendien zijn belangrijke verschillen gevonden in S en Γ_e als functie van de neutralisatiegraad. Daarentegen zijn S en Γ_e niet afhankelijk van het feit of het molecuul in de a- of b-conformatie opgelost is. Ca^{2+} tegenionen hebben een grote invloed op de emulsie eigenschappen; t.o.v. Na^+ tegenionen is S sterk verlaagd en Γ_e sterk verhoogd. Hetzelfde geldt voor emulsies, gestabiliseerd door de veresterde polyelektrolyten voor $\alpha \leqslant 0.30$. Een vergelijking met de adsorptie aan polystyreen latex leert, dat de verhoogde adsorptie aan het emulsie grensvlak voor Ca^{2+} tegenionen en voor $\alpha \leqslant 0.30$ bij Na^+ tegenionen, het gevolg is van een extra coalescentie zonder desorptie van het polyelektrolyt. Op deze manier kan verklaard worden, dat Γ_e oploopt tot ongeveer 10 mg m^{-2}. Omdat de emulsies gemaakt zijn onder standaardomstandigheden en S en Γ_e niet afhankelijk zijn van de tijd na emulgeren, geeft het verloop van S als functie van c_p' informatie over het emulgeermechanisme voor verschillende neutralisatiegraden. De wijze waarop de bij de nieuw gevormde druppeltjes ontstane gradienten in γ ongedaan gemaakt worden, speelt hierbij een belangrijke rol. Het opheffen van deze gradienten kan geschieden door diffusie van het polyelektrolyt naar het grensvlak en/of door spreiding en reconformatie van reeds geadsorbeerde moleculen in het grensvlak. Uit het reeds eerder onderzochte gedrag van polyvinyl alcohol (PVA) als emulgator is bekend, dat voor een weinig flexibel polymeer S als functie van c_p' door een maximum gaat. Voor flexibele polymeren bereikt S een plateau waarde. Voor PMA-pe kunnen beide mogelijkheden zich voordoen. Voor $\alpha \geqslant 0.70$ is de flexibiliteit gering (t.g.v. de grote ladingsdichtheid) en wordt een maximum in S gevonden. Bij hogere α wordt het maximum geleidelijk minder duidelijk, omdat de elektrostatische repulsie tussen de druppeltjes, waarop het geladen polyelektrolyt geadsorbeerd is, toeneemt en omdat de diffusie van polyelektrolyt naar het grensvlak afneemt. Beide factoren werken de coalescentie tegen. Voor $0.30 \leqslant \alpha \leqslant 0.50$ bereikt S bij toenemende c_p' een plateau waarde.

In hoofdstuk 6 is de viscositeit van de emulsies onderzocht. Bij een volumefractie olie van 0.50 is de viscositeit in bijna alle gevallen lager dan ongeveer 150-300 cP. Alleen de emulsies, gestabiliseerd door PMA-pe bij $\alpha \leqslant 0.30$ zijn veel viskeuzer. O.a. uit mengproeven, waarbij PMA-pe en PAA-pe als emulgator gebruikt zijn, werd aangetoond dat de zeer sterk verhoogde viscositeit geheel is toe te schrijven aan attractiekrachten tussen de geadsorbeerde moleculen van verschillende druppeltjes en niet aan het z.g. brugvormingsmechanisme, waarbij één molecuul op verschillende druppeltjes geadsorbeerd is. Deze attractiekrachten zijn dezelfde als die, welke de a-conformatie in oplossing stabiliseren. Op grond van emulsie experimenten, waarbij een water–methanol

mengsel als continue fase gebruikt is, werd aangetoond, dat hydrofobe binding verantwoordelijk is voor de stabilisatie van de a-conformatie.

Het voorspellen van emulsie eigenschappen op grond van grensvlakspanningsmetingen aan statische grensvlakken en op grond van de bulk eigenschappen van de polyelektrolyten is uiterst moeilijk, vanwege het complexe dynamische gedrag tijdens het emulgeren. In dit onderzoek is nagegaan in hoeverre de invloed van een aantal parameters op statische grensvlak eigenschappen is terug te vinden in één of meerdere emulsie eigenschappen. Dit leidt tot een beter inzicht in de factoren, welke van invloed zijn op het grensvlakgedrag van polyelektrolyten aan statische en aan dynamische vloeistof–vloeistof grensvlakken. Bovendien geeft dit modelsysteem ons de mogelijkheid na te gaan welke factoren wel of geen rol van betekenis spelen bij het gedrag van eiwitten aan vloeistof–vloeistof grensvlakken in meer praktische toepassingen.

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LIST OF SYMBOLS

A	area per mg of adsorbed polyelectrolyte, $m^2\ mg^{-1}$
A_0	limiting area per adsorbed segment ($= 0.20\ nm^2$)
a	exponent in MARK-HOUWINK equation (eq. 2.9.)
a_1	proportionality constant between Π and ε (eq. 3.2.)
c_a	polyelectrolyte concentration in the a-conformation, ppm
c_b	polyelectrolyte concentration in the b-conformation, ppm
c_p	polyelectrolyte concentration, ppm; $c_p = c_a + c_b$
$c_p{'}$	polyelectrolyte supply, mg/ml paraffin oil
D_s	rate of shear, sec^{-1}
d	droplet diameter, μm
d_m	maximum droplet diameter, μm
d_1	auxiliary droplet parameter (eq. 5.1.)
$\bar{d}_{vs}(= \bar{d}_{32})$	volume surface droplet diameter, μm
E	optical density; $E = \log I_0/I$
$\Delta G°$	standard free energy change of dissociation (eq. 2.4.)
ΔG_{el}	electrostatic free energy change for dissociation of polyacid (eg. 2.5.)
ΔG_{ads}	free energy gain of adsorption of polymer segment
I	intensity of transmitted light
I_0	intensity of incident light
K	apparent ionization constant (eq. 2.5.)
K_0	intrinsic ionization constant (eq. 2.2.)
K_{av}	averaged ionization constant in H−H equation (eq. 2.7.)
k	constant in MARK-HOUWINK equation (eq. 2.9.)
L	length of the vessel for dynamic interfacial or surface tension measurements, cm (section 3.6.)
l	optical path length of cuvette, cm
$\bar{M}_\eta$	viscosity averaged molecular weight of the polyelectrolytes
N	number of emulsion droplets per unit volume
n	constant in H−H equation (eq. 2.7.)
n_c	refractive index of continuous phase
n_d	refractive index of dispersed phase
p	fraction of segments per polyelectrolyte molecule, adsorbed in the first layer
p_{ad}	ibid. by adsorption from solution
p_{sp}	ibid. by spreading
Q	light scattering coefficient (eq. 5.2.)
$Q*$	ibid. corrected for forward scattering
q	proportionality constant between θ and Π, $mM\ m^{-1}$ (eq. 3.1.)
R	gas constant
R_G	radius of gyration, nm
$r\ (= d_m/d_1)$	truncation parameter (eq. 5.1.)
S	interfacial area of the emulsion per ml oil phase, m^2/ml

x	distance from the interface, nm
y	distance from the movable barrier in the vessel for dynamic interfacial tension measurements, cm (section 3.6.)
Z	reduced turbidity (eq. 5.4.)
α	degree of neutralization, i.e. the fraction of the equivalent amount of NaOH to neutralize the anionic polyelectrolyte solution ($\alpha = C_{NaOH}/C_M$; C_M stands for the concentration of polyelectrolyte in monomeric equivalents)
α'	degree of ionization, i.e. the fraction of acid groups that is dissociated ($\alpha' = C_{NaOH} + C_{H+}/C_M$)
α'_a	ibid. for the a-conformation
α'_b	ibid. for the b-conformation
α_η	linear expansion factor (eq. 2.10.)
$\beta\ (= -d\ln\Delta\gamma/d\gamma)$	damping coefficient of longitudinal wave (section 3.6.)
Γ	adsorbed amount of polyelectrolyte per unit area, mg m^{-2}
Γ_e	ibid. at an emulsified interface, mg m^{-2}
Γ_f	ibid. in the first layer of the interface, mg m^{-2}
Γ_l	ibid. for adsorption on the polystyrene latex, mg m^{-2}
Γ_{ad}	ibid. for adsorption from solution on L/L interface, mg m^{-2}
Γ_{lp}	ibid. for adsorption in loops, mg m^{-2}
Γ_{sp}	ibid. for a spread layer, mg m^{-2}
γ	surface, interfacial tension, mN m^{-1}
$\Delta\gamma$	change in surface, interfacial tension, mN m^{-1}
$\gamma(t)$	interfacial tension as a function of time, mN m^{-1}
$\gamma(\infty)$	steady state interfacial tension, mN m^{-1}
$\varepsilon\ (= d\gamma/d\ln A)$	surface, interfacial dilational modulus, mN m^{-1}
η	viscosity, dl/g
$[\eta]$	intrinsic viscosity, dl/g
η_{sp}	viscosity ratio excess
η_r	emulsion viscosity relative to $\eta(D_s = 7.05\ \text{sec}^{-1})$
Θ	theta condition
θ	fraction of the interface occupied by polyelectrolyte
θ_{ad}	ibid. for adsorption from solution
θ_{sp}	ibid. for spreading
θ_{mpx}	maximum occupation of the interface ($= 0.70$)
λ	wavelength, nm
$\nu (= c_b/c_p)$	fraction of polyelectrolyte in the b-conformation
Π	surface or interfacial pressure, mN m^{-1}
$\Pi(t)$	interfacial pressure as a function of time, mN m^{-1}
$\Pi(\infty)$	steady-state interfacial pressure, mN m^{-1}
ρ	dimensionless droplet-size diameter (eq. 5.3.)
ρ_1	dimensionless auxiliary parameter (eq. 5.7.)
$\overline{\rho}_{32}$	dimensionless volume-surface diameter
$\rho_p(x)$	polymer density as a function of the distance from the interface, surface

σ	spreading parameter in droplet-size distribution (eq. 5.1.)
σ_0	surface charge of polystyrene latex
τ	phase angle difference between surface change and surface tension (section 3.6.)
φ	volume fraction of dispersed phase
ω	angle frequency of the longitudinal wave, $rad.sec^{-1}$