ADSORPTION OF POLYVINYLALCOHOL ON PARAFFIN-WATER INTERFACES AND THE PROPERTIES OF PARAFFIN-IN-WATER EMULSIONS STABILIZED BY POLYVINYLALCOHOL

AN EXPERIMENTAL STUDY

J. M. G. LANKVELD

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Dit proefschrift met stellingen van

JOSEPH MARIA GERARDUS LANKVELD,

landbouwkundig ingenieur, geboren te Arnhem, 17 mei 1943, is goedgekeurd door de promotor, Dr. J. LYKLEMA, hoogleraar in de Fysische- en Kolloidchemie.

De Rector Magnificus van de Landbouwhogeschool,
J. M. POLAK

Wageningen, November 1970

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AN EXPERIMENTAL STUDY

(with a summary in Dutch)

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD
VAN DOCTOR IN DE LANDBOUWWETENSCHAPPEN
OP GEZAG VAN DE RECTOR MAGNIFICUS, MR. J. M. POLAK,
HOOGLERAAR IN DE RECHTS- EN STAATSWETENSCHAPPEN
VAN DE WESTERSE GEBIEDEN,
IN HET OPENBAAR TE VERDEDIGEN
IN DE AULA
VAN DE LANDBOUWHOGESCHOOL TE WAGENINGEN
OP DONDERDAG 17 DECEMBER 1970 TE 16 UUR

DOOR

J. M. G. LANKVELD

H. VEENMAN & ZONEN N.V. - WAGENINGEN - 1970

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STELLINGEN

I

Een hoofdwasmiddel dient bij voorkeur niet als zodanig te worden gebruikt.

II

De theoretische interpretatie van de gemeten grensvlakspanningsdaling, veroorzaakt door geadsorbeerde polymeren, in termen van polymeeradsorptie is complex vanwege het irreversibel karakter van de adsorptie. Toepassing van de Gibbsvergelijking is daardoor niet geoorloofd.

Dit proefschrift, hoofdstuk 2 en 5

III

De tijdsafhankelijkheid van de grensvlakspanningsdaling tengevolge van polymeeradsorptie kan worden toegeschreven aan twee verschillende mechanismen: diffusie en reconformatie.

Dit proefschrift, hoofdstuk 3.

IV

Jaffe et al. hebben niet onderkend dat de uitkomst voor de berekende interactieenergie tussen de monomeereenheden in een polymeerlaag, via de theorie van Motomura en Matuura, zeer gevoelig is voor de keuze van het coördinatiegetal.

Motomura, K. en Matuura, R., J. Colloid Sci. 18, 52 (1963).
Jaffe, J., Bricman, G. en Gelbcke, A., J. Chim, Phys. 64, 942 (1967).
Dit proefschrift, hoofdstuk 4.

V

De tegenstrijdige resultaten van O'Donnell et al. enerzijds en van Dunn en Taylor anderzijds bij hun onderzoekingen naar het effect van de PVA concentratie op de polymerisatiesnelheid van vinylacetaat moet waarschijnlijk worden toegeschreven aan het anomale emulgeergedrag van het meer hydrofobe PVA.

O'Donnell, J. T., Mesrobian, R. B. en Woodward, A. E., J. Polymer Sci. 28, 171 (1958).
Dunn, A. S. en Taylor, P. A., Makromolek. Chem. 83, 207 (1965).
Reynolds, G. E. J. en Gulbekian, E. V., Soc. Chem. Ind. Monograph nr. 30, 131 (1968).
Dit proefschrift, hoofdstuk 5 en 6.

VI

Het is onjuist het werk van Cockbain aan te halen als voorbeeld waarbij de emulgeertechniek is gebruikt als directe methode voor de bepaling van de adsorptie aan vloeistof/vloeistof grensvlakken omdat door Cockbain de specifieke oppervlakken van de emulsies niet onafhankelijk zijn bepaald.

Cockbain, E. G., Trans. Faraday Soc. 50, 874 (1954).
Davies, J. T. en Rideal, E. K., 'Interfacial Phenomena' Acad. Press p. 210 (1963)
Kitchener, J. E. en Musselwhite, P. R., 'Emulsion Science' editor P. Sherman, Acad. Press p. 90 (1968)

VII

De door de IUPAC gegeven definitie van een emulsie luidt: 'An emulsion is a dispersion of droplets of one liquid in another one with which it is incompletely miscible'. Volgens deze definitie kan melk alleen dan een emulsie zijn als het zich buiten de koelkast bevindt.

IUPAC Information Bulletin nr. 3 (1970)

VIII

Chen en Joslyn hebben bij de bestudering van de invloed van suikers op de viscositeit van pektine-oplossingen onvoldoende rekening gehouden met de complexe verandering van pH, ionsterkte en diëlectrische constante van de oplossing ten gevolge van de suikertoevoeging.

Chen, Tung-Shan en Joslyn, M. A., J. Colloid Interface Sci. **23**, 399 (1967).
Ibid: **25**, 346 (1967)

IX

De bewering van Bender dat de dosering van een nutriënt boven het fysiologisch minimum geen enkel aantoonbaar gunstig effect heeft is aanvechtbaar.

Bender, A. L., Royal Soc. Health J., **5** 221 (1969).

X

De conclusie van Engelberg en Artman dat het RNA van levensvatbare bacteriofagen tijdens de replicatie van het virus kwantitatief in een dubbelstrengige vorm wordt omgezet is logisch doch niet gebaseerd op door hen verkregen experimentele resultaten.

Engelberg, H. en Artman, M., J. Mol. Biol. **48** 181 (1970)

XI

De conclusie van Holland et al. dat, op grond van de waargenomen koppelingsconstanten bij 1-Thio-ß-D-glucopyranose Penta acetate de C-6 acetoxygroep antiparallel staat met C-4, is aanvechtbaar.

Holland, C. V., Horton, D. Miller, M. J., en Bhacca, N. S., J. Organic Chem. **32**, 3077 (1967)

XII

Het normaliseren van St. Nicolaaskleding dient te worden overwogen.

J. M. G. Lankveld
17 december 1970

Aan de nagedachtenis van Vader
Aan Moeder
Aan Ria, Marc en Nicole

VOORWOORD

Bij het gereedkomen van dit proefschrift realiseer ik mij aan hoevelen ik dank verschuldigd ben; dank aan hen die bijdroegen tot mijn wetenschappelijke vorming, en aan hen, die medewerkten bij het tot stand komen van dit proefschrift.

In de eerste plaats geldt deze dank mijn ouders, die mijn studie krachtig hebben gestimuleerd. Vader, helaas ging je te vroeg heen om het resultaat ervan te kunnen zien.

U, Hoogleraren en Lectoren van de Landbouwhogeschool dank ik voor alles wat ik op Uw colleges en practica, alsook in persoonlijk contact heb mogen leren.

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Zeergeleerde WALSTRA, de methode voor het bepalen van emulsieoppervlakken, waarin U mij hebt geadviseerd, is voor mij van grote waarde gebleken.

De prettige en collegiale sfeer op de afdeling Fysische en Kolloidchemie heeft stellig bijgedragen tot een snelle afronding van dit onderzoek.

Geleerde FLEER, jou wil ik in dit verband speciaal noemen omdat het PVA waarmee jij was gestart, in mijn onderzoek interessante eigenschappen bleek te bezitten. De vele discussies die we over PVA hebben gehad waren bijzonder nuttig.

De waardevolle hulp, bij de uitvoering van de metingen aan emulsies, van de de studenten VAN LEEUWEN, LANGENBERG, SCHELLART, HARTOG en JOOSTEN wil ik niet onvermeld laten. De heer H. VAN BEEK wil ik danken voor het vervaardigen van de figuren. Speciale dank geldt Mej. MOLLEN en Mevr. VAN DER MADE-KLEIJNE voor de snelheid waarmee zij het manuscript hebben getypt.

De heer J. GILBERT M.A. ben ik bijzonder dankbaar voor het verzorgen van de Engelse tekst.

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CONTENTS

1. INTRODUCTION

1.1. GENERAL

A look at the literature of recent years reveals that the adsorption of polymers is receiving much attention, both practical and theoretical. This is not so surprising in view of the enormous expansion in the application of polymers during the last decade. This expansion explains the need for fundamental knowledge about the factors affecting the physical properties of polymers. One of these properties is the behaviour of polymers at phase interfaces. More knowledge of this would give a better insight into the mode of action of polymers as dispersing agents, flocculating agents, adhesives, emulsion stabilizers, and the like.

Most of the studies on polymer adsorption have so far concerned adsorption at liquid-solid interfaces and, to a lesser extent, gas-liquid interfaces. Much less is to be found in the literature about the adsorption of polymers at liquid-liquid interfaces. Nevertheless, this subject most certainly deserves attention, for polymers play an important role in the stabilization of emulsions (KITCHENER and MUSSELWHITE, 1968). An emulsion is a distribution of droplets of one liquid in another liquid, the two of which are immiscible. Emulsions are thermodynamically unstable. The existence of the individual droplets is prolonged considerably when a third substance (the stabilizer) is present which reduces the chance of a break in the film between two droplets close to one another. Polymers are very suitable as stabilizers, and there are numerous examples to be found in practice. Milk is an emulsion of fat in an aqueous phase containing milk proteins, which act as stabilizers. Various hydrocolloids are used as emulsion stabilizers in the pharmaceutical industry (SCHWARZ, 1962). Polymers can also be used to stabilize monomers during the preparation of polymers by emulsion-polymerisation (SCHULLER, 1965).

The interfacial activity of polymers can be important not only in the stabilization of emulsions but also in the field of biochemistry. Some enzymes are more active when adsorbed. Lipase, for instance, is most active with emulsified triglycerides (FRUTON, 1953); this can be ascribed to the conformation which the enzyme can assume at the interface. The formation of plaques on the walls of arteries may also have something to do with the properties of macromolecules at a phase interface.

The aim of our investigation is to find out more about the adsorption of polymers at oil-water interfaces. Since the polymer adsorption is irreversible and because the properties of the interface are dependent on its history, it is necessary to approach the problem from different angles and to interpret the results critically. In this study, therefore, measurements have been made on adsorbed and spread monolayers as well as on emulsions.

Paraffin – polyvinylalcohol – water was chosen as the model system. Paraffin was chosen on account of its very low solubility in water. Polyvinylalcohol

(PVA) is water-soluble, non-ionic, and readily determined quantitatively in solution, all of which makes this polymer suitable for model experiments. The effects of the factors time and the concentration, molecular weight and hydrophobicity of the PVA on the interfacial tension of adsorbed and spread monolayers have been studied. In addition, the adsorption of the PVA at the interface of an emulsion obtained by emulsifying the same model system has been measured; these latter measurements were also useful in providing information about the effectiveness of the polymer as an emulsifier.

1.2. POLYMER ADSORPTION

A polymer molecule consists of a chain of segments, some of which will be caught up in the interface during adsorption. The segments which have not been adsorbed in the interface stick out like loops into the liquid. A polymer molecule adsorbed in this way can, depending on various factors, assume different conformations at the interface. This is in contrast to a low-molecular-weight substance which usually adopts a single uniform orientation at the interface. Some possible conformations of an adsorbed polymer molecule are sketched in fig. 1.1. It can be seen that both the surface taken up by one molecule and the fraction of segments adsorbed per molecule decreases from a to c, whereas the total adsorption in fact increases. The principal factors determining the conformation of the polymer at the interface are the flexibility of the polymer chain, the mutual interaction of the polymer segments, and the interaction between the polymer and both the solvent and the interface. The polymer concentration in the solution is also important, since kinetic factors, such as the relative rates of supply to the interface by diffusion and of the unfolding of partially adsorbed molecules, can substantially influence the final conformation of the polymer during the formation of the interface.

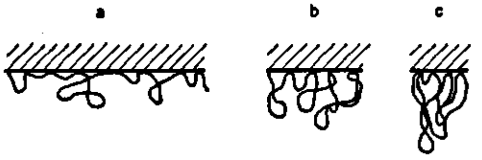

FIG. 1.1. Some possible conformations of a polymer molecule adsorbed at an interface.

The adsorption of polymers has been reviewed by, amongst others, SILBERBERG (1962b), PATAT et al. (1964) and STROMBERG (1967). From the publications it appears that polymer adsorption usually satisfies all, or in any case many, of the following conditions:

1. Attainment of the steady state[1] takes very much time.
2. The rate of desorption of complete molecules is so low that the adsorption of the polymer can be considered as irreversible.

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[1] The term steady state is used here and below to indicate that the final values are independent of time without implying that equilibrium has been attained.

3. The polymer is totally adsorbed at low concentrations, i.e. the adsorption isotherms have a 'high-affinity' character.
4. Only a fraction of the segments comprising the polymer molecule are adsorbed on the interface, so that parts of the polymer chain stick out like loops into the solutions (fig. 1.1.), at least at high coverages.
5. Generally, the temperature-dependence is slight, while adsorption increases with increasing molecular weight. There is, however, much less agreement in the literature on these aspects. In this context, ons should take into account that the quality of the solvent is also important.

In recent years, various workers have tried to approach the problem of polymer adsorption theoretically, with the aid of models and statistical methods. The principal theories are those of FRISCH and SIMHA (1954, 1955, 1957), SILBERBERG (1962, 1967, 1968), HOEVE (1965, 1966) and CLAYFIELD and LUMB (1966, 1968). The basis of their approach is a model defined by various parameters, the adsorption being calculated as a function of the concentration and of these parameters. At present, however, it is impossible to determine independently the various parameters which describe the polymer adsorption, so that the theories cannot be verified. These theories are, therefore, restricted in their usefulness. They do, however, enable insight to be gained in the effect which different factors, such as molecular weight, quality of the solvent and flexibility of the polymer chain, have on the adsorption of the polymer.

1.3. MATERIALS

1.3.1. *Paraffin*

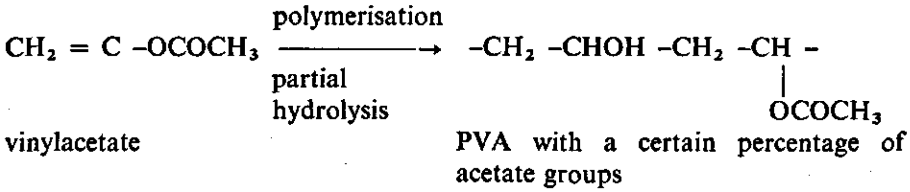
Paraffin was selected because of its very poor solubility in water and because the different alkanes have almost the same interfacial tension against water (REHFELD, 1967). The interfacial tension measured against distilled water was 50.5 ± 0.2 mN m^{-1} with a spread of ± 0.8 mN m^{-1} between the different paraffin samples. The paraffin was only judged suitable if the interfacial tension against distilled water decreased by less than 1.0 mN m^{-1} in 24 hours. The liquid paraffin was form E. Merck A.G., Darmstadt; its density was 880 kg/m^3 and its viscosity at 25°C was about 8.0 N sec m^{-2}.

1.3.2. *Polyvinylalcohol (PVA)*

PVA is soluble in water but not in paraffin and is, on account of its lack of groups which can dissociate, little sensitive to changes in pH and electrolyte concentration. Moreover, it is fairly easy to determine quantitatively very low concentrations of PVA in solution. Much information about the properties and use of PVA was given at a recent symposium devoted to it (FINCH, 1968).

1.3.2.1. Synthesis and structure

The polyvinylalcohol is prepared by polymerisation of vinylacetate to polyvinylacetate (PVAc) and subsequent partial hydrolysis. The PVA contains a certain percentage of acetate groups, depending on the degree of hydrolysis:



$$CH_2 = C\text{-}OCOCH_3 \xrightarrow[\text{partial hydrolysis}]{\text{polymerisation}} \text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}\underset{\displaystyle OCOCH_3}{\underset{|}{CH}}\text{-}$$

vinylacetate

PVA with a certain percentage of acetate groups

The polymer obtained may be considered as a copolymer of vinylalcohol and vinylacetate. It is probable that the acetate groups are distributed not uniformly along the chain but in blocks (HACKEL, 1968). It has been found that the rate of hydrolysis increases with time, which implies that hydrolysis proceeds more quickly once free OH–groups have been formed. It is therefore likely that an acetate group next to a free OH-group is more readily hydrolysed, which results in a non-random distribution of the remaining acetate groups along the chain. The non-random distribution can also be deduced from the fact that the surface activity of partially acetylated PVA, in which it is assumed that the distribution is random, is different from that of PVA obtained by partial hydrolysis of polyvinylacetate (HAYASHI et al., 1964). The structure of the polymer chain can also be influenced by the tacticity and the 1,2-diol content (MOORE and O'DOWD, 1968), as well as by other factors which are summarized by ZWICK (1964).

1.3.2.2. Solubility

The solubility characteristics of PVA depend strongly on its degree of hydrolysis. When the latter exceeds 90%, the polymer is poorly soluble in water at room temperature but dissolves readily at 80°C. Upon cooling the polymer remains in solution. When the degree of hydrolysis is less than 90%, PVA dissolves at room temperature but becomes insoluble at higher temperatures (~ 70°C). The effect of the acetate content on the behaviour of PVA samples in solution thus seems to be characterized by a fairly sharp boundary at about 10% acetate groups (PETER and FASBENDER, 1964). Further evidence for this is provided by the intrinsic viscosity of PVA which is substantially independent of the acetate content up to 10%, but thereafter decreases sharply with increasing acetate content (TOYOSHIMA, 1968) indicating a reduction in the predominantly hydrophilic character.

The solutions are stable although fully hydrolysed PVA in concentrated solution can aggregate after a time (TOYOSHIMA, 1968).

PVA is completely insoluble in paraffin. We confirmed this by shaking a concentrated aqueous PVA solution (4000 ppm[1]) with paraffin; after centrifuging, part of the paraffin was shaken with a little distilled water. No PVA could be detected in the water.

1.3.2.3. Types of PVA used

In all experiments commercial preparations, from a variety of suppliers, were used. The PVA was usually coded by two numbers, the first indicating

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[1] All concentrations are expressed as parts per milion by weight.

TABLE 1.1. Specification of polyvinylalcohol samples

Sample code	Molecular weight	Degree of polymerisation	Manufacturer
8 - 98	35,000	780	KONAM, The Netherlands
16 - 98	55,000	1230	KONAM, The Netherlands
32 - 98[b]	80,000	1780	KONAM, The Netherlands
3 - 98.5	13,000	290	WACKER, Germany
28 - 98.5	72,000	1600	WACKER, Germany
48 - 98	91,000	2040	WACKER, Germany
60 - 99	105,000	2340	WACKER, Germany
(105)[a]	24,000	535	KURASHIKI, Japan
(124)[a]	110,000	2450	KURASHIKI, Japan
4 - 88	22,000	450	KONAM, The Netherlands
16 - 88	60,000	1220	KONAM, The Netherlands
3 - 88	16,000	325	WACKER, Germany
5 - 88	26,000	530	WACKER, Germany
13 - 88	53,000	1080	WACKER, Germany
25 - 88	85,000	1730	WACKER, Germany
40 - 88	106,000	2160	WACKER, Germany
(204)[a]	20,000	410	KURASHIKI, Japan
25 - 82.5	90,000	1830	WACKER, Germany
25 - 76.5	95,000	1760	WACKER, Germany

[a] The degree of hydrolysis of PVA samples 105 and 124 from KURASHIKI is about 98%, that of PVA 204 about 88%.

PVA 32–98 contains some alkyl residues.

the viscosity of a 4% aqueous solution at 20°C and the second the degree of hydrolysis. The PVA samples used in this investigation are listed in table 1.1., together with the suppliers' quotations of their viscosity-average molecular weights. Incidental checks of the molecular weights by viscosity measurements showed that the quoted values were reliable. The average molecular weight $\overline{M}$ was calculated from the intrinsic viscosity, $[\eta]$, from the relationship:

$$[\eta] = k\overline{M}^{\alpha}$$

At 25°C values for k (dl/g) and α were taken to be 8.8×10^{-4} and 0.61 respectively at an acetate content of about 2%, and 9.9×10^{-4} and 0.59 respectively at an acetate content of about 12%. The k and α values were derived from viscosity measurements with the PVA samples from Kurashiki, for which the molecular weight was given. There is close agreement between the values derived for k and α and those quoted by BRANDRUP and IMMERGUT (1965).

The different PVA samples were obtained by courtesy of Konam N.V., Amsterdam, except for the three lots of PVA from Kurashiki which were supplied by the Fresal Company, Amsterdam.

1.3.2.4. Quantitative determination in solution

Quantitative determination of PVA in solution can be done colorimetrically.

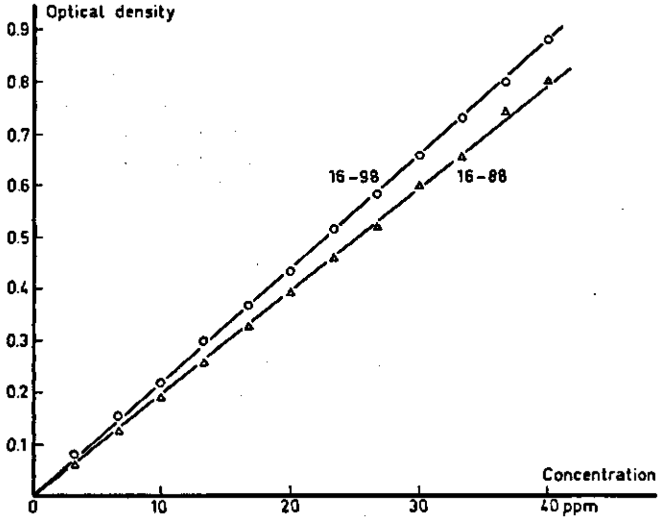


FIG. 1.2. Calibration curves for the determination of PVA in solution with boric acid and potassium iodide.

By treatment with boric acid the polymer is brought into a helix conformation, in which iodine can be entrapped to give a blue complex analogous to the starch-iodine complex (ZWICK, 1965). The method can be made quantitative by a suitable choice of concentrations. It has already been applied by several workers (HORACEK, 1962; CHENE, 1966; and MONTE BOVI, 1969).

To 6 ml of an aqueous solution of between 0 and 40 ppm PVA, 4 ml of an aqueous solution of 0.64 M H_3BO_3, 0.06 M I_2 and 0.018 M KI is added. Extinction is measured at 670 nm in a 1 cm cuvette against a blank sample. The measured extinction is proportional to PVA concentration in the range 0–40 ppm, as is shown for two PVA samples in fig. 1.2. The slope of the line decreases slightly with decreasing molecular weight and increasing acetate content. With increasing acetate content, maximum absorption shifts to a lower wavelength. According to ZWICK (1966) this can be ascribed to the shorter helices which are formed at higher acetate contents as a result of the hindrance of the acetate groups to helix formation.

1.3.3. *Water*

For the measurement of interfacial tensions and for the preparation of emulsions, the polymer was dissolved in distilled water. The surface tension of the distilled water was measured to check whether it was free from surface-active substances, 72.0 mN m^{-1} being taken as the minimum permissible value at 20°C.

2. STEADY-STATE INTERFACIAL TENSION BETWEEN PARAFFIN AND POLYVINYLALCOHOL SOLUTIONS

2.1. INTRODUCTION

Few systematic studies have been made of the lowering, $\triangle\gamma$, of the interfacial tension as a result of the adsorption of a polymer ($M > 10{,}000$) at air-liquid and liquid-liquid interfaces. Those studies so far reported in the literature on the effect of polymer adsorption on the interfacial tension generally reveal the size of the drop in interfacial tension but provide little information on polymer adsorption as such. In addition, if improperly done, the results will depend on the method of measurement. This is to be expected with an irreversible process like polymer adsorption and has been clearly demonstrated for PVA (KUHLMAN, 1965; LANKVELD and LYKLEMA, 1968). The conformation of the adsorbed polymer molecule will depend on the way in which the interface is formed. When an interface is stretched, more segments of an already partially adsorbed polymer will be pulled into the interface, thus causing a change in the conformation of the polymer and consequently a different value of $\triangle\gamma$. Methods of measurement in which the interface does not attain the steady state must therefore be rejected. Stretching of an interface during its formation occurs for instance with the drop-weight method. Since the attainment of the steady state often takes more than 12 hours (chapter 3), a static method is required.

Previous papers about the effect of adsorbed polymers ($M > 10^4$) on the reduction in interfacial tension are summarized in table 2.1. Careful note should be made of the method of measurement. Most of the investigations are limited in their scope and not very systematic; moreover they enable little comparison because the polymer has been inadequately characterized and the methods of measurement are different. Probably the most systematic investigation to date is that of GLASS (1968), although his quantitative interpretation of the results raises many doubts.

One facet of the investigation to be described here has already been published (LANKVELD and LYKLEMA, 1968). This article outlined several important differences in interfacial activity between PVA with about 2% acetate groups and PVA with about 12% acetate groups. The principal point to emerge was the discontinuity in the γ-log c_p curve at the lower acetate level (c_p = polymer concentration). The dependence of γ on time was also irregular for the polymer with the lower acetate content for certain levels of c_p. HUBER and THIES (1970) obtained analogous results with polymethyl methacrylate at a toluene-water interface.

2.2. THEORY

2.2.1. *Introduction*

The problem is how to interpret the measured interfacial tensions in terms of polymer adsorption. The adsorption of a polymer molecule is irreversible, for

TABLE 2.1. A summary of the literature on the effect of polymer adsorption on interfacial tension

Author	Interface	Polymer	Method of Measuring	Remarks
MATTHEWS (1939)	cyclohexane – water	natural carbohydrate polymers	drop-weight	steady state within about 3 min.; high concentrations
KATCHALSKY and MILLER (1951)	air – water	polymethacrylic acid	drop-weight	steady state within about 5 min.; $\Delta\gamma$ proportional to ln c_p and $P^{-1/2}$
FRISCH and AL-MADFAI (1958)	air – water tetraline – water	polyvinylalcohol polystyrene	drop-weight	steady state within 20–100 min.; concentration 1%
SHOTTON and KALYAN (1960)	benzene – water	sodium alginate gelatin	sessile drop	steady state within about 74 hours
FUKAWA et al. (1961)	air – water	polyvinylalcohol	static Wilhelmy-plate	steady state within about 15 hours; exponential decrease of γ with time; concentrations $\geqslant$ 100 ppm
MACRITCHIE and ALEXANDER (1963)	air – water	proteins	static Wilhelmy-plate	low concentrations 1–30 ppm
HAYASHI et al. (1964)	air – water	polyvinylalcohol	drop-weight	the effect of the distribution of the residual acetate groups is shown
MUKERJEE and SHUKLA (1967)	kerosene – water olive oil – water	natural carbohydrate polymers and gelatin	du Nouy ring	concentration 10^3–10^4 ppm
GROMOV et al. (1967)	styrene – water	polyvinylalcohol	du Nouy ring	concentration 1–10,000 ppm

TABLE 2.1. Continued

Author	Interface	Polymer	Method of Measuring	Remarks
BLOCK and LAMY (1968)	cyclohexane – water n-octanol – water	sodium carboxymethylcellulose hydroxypropylcellulose	drop-weight	few measurements
GLASS (1968)	air – water	polyvinylalcohol polyvinyl pyrrolidone polyethylene oxide	drop-weight	steady state within about 1 min.
JOOS (1968)	air – water	proteins	static Wilhelmy-plate	$\Delta\gamma$ proportional to ln c_p
LANKVELD and LYKLEMA (1968)	paraffin – water	polyvinylalcohol	static Wilhelmy-plate	anomalous behaviour as function of concentration and time for low acetate content
ABRAMZON and GROMOV (1969)	air – water isopentane – water toluene – water	polyvinylalcohol		
KUHLMAN et al. (1968, 1969)	air – water	polyvinylalcohol	sessile bubble	steady state within about 2 hours, concentration 1%
HUBER and THIES (1970)	toluene – water	polystyrene; polyethylene; ethylcellulose; polymethyl methacrylate	du Nouy ring	anomalous behaviour of polymethyl methacrylate as funtion of concentrations; 1–100 ppm hardly any effects of time; > 100 ppm steady state after more than 11 hours

it is adsorbed by way of many tens of segments, all of which would have be desorbed simultaneously if the molecule itself is to be desorbed. The probability of this happening is very slight. Consequently, the conformation of the polymer, and hence the reduction in interfacial tension, can depend on the history of the interface. On the other hand, the adsorption of a single segment probably is a reversible process, so that an equilibrium will be established locally. An indication for this can be found in the work of COCKBAIN (1956). He found that a layer of serum albumin adsorbed on an emulsion interface could be completely replaced by sodium dodecyl sulfate (SDS). This means that the segments of the albumin must be desorbed and the adsorption sites occupied by SDS. In this way the albumin is gradually removed from the interface. If the adsorption of individual segments is indeed reversible, the theoretical interpretation becomes somewhat less difficult. One can then apply statistical-thermodynamic methods to the individual segments. Results for polymer molecule as a whole can not be compared with experiments because equilibrium is not experimentally attainable.

A brief account will be given of the various theories on the reduction in interfacial tension as a result of polymer adsorption.

2.2.2. *Gibbs' law of adsorption*

The occupation of a surface by low-molecular-weight substances can be calculated from the reduction in interfacial tension for different concentrations of the substances from the well-known equation of GIBBS:

$$\Gamma = -\frac{1}{RT}\cdot\frac{d\gamma}{d(\ln c)} \qquad 2.1.$$

where Γ = the absorption of the low-molecular-weight substance per unit interface (if $\Gamma_{solvent} = 0$)
c = the equilibrium concentration of the low-molecular-weight substance
γ = interfacial tension
R = the gas constant
T = the absolute temperature.

It is assumed here that the low-molecular-weight substance does not dissociate, that its adsorption is reversible, and that corrections for the activity in the solution can be neglected. The adsorption of polymers, however, is irreversible, which makes the use of GIBBS' law to calculate the level of adsorption from the reduction in interfacial tension highly questionable, despite what is often done in the literature (e.g. FUKAWA et al., 1961; GLASS, 1968).

When, however, we assume reversibility for the adsorption of individual segments, the GIBBS' equation can be applied to this local equilibrium. This means that the adsorption calculated according to GIBBS' law may not be interpreted in terms of molecules but in terms of smaller units, for example the statistical chain element (s.c.e.) For the equilibrium concentration one should take the concentration of s.c.e.'s in the subsurface. The subsurface concentration will be correlated with the bulk concentration only if the latter is not altered after the adsorption process (Kuklman, 1965; Lankveld and Lyklema, 1968).

When using the Gibbs equation, therefore, one should always be clear what the unit of Γ is and how the subsurface concentration is correlated with the bulk concentration. Use of the law of Gibbs as it stands is not permissible and results in improbably high adsorption value (Glass, 1968; Abramzon, 1969).

2.2.3. *Theory of Katchalsky and Miller*

Katchalsky and Miller (1951), with the aid of a simple model, have derived an equation for the reduction in interfacial tension due to polymer adsorption as a function of the polymer concentration c_p. The equation gives reasonable predictions, despite a number of unjustifiable assumptions such as the applicability of the Gibbs equation.

Katchalsky and Miller formally divide the system into a boundary and a bulk phase. When dn molecules are added, their distribution between the boundary layer and the bulk phase is determined by the relative proportion of free space in the two and by a Boltzmann factor containing the free energy of adsorption:

$$\frac{\mathrm{d}n_s}{\mathrm{d}n_b} = \frac{\delta A_i - n_s P w}{V - n_b P w} \cdot e^{\frac{\psi}{kT}} \qquad 2.2.$$

In this equation

n_s = number of polymer molecules in the boundary layer
n_b = number of polymer molecules in the bulk
δ = thickness of the boundary layer containing n_s molecules
A_i = area of the boundary layer interface
V = volume of the bulk phase
P = degree of polymerisation
w = volume per segment
ψ = free energy of adsorption per molecule.

By combining equation 2.2. with the law of Gibbs, Katchalsky and Miller derived the following relationship:

$$\Delta\gamma = \frac{\delta kT}{Pw}\left(0.577 - \frac{\psi}{kT} + \ln V_b\right) \qquad 2.3.$$

in which $V_b = n_b Pw/V$, the volume fraction of the polymer in the bulk.

In the derivation of this equation δ and ψ are considered to be independent of c_p; this is questionable, certainly at low concentrations. At low concentrations, one would expect δ to increase sharply and ψ to decrease with increasing concentration.

Equation 2.3. thus predicts a linear relationship between γ and log c_p:

$$\gamma = \alpha - \beta \log c_p \qquad 2.4.$$

where β is the slope and α the intercept of the γ-log c_p curve.

The factors δ and ψ/kT can be written as follows:

$$\delta = 0.434 \frac{BPw}{kT} \qquad 2.5.$$

$$\frac{\psi}{kT} = \frac{2.3(\gamma_0 - \alpha)}{\beta} - 0.577 \qquad 2.6.$$

The question remains as to how much the assumptions made in this derivation, which is based on an incomplete picture of polymer adsorption, will influence the values calculated for δ and ψ.

2.2.4. *Theory of Frisch and Simha*

Frisch and **Simha** (1957) give a relationship between the proportion Θ of the interface occupied by the polymer and the polymer concentration c_p:

$$Kc_p = \frac{\Theta\left[1 - \frac{2}{z}\left(1 - \frac{1}{P}\right)\Theta\right]^{\nu - 1}}{\nu\,[1 - \Theta]^{\nu}} \qquad 2.7.$$

in which the symbols not already mentioned are:
K = adsorption constant
z = coordination number of the polymer segment in the interface
ν = number of segments per polymer molecule that are adsorbed in the interface.

The theory is based on a model, in which the polymer contacts the interface by random walk and the interface is considered as a reflecting surface. When the segments contact the interface, some of them are bound by adsorption, the number retained being given by a Boltzmann factor. **Frisch** and **Simha** also give a relationship between the interfacial pressure and the extent of occupation of the interface (equation 2.8.) in which the thermodynamic definition of the interfacial pressure is utilized. The equation of state for the adsorbed polymer is as follows:

$$\frac{\Pi A_0}{kT} = \frac{z}{2}\,\frac{\nu - 1}{\nu\left(1 - \frac{1}{P}\right)} \ln\left[1 - \frac{2}{z}\left(1 - \frac{1}{P}\right)\Theta\right] - \ln(1 - \Theta) \qquad 2.8.$$

in which the symbols not already mentioned are:
Π = interfacial pressure
A_0 = limiting surface area per segment.

From equation 2.7. it follows that:

$$(v-1)\ln\left[1-\frac{2}{z}\left(1-\frac{1}{P}\right)\Theta\right]=\ln c_p+\ln\frac{Kv(1-\Theta)^v}{\Theta}$$

which, when substituted in equation 2.8. gives:

$$\frac{\Pi A_0}{kT}=\frac{z}{2}\frac{1}{v\left(1-\frac{1}{P}\right)}\ln\frac{Kv(1-\Theta)^v}{\Theta}-\ln(1-\Theta)-$$

$$-\frac{z}{2v\left(1-\frac{1}{P}\right)}\ln c_p \qquad 2.9.$$

It follows from equation 2.9. that

$$\frac{d\Pi}{d(\ln c_p)}=-\frac{k\,T\,z}{2\,A_0\,v\left(1-\frac{1}{P}\right)} \qquad \text{or}$$

$$v=-\frac{k\,T\,z}{2\,A_0\,\frac{d\Pi}{d(\ln c_p)}} \qquad 2.10.$$

Equation 2.10. gives the relation between the number of adsorbed segments per molecule and the slope of the Π – ln c_p curve.

Using the same equations 2.7. and 2.8. but a different method of derivation, Joos (1968) arrived at a relationship analogous to equation 2.10. with the only difference that the term $\frac{z}{2\left(1-\frac{1}{P}\right)}$ was absent. This results in lower values of v.

2.2.5. *Discussion of the theories reviewed*

For the calculation of the proportion of surface occupied on the basis of the three above-mentioned theories, the gradient β of the plot of γ against c_p (see equation 2.4.) is an important experimental quantity. Comparison of the three theories shows that the values of β are almost equal. For a low-molecular-weight substance it follows from equation 2.1. that

$$\frac{0.434}{RT}\beta = \frac{1}{\text{surface area per active group}} \qquad 2.11a$$

In the case of a polymer one might consider the active group as a statistical chain element of the polymer.

Since KATCHALSKY and MILLER used the GIBBS' equation in the deviation of their equation, they find an analogous relationship, namely:

$$\frac{0.434}{RT}\beta = \frac{\delta}{P_w} \cdot \frac{1}{\text{surface area per polymer molecule}} \qquad 2.11b.$$

According to equation 2.10., the theory of FRISCH and SIMHA predicts the following relationship for $\frac{1}{P} << 1$:

$$\frac{0.434}{RT}\beta = \frac{z}{2vA_0} = \frac{z}{2}\,\frac{1}{\text{surface area per polymer molecule}} \qquad 2.11c.$$

Thus, the three theories discussed give an answer which is the same but for a single factor.

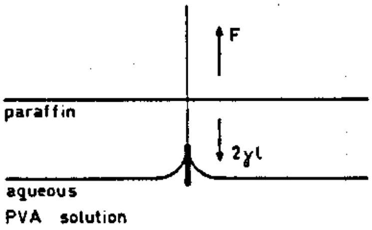
From the above discussion it is clear just how little is known in theory about the influence of polymer adsorption on the reduction in interfacial tension. With the aid of a model for polymer adsorption, SILBERBERG (1962b) has also derived an equation for $\Delta\gamma$ as a function of c_p. Its applicability is however decidedly limited by the many parameters which are either unknown or which can only be estimated with difficulty. When the conformation of the adsorbed polymer is known, the theory enables in principle the reduction in interfacial tension to be predicted by a statistical-thermodynamic approach. In practice the polymer conformation is not only dependent on the variables accounted for by the theory but also on the way in which the interface has been formed. This constitutes an additional difficulty in the experimental verification of the theory. Finally, the many parameters can seldom be verified independently, which makes the theory difficult to test. Still an attempt will be made to interpret the measured effect in the light of the theoretical considerations above.

2.3. MEASUREMENT OF INTERFACIAL TENSION

2.3.1. *Method*

The interfacial tension between the PVA solutions and paraffin was measured by the static Wilhelmy-plate method. We used the Prolabo-tensiometer of Dognon-Abribat, the operational principle of which has been described by PADDAY (1957). A small roughened platinum plate, which had been tempered and wetted with the aqueous phase, was brought through the paraffin layer up to the interface between the paraffin and the aqueous PVA solution below it (see 2.3.2.). Upon contact with the interface the plate is pulled into the aqueous

FIG. 2.1. Principle of measuring the interfacial tension by the static Wilhelmy-plate method.



phase as a result of the interfacial tension. The plate, which is suspended from an electromagnetic balance, is brought to balance by the application of a force F (fig. 2.1.). The value of F can be read off, thus enabling the interfacial tension to be calculated. The reading was corrected for the buoyancy of the plate due to its submersion in the paraffin. The length of the plates was always 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 always within 0.4 mN m^{-1}. It is important that the plate is well wetted with the aqueous phase. This can be seen from its reflectivity. Another indication of good wetting is when the displacement force, necessary to bring the plate out of balance, is slight.

2.3.2. *Experimental*

PVA solutions of different concentrations were made by dilution of a stock 4000 ppm solution. Of one of the PVA solutions, 15 ml was put into a 50 ml vessel with a diameter of about 4.6 cm. To avoid possible effects due to the ageing of PVA solutions, only those solutions which were less than a week old were used. A paraffin layer of about 1 cm was introduced on the PVA solution and the vessel was put into a bath thermostated at 20.0 ± 0.2°C. The interfacial tension was measured three times between 18 and 30 hours after the formation of the interface. The average of the three measurements, which seldom differed by more than 0.2–0.3 mN m^{-1} from one another, was taken as the steady-state value. The long interval between formation of the interface and the first measurement is necessary to ensure that the steady state has been attained (chapter 3).

All glassware was cleaned before use with a solution of potasium dichromate and sulphuric acid, and then rinsed with distilled water.

2.4. RESULTS AND DISCUSSION

The interfacial tension between the paraffin and the aqueous phase was measured as a function of the PVA concentration in the aqueous phase for the PVA samples listed in table 1.1. The results are given in figures 2.2. to 2.8. The concentration by weight of the polymer and not the molar concentration has been set out along the abscissae. This implies that the segment concentration has been taken as a unit and not the concentration of polymer molecules. The

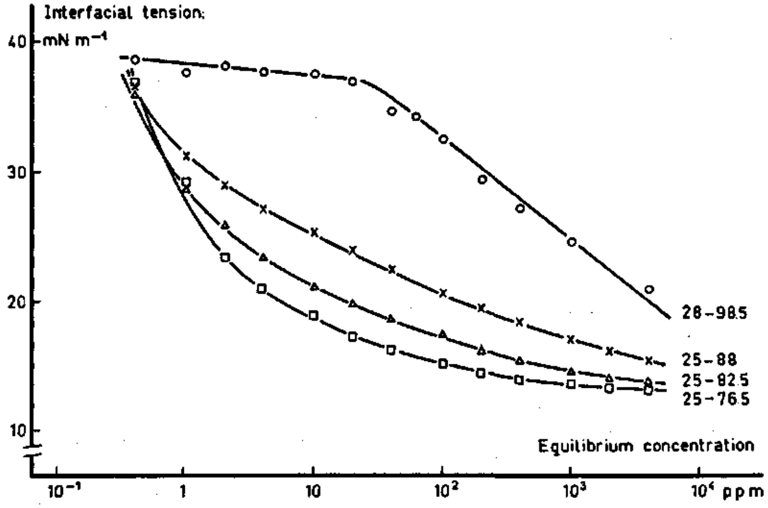


FIG. 2.2. Influence of the acetate content of PVA ($\bar{P} \backsim 1700$) on the interfacial tension.

equilibrium concentration of polymer in solution may be taken as being equal to the initial concentration, because adsorption does not significantly influence the polymer concentration provided the initial value of the latter is not too low ($\geqslant$ 1 ppm).

The effect of the acetate content and molecular weight of the PVA on the interfacial tension will be discussed in turn below, and an attempt will be made to interpret the measurements in terms of the adsorption of the polymer.

2.4.1. *Effect of the acetate content*

Fig. 2.2 shows the measured interfacial tension as a function of concentration for four types of PVA with different acetate contents but with comparable degrees of polymerisation. Two important aspects emerge; firstly, the reduction in interfacial tension increases with increasing acetate contents and, secondly, the plot of interfacial tension against concentration for a low acetate content (1.5%) is characterized by a discontiniuty which is not found for the higher acetate contents ($\geqslant$ 12%).

Lowering of the interfacial tension with increasing acetate content, at a given concentration, is what would be expected, since the acetate groups convey a more hydrophobe character to the molecule (KUHLMAN, 1968) thus causing the surface activity to increase. The marked effect of the acetate groups is clearly illustrated in fig. 2.3. in which the interfacial tension for mixtures of PVA 16–98 and PVA 16–88 is plotted against the total concentration of polymer. It can be seen that, except at low polymer concentrations, $\Delta\gamma$ is principally determined by the PVA 16–88. A larger reduction in interfacial tension at higher acetate contents has also been found by KUHLMAN (1968) for the interfaces

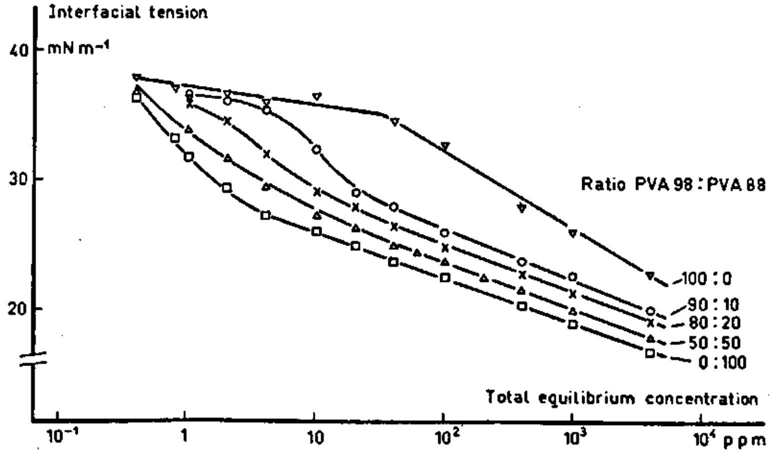


FIG 2.3. Interfacial tension for mixtures of a hydrophilic (16–98) and a more hydrophobic (16–88) PVA ($\bar{P} \backsim 1200$).

between a 0.5% solution of PVA in water and both benzene and air. GROMOV et al. (1967). likewise found $\triangle\gamma$ for the styrene-water and toluene-water interfaces to increase with increasing acetate content, as did FUKAWA et al. (1961), HAYASHI et al. (1964), and GLASS (1968) for the water-air interface.

It is, however, feasible that the lower interfacial tensions at higher acetate contents are not only due to the more hydrophobic character of the molecule but that interactions between the loops also has an effect. According to theory (SILBERBERG, 1968; HOEVE, 1969) the average loop length of an adsorbed polymer is larger with poorer solvents. This may cause the loop length of the more hydrophobic PVA samples to be greater than that of PVA 98, and the mutual entropic repulsion between the loops may results in an extra reduction of the interfacial tension.

The discontinuity in γ as a function of log c_p is found only at a low acetate content. Similar discontinuities have been found for other polymers in interfacial tension measurements (GLASS, 1968) and in work on monolayers (ISEMURA, 1952; LOEB, 1968). In the latter case this is explained by a conformational change of the polymer at the surface as a result of compression of the monolayer. With an adsorbed polymer layer, a change of conformation can occur only when the mechanism of adsorption changes. When one or more segments of a diffusing polymer molecule contact the interface, the local interfacial tension at the points of contact will be lower than for the free interface. The interface which is still free of adsorbed polymer can now be occupied in either of two ways, namely by supply of new polymer molecules from the bulk or by the unfolding of polymer molecules which have already been partially adsorbed. When the polymer concentration is low, the interface can be occupied by the unfolding mechanism, which will result in a flat conformation of polymer at the interface. At low concentrations, therefore, the molecules arriving first can completely occupy the interface in this way, so that an increase in concentration will cause no further increase in adsorption and hardly any further decrease in interfacial tension. Above a certain polymer concentration, however, the polymer molecules at the interface will be able to unfold much less readily or hardly at all, because the neighbouring sites will have been already occupied as a result of the higher rate of supply by diffusion. The occupation of the interface is thus determined by kinetic factors. The discontinuity in the γ-log c_p curve thus corresponds to the concentration at which adsorption due to supply from the bulk occurs just that bit more quickly than adsorption due to unfolding. Entropic repulsion between the loops formed in this way can also be partially responsible for the sharper rate of decline of the interfacial tension. Since the adsorption is irreversible, the way in which the interface is occupied can be an important factor. Similar effects were found in the investigation of the time-dependence of the reduction in the interfacial tension and with the work on monolayers (chapter 3 and 4).

From ellipsometry measurements on metal surfaces onto which polystyrene had been adsorbed from a solution, STROMBERG (1965) found that the rate of occupation by unfolding of the molecule can be quicker than that by diffusion from the bulk. This agrees with the mechanism assumed above. The question remains, however, as to why the discontinuity is only found with the PVA 98 samples (see also figures 2.4 to 2.6). This is probably due to a difference in flexibility of the polymer molecule and a difference in its affinity for the interface. Polyvinylalcohol is a very flexible polymer (ZWICK, 1965) and will expand markedly upon solvation. This will be less marked with PVA 88 samples on account of their more hydrophobic character. A lower flexibility can cause the unfolding process to be slow in comparison with the rate of supply from the bulk, and thus no clear transformation in conformation can be expected for this concentration range. A higher affinity for the interface means that a segment, once adsorbed, will be less readily desorbed. As a result, changes in conformation of the molecule at the interface, necessary for it to be able to unfold, will be less easy.

2.4.2. *Effect of molecular weight*

The effect of the molecular weight on the interfacial tension is shown in figs. 2.4., 2.5. and 2.6. for the PVA 98 samples and in figs. 2.7. and 2.8. for the PVA 88 samples. There is not always agreement in the literature about the effect of the molecular weight. PVA samples were therefore obtained from a number of different sources to check whether different methods of preparation could account for the observed discrepancies. HAYASHI (1964) has already shown that slight difference in secondary structure as a result of another method of preparation can influence the measured reduction in interfacial tension.

With the PVA 98 samples from Konam, the reduction in interfacial tension increases with increasing molecular weight (fig. 2.4.). With the samples from Wacker (fig. 2.5.) and Kurashiki (fig. 2.6.) the effect of molecular weight is

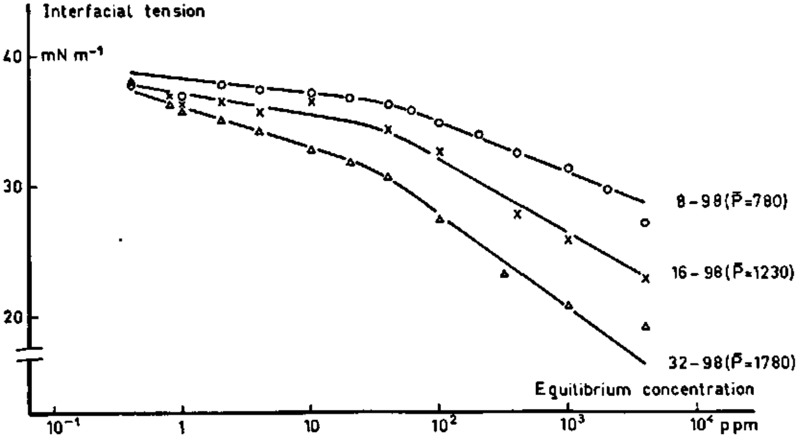


FIG. 2.4. Influence of molecular weight on the interfacial tension for PVA 98 ex Konam.

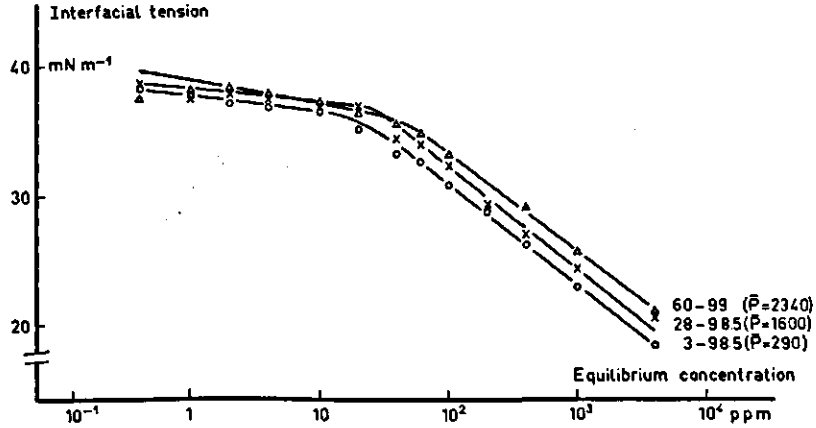


FIG. 2. 5. Influence of molecular weight on the interfacial tension for PVA ex Wacker.

just the opposite. This could indicate that in the latter case the larger molecules unfold less at the interface. The shift in the discontinuity to a lower concentration is possibly a further indication of a less flexible molecule, for, at the discontinuity, the rate of supply by unfolding is roughly equal to the rate of supply from the bulk, and a shift of the discontinuity to lower concentrations means that the unfolding is slower. A similar difference with respect to the molecular weight dependence, was found between the Konam PVA 88 samples (fig. 2.7.) and those from Wacker (fig. 2.8.). In the former case molecular weight had no effect, while for the Wacker samples the reduction in interfacial tension was again least for the highest molecular weight. On the whole, the differences

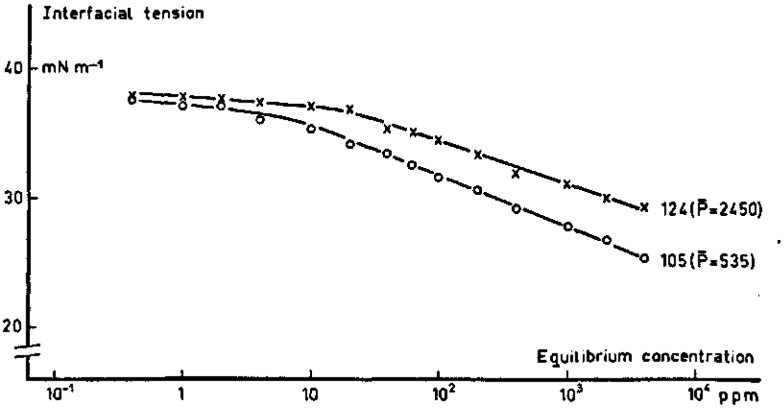


FIG. 2.6. Influence of molecular weight on the interfacial tension for PVA 98 ex Kurashiki.

are not large, from which one can conclude that the degree of lateral unfolding is such that it does not much matter whether the polymer molecule is made up of 350 or 2500 segments. In addition, polymer segments far removed from the interface, of which there will be more with a larger molecule, will not contribute so much to the reduction in interfacial tension.

The slight differences in the effect on $\triangle\gamma$ of the various PVA samples can probably be attributed to differences in the stereochemical structure of the molecules, such as differences in the distribution of acetate groups along the chain, which depends on the polymerisation conditions. The influence of the acetate group distribution on interfacial tension was demonstrated by HAYASHI

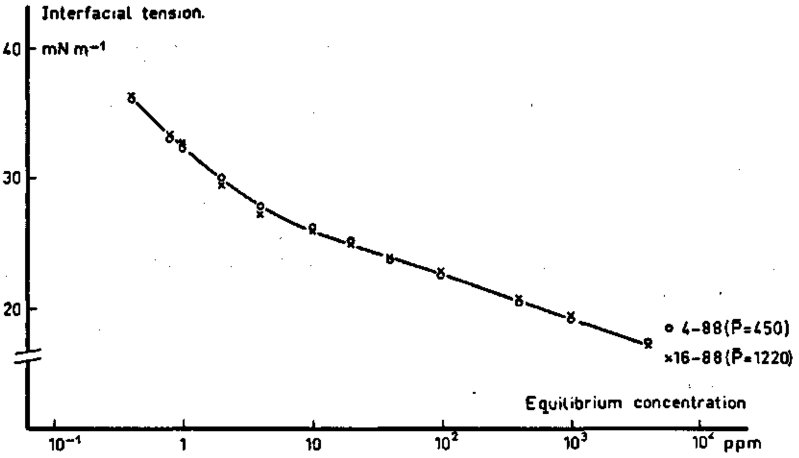


FIG. 2.7. Influence of molecular weight on the interfacial tension for PVA 88 ex Konam.

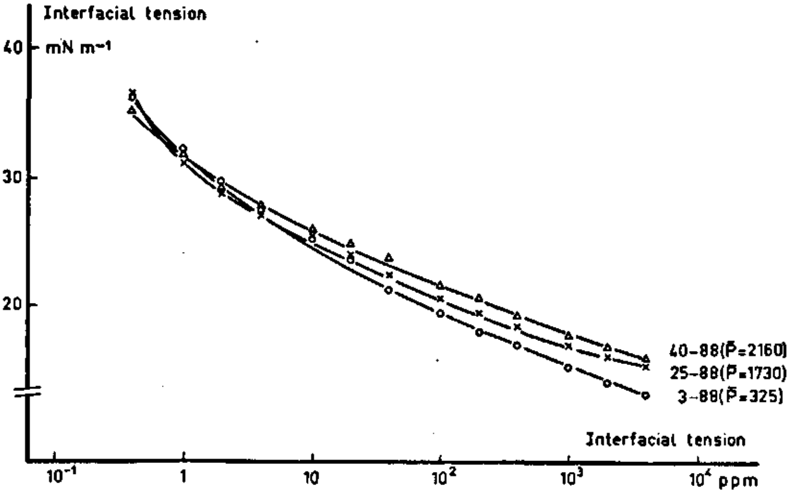


FIG. 2.8. Influence of molecular weight on the interfacial tension for PVA 88 ex Wacker.

(1964) for the water-air interface. The tacticity of the polymer can also have an effect, as was shown by JAFFE et al. (1967) for polymethacrylates. These factors, together with small differences in the 1,2-diol content and the acetate content, differences in the latter probably being the most important especially for the PVA 98 samples, can account for the slight dissimilarities between the various preparations. One must conclude that the molecular weight is hardly important, but that the total number of segments is the determining factor and is one reason for approaching the problem in terms of statistical chain elements. At the same time one can see that, in an investigation with a polymer series, it is important to know that the stereochemical structure remains identical, as this can affect the measured effects.

2.4.3. *Semi-quantitative interpretation*

In the theoretical discussion of the reduction in interfacial tension (2.2.) it was pointed out that the theories are only valid when adsorption is reversible a condition which is not in general fulfilled for polymer adsorption (KUHLMAN, 1965; LANKVELD and LYKLEMA, 1968). It was, however, also mentioned that the adsorption of individual segments is probably reversible, so that locally there will be equilibria to which the theories can be applied. The reduction in interfacial tension is then no longer a definitive function of the bulk concentration, but of the subsurface concentration which is unknown. The subsurface concentration will be a function of the bulk concentration provided the history of the interface remains the same. Thus, a definitive relationship betwee γ and c_p can be expected only when the history of the interface is fixed. From the above it appears that the usefulness of the theories discussed is highly questionable. Nevertheless, it is still of interest to calculate the order of magnitude of the

Table 2.2. Adsorption data derived from interfacial tension measurements

1 Sample	2 $\bar{P}$	3 c_p (ppm)	4 β	5 $\frac{1}{\Gamma}$(Å^2)	6 ν	7 $\frac{\nu}{\bar{P}} \cdot 100$
8 - 98	780	2 - 25	0.75	1240	124.0	15.9
		40 - 4000	4.65	200	20.0	2.6
16 - 98	1230	0.4 - 25	1.45	640	64.0	5.2
		40 - 4000	6.45	144	14.4	1.2
32 - 98	1780	0.4 - 25	2.05	454	45.4	2.6
		40 - 4000	6.95	134	13.4	0.8
3 - 98.5	290	0.4 - 10	1.15	810	81.0	27.9
		40 - 4000	7.85	118	11.8	4.1
28 - 98.5	1600	0.4 - 25	0.95	980	98.0	6.1
		60 - 4000	7.55	123	12.3	0.8
60 - 99	2340	0.4 - 25	1.75	530	53.0	2.3
		60 - 4000	7.65	122	12.2	0.5
105	535	0.4 - 10	1.25	744	74.4	13.9
		25 - 4000	4.05	298	29.8	4.3
124	2450	0.4 - 10	0.65	1430	143.0	5.8
		25 - 4000	3.40	274	27.4	1.1
4 - 88	450	4 - 4000	3.50	266	26.6	5.9
16 - 88	1220	4 - 4000	3.50	266	26.6	2.2
3 - 88	325	4 - 4000	4.25	218	21.8	6.7
25 - 88	1730	4 - 4000	3.95	236	23.6	1.4
40 - 88	2160	4 - 4000	4.10	227	22.7	1.1
25 - 82.5	1830	4	6.75	138	13.8	0.8
		100	3.60	258	25.8	1.4
25 - 76.5	1760	4	5.95	156	15.6	0.9
		100	3.50	266	26.6	1.5

β = slope of γ-log c_p curve

$\frac{1}{\Gamma}$ = area per adsorbed unit according to Gibbs' law

ν = number of segments adsorbed per molecule according to Frisch and Simha.

adsorption which, according to the several theories, corresponds to the measured reduction in interfacial tension. These calculated adsorption values can then be compared with the directly measured adsorptions (chapter 5).

Table 2.2. summarizes the measured values of the slopes β (column 4) of the γ-log c_p plots for the diverse PVA samples at the stated concentrations. The surface occupied per surface-active group, calculated on the basis of the Gibbs theory (equation 2.1.), is given in column 5. The nature of the adsorbed group is not specified. Column 6 gives the number of adsorbed segments per molecule according to the Frisch-Simha equation (equation 2.10. in which A_0 = 30 Å^2 and z = 6), while in column 7 this number is expressed as a percentage of the total number of segments.

If Gibbs' law is used and Γ is expressed as the number of polymer molecules per unit surface, the predicted adsorption values are improbably high. For instance, for PVA 40–88 the predicted adsorption is 80 mg m^{-2} which is about 20 times as high as is found by direct measurements on emulsion interfaces (chapter 5). Thus, the surface given in column 5 is not that of a polymer molecule but of a smaller unit, possibly that of a statistical chain element, which is the reversibly adsorbed unit.

The percentage of segments adsorbed per molecule (column 7) decreases with increasing molecular weight, which implies that the adsorbed polymer layer becomes thicker the higher the molecular weight. This agrees with the measurements of the adsorption on emulsion interfaces. It has been shown, however, that γ is fairly insensitive to changes in molecular weight, which underlines the fact that γ is not directly related to the number of molecules adsorbed, but rather reflects the level of adsorption of segments and/or statistical chain elements, in addition to possible interactions between the loops. Comparison between the PVA 98 and PVA 88 samples shows that, at low concentrations, the percentage of adsorbed segments is greater for the 98 than for the 88 samples, but that at high concentrations the situation is just the reverse. According to the theories of SILBERBERG (1968) and HOEVE (1969), a polymer adsorbed from a good solvent should have a flatter conformation than when adsorbed from a poor solvent. This would mean that PVA 98 is flatter when adsorbed, and hence that the percentage of adsorbed segments is higher. At low concentration, therefore, the experiment is in agreement with the theory of SILBERBERG and that of HOEVE. At higher concentrations, the greater hydrophobicity of the PVA 88 samples may be responsible for the higher percentage of adsorbed segments.

With the 98 samples, a higher percentage of adsorbed molecules was found before the discontinuity than thereafter. This suggests that the conformation is less flat after the discontinuity. The percentage before the discontinuity, however, is still but small, which implies that unfolding occurs only partly. It should be noted that the slope of the plot is very difficult to determine experimentally at low concentrations.

The figures in columns 5 and 6 differ by a factor to exactly 10. In 2.2.5. we already learned that the theory of FRISCH and SIMHA shows a close agreement with the theory of GIBBS (compare equations 2.11.a and 2.11.c). The factor is exactly 10 on account of the choice of $z = 6$ and $A_0 = 30$ Å^2.

From the theory of KATCHALSKY and MILLER one can calculate the free energy of adsorption per molecule (ψ) and the thickness (δ) of the adsorbed layer. If one assumes the density of PVA to be 1.30 g/cm^3 (BRANDRUP, 1965), the volume per segment, w, can be calculated as 5.72×10^{-23} cm^3 for PVA 98 and 6.30×10^{-23} cm^3 for PVA 88 samples. The layer thickness, δ, can be calculated with equation 2.5. For the calculation of the free energy of adsorption, the volume fraction in the bulk in equation 2.6. has to be converted into the concentration in ppm. Equation 2.6. then becomes

$$\frac{\psi}{kT} = 2.3 \left(\frac{\gamma_0 - \alpha}{\beta}\right) + 13.5 \tag{2.6a}$$

TABLE 2.3. Adsorption data calculated from interfacial tension measurements with the theory of KATCHALSKY and MILLER

1 PVA sample	2 $\bar{P}$	3 c_p (ppm)	4 α (mNm^{-1})	5 β	6 δ (Å)	7 end-to-end distance (Å)	8 ψ/kT
3 – 98.5	290	0.4 – 10	37.8	1.15	20	70	38.9
		40 – 4000	47.0	7.85	140		14.5
60 – 99	2340	0.4 – 25	38.8	1.75	342	198	28.9
		60 – 4000	49.1	7.65	1100		13.9
3 – 88	325	4 – 4000	28.2	4.25	94	74	25.6
40 – 88	2160	0 – 4000	30.4	3.95	578	190	25.2

α, β = slope and intercept of γ-log c_p curve
δ = thickness of adsorbed polymer layer
ψ = adsorption free energy

The calculated values of δ and ψ/kT are given in Table 2.3. for several PVA samples. The calculated values probably have but little absolute significance because the theory is based on a somewhat too simple picture of polymer adsorption for which the GIBBS equation is assumed to hold. The tabulated values for δ and ψ, however, are of the right order of magnitude. At low concentrations the calculated layer thicknesses (column 6) agree with estimates made on the basis of direct adsorption measurements with emulsions, and are also of the same order of magnitude as the 'end-to-end distance' of the polymer in solution (column 7). If we assume a free energy of adsorption of 0.5–1.0kT per segment, the calculated free energy of adsorption per molecule (column 8) agrees fairly well with the value expected in view of the number of segments adsorbed (table 2.2., column 6).

The close agreement between the calculations according to the several theories was to be expected, since the theories are closely analogous (equations 2.11.a,b,c). Moreover the calculations are primarily based on a single factor, the slope of the γ-log c_p curve. For the calculation of the free energy of adsorption according to the theory of KATCHALSKY and MILLER, however, the absolute value of γ (α, column 4) is needed. If the adsorption free energy per segment assumed to be 0.5–1.0 kT the number of adsorbed segments can be estimated. This estimated value agrees with the value calculated from the FRISCH-SIMHA equation. This agreement is perhaps an indication of the applicability of these theories.

2.5. CONCLUSIONS

The reduction ($\Delta\gamma$) in interfacial tension as a consequence of the adsorption of PVA at the paraffin-water interface is directly proportional to log c_p over a wide range of concentrations. In addition $\Delta\gamma$ increases with increasing acetate content of the PVA, which can be explained by the increasing hydrophobic character of the polymer molecule. At a low acetate content (about 2%) the

γ-log c_p curve shows a discontinuity which must be ascribed to a change in the conformation of the adsorbed polymer at the corresponding value of c_p. Kinetic factors during the formation of the polymer layer are probably responsible for this discountinuity. That the kinetics of the formation of the polymer layer can determine the final interfacial tension must be tied up with the irreversible nature of polymer adsorption.

It is this very irreversibility which complicates the quantitative interpretation of the reduction in interfacial tension due to polymer adsorption. A semi-quantitative interpretation indicated that the percentage of segments per molecule adsorbed in the layer is low, which agrees with the measurement on emulsions. Although the current theories do not enable an exact quantitative interpretation of the measured effects, the many experiments described in this chapter make an important contribution to the understanding of the effect of polymer adsorption on the reduction in interfacial tension.

3. TIME-DEPENDENCE OF THE INTERFACIAL TENSION

3.1. INTRODUCTION

When polymers are adsorbed, it usually takes a long time before the steady state is reached (SILBERBERG, 1962b; PATAT et al., 1964). It is therefore understandable why the interfacial tension can depend markedly on time. There are two factors which determine this time-dependence, namely the rate of supply by diffusion and the rate of reconformation of the polymer in the interface once it is adsorbed. If one wants to study the influence of time on γ, one should use a static method. With a dynamic method the interface is continuously disturbed, which can have a marked effect on the rates of adsorption and reconformation of the polymer at the interface. This influences not only the size of the measured reduction in interfacial tension, but also the time taken for the steady state value to be reached. Therefore measurement of the interfacial tension by the drop-weight method and by the dynamic Wilhelmy plate and du Nouy ring methods are unsuitable. From table 2.1., which summarizes the work of others on the effect of polymer adsorption on interfacial tension, it is clear that the time recorded for the attainment of the steady state is longer for the static methods.

The time-dependence of the surface-tension of PVA solutions has been measured by FUKAWA et al. (1961) and GLASS (1968a) by different methods. FUKAWA et al. measured the time-dependence by the static Wilhelmy plate method for concentrations of 10^2–10^5 ppm and found that the steady state was often not reached even after 20 hours. The measurements of GLASS were, unjustifiably, made with a stalagmometer at somewhat lower concentrations. GLASS found that the surface tension had almost reached its steady-state within about 60 seconds. It is not surprising, therefore, that the diffusion coefficients which he calculated (10^{-15}–10^{-18} cm^2/s) differ greatly from the diffusion coefficients of PVA quoted elsewhere in the literature. FUKAWA et al. also attribute the measured effects of time to a limited supply by diffusion. It is, however, unlikely that the supply can be limited by diffusion at the high concentrations which they used. KUHLMAN (1969) has shown how the time-dependence at high concentrations may well be caused by a slow exchange of adsorbed segments with more hydrophobic segments in the chain, with a consequent reconformation of the polymer at the interface.

In the interpretation of the measurements of γ_t, both of the above mentioned causes of the time-dependence, namely the diffusion and reconformation mechanisms, must be taken into consideration. It can be noted here that diffusion-determined time-dependence of the interfacial tension is only conceivable at low concentrations.

3.2. THEORY

3.2.1. *Diffusion-determined time-dependence*

The supply by diffusion of a low-molecular-weight compound to a phase interface can be expressed by the well-known equation of WARD and TORDAI (1946):

$$n_t = 2\,c\sqrt{\frac{D}{\pi}} \cdot \sqrt{t} \qquad (3.1.)$$

where n_t = the number of molecules per unit area which have been supplied to the interface by diffusion at time t
c = concentration of the low-molecular-weight substance (molecules/volume)
D = diffusion coefficient
t = time during which diffusion has taken place.

Equation 3.1. is only valid for the intitial phase of the adsorption process, since it does not fulfill the condition that the level of adsorption should be finite.

The equation of WARD and TORDAI can be combined with the simple two-dimensional equation of state, $\Pi A = kT$, in which Π the interfacial pressure, is defined as $\gamma_0 - \gamma$ (γ_0 = interfacial tension of clean interface). In this way an expression can be derived for γ as a function of time:

$$\gamma_t = \gamma_0 - 2\,ckT\sqrt{\frac{D}{\pi}} \cdot \sqrt{t} \qquad (3.2.)$$

If the interfacial tension is now measured as a function of t for known c, the diffusion coefficient can, in principle, be calculated from the slope of the $\gamma - \sqrt{t}$ curve.

Equation 3.1. will also be valid for the supply of polymers by diffusion, but with polymer adsorption there is the added complication that the supply of a single molecule results in many segments being adsorbed. The reduction in interfacial tension will be related the number of statistical chain elements adsorbed. It was in fact shown in Chapter 2 that the segment concentration in the bulk and not the molecular concentration was important for $\triangle\gamma$. When ν segments per molecule are adsorbed, νc_p should be taken for the concentration in equation 3.2., where c_p is the polymer concentration. Equation 3.2. then becomes:

$$\gamma_t = \gamma_0 - 2\nu c_p kT\sqrt{\frac{D}{\pi}} \cdot \sqrt{t} \qquad (3.3.)$$

or

$$\gamma_t = \gamma_0 - \beta_1 \sqrt{t} \qquad (3.4.)$$

in which

$$\beta_1 = 2\nu c_p kT\sqrt{\frac{D}{\pi}} \qquad (3.5.)$$

When c_p and D are known, it should be possible to calculate the number of segments per molecule adsorbed.

When equation 3.3. is combined with the equation of state,

$$\Pi(A - A_0) = kT \tag{3.6.}$$

the equation of Bartholomé-Shäfer (1950), modified by the factor ν, is found:

$$\frac{1}{\Pi_t} = \frac{1}{2\nu c_p kT\sqrt{\frac{D}{\pi}}\cdot\sqrt{t}} - \frac{A_0}{kT} \tag{3.7.}$$

or

$$\frac{1}{\Pi_t} = \frac{1}{\beta_1\sqrt{t}} - \frac{A_0}{kT} \tag{3.8.}$$

When Π_t^{-1} is plotted against $t^{-\frac{1}{2}}$, the value derived for β_1 from equation 3.8. should be identical to that found for β_1 from the plot of γ_t against $t^{\frac{1}{2}}$. One finds in fact that this is only the case when Π_t is defined as $\Pi_t = \gamma_{t\to 0} - \gamma_t$, in which $\gamma_{t\to 0}$ is obtained by extrapolation of γ to $t=0$. At the start of the experiment ($t=0$), the interfacial tension is not equal to γ_0 but is lower, since the water phase contains polymer, some of which will be present at the interface at $t=0$. This amount of polymer already present will no longer have to be supplied by diffusion. The advantage of using the Barthlomé-Schäfer equation rather than equation 3.4. is that the slope can be read off better from the corresponding graph. This is because, for small t, the interfacial pressure Π is also small and hence Π^{-1} and $t^{-\frac{1}{2}}$ are large in the range where diffusion is to be studied. The Bartholomé-Schäfer method of interpretation has also been used for low-molecular weight substances by Baret and Roux (1968a) who, however, did not take into account that γ_0 should be taken as $\gamma_{t\to 0}$. The value of $\gamma_{t\to 0}$ must be calculated by extrapolation of γ to $t \to 0$, which inevitably introduces a certain inaccuracy and makes the method somewhat less attractive.

3.2.2. *Time-dependence not determined by diffusion*

At higher polymer concentrations, one cannot expect diffusion to be responsible for the long times required for the interfacial tension to reach its final value. Ward and Tordai (1946) assumed that an adsorption barrier must then be the limiting factor. In this case, though, it becomes questionable whether the process can be treated as a diffusion problem. The treatment of Ward and Tordai has been adopted by Vochten et al. (1968), Glass (1968) and others.

The time-dependence observed after long times at high concentrations should rather be interpreted in terms of adsorption-desorption antagonism. This involves replacement of surface active substances, or polymer segments, with low affinity for the interface by components with a higher affinity for the interface. This can result in long times being required for the attainment of the final value. This picture, which predicts an exponential decrease of the interfacial tension with time, is outlined by BARET (1968b). There are, however, alternative models likewise predicting an exponential decrease with time (MAC RITCHIE and ALEXANDER, 1963; FAINERMAN et al., 1969). The general expression is:

$$\Pi_t = \Pi_\infty(1 - e^{-t/\tau}) \tag{3.9.}$$

or

$$\log\left(\frac{\gamma_t - \gamma_\infty}{\gamma_0 - \gamma_\infty}\right) = -\,0.434\,\frac{t}{\tau} \tag{3.10.}$$

in which $\Pi_t = \gamma_0 - \gamma_t =$ interfacial pressure at time t
$\Pi_\infty = \gamma_0 - \gamma_\infty =$ final value of interfacial pressure
$\tau =$ relaxation time for the attainment of the steady state interfacial tension.

In fact, for γ_0 one should again take the interfacial tension at the time when the mechanism, on which equation 3.9. is based, begins. These values of γ are of course unknown but, according to equation 3.10., they do not effect the slope of the curves. In addition to the investigations already mentioned, exponential relationships similar to that in 3.9. have also been found by, amongst others, HANSEN and WALLACE (1959), FRISCH and AL-MADFAI (1958) and GLASS (1968).

3.3. EXPERIMENTAL

The interfacial tension was measured as described in 2.3. The time-dependence of the interfacial tension has been followed by two methods. On the one hand, the interfacial tension was measured at various times after the formation of the interface for the experiments described in chapter 2. On the other hand, the interfacial tension was followed continuously as a function of the time after formation of the interface by suspending the platinum plate in the interface throughout the experiment. The difference between the two techniques is that, with the latter, the interface is not disturbed during the whole experiment, while with the first method the interface is temporarily disturbed by the renewed introduction of the plate. With this discontinuous technique, the first measurement was made after 15 minutes and the method employed was that which is described in 2.3.

For the continuous recording of the interfacial tension larger volumes were used because these experiments were mostly carried out at very low concentrations to investigate the limits of diffusion-determined time-dependence. Paraffin was brought onto the surface of 100 ml of a PVA solution in a vessel of about 250 ml and diameter 7.4 cm. The time was recorded from the moment of introduction of the paraffin and the interfacial tension was read off at various intervals. The vessel was thermostated at 20 °C.

It made no difference whether the paraffin had been equilibrated with water or not. The interfacial tension recorded in this way between paraffin and distilled water dropped gradually by about 1 mN m^{-1} in the course of 8 hours. To check that low-molecularweight substances, which might influence the time-dependence, are absent from the PVA, a concentrated solution of PVA 3–88 was dialysed for one week. The time-dependence measured with diluted dialysed solution did not differ from that of non-dialysed solution. Thus, low-molecular-weight components, which diffuse more quickly to the interface, cannot be expected to have a disturbing effect on the measurements.

3.4. RESULTS AND DISCUSSION

3.4.1. *Discontinuous measurements*

The interfacial tensions measured at different times after the formation of the interface are given in figures 3.1.–3.8. for the different PVA samples and for different concentrations. A marked difference in the interfacial activity between PVA samples with a low acetate content (2 %) and those with a higher acetate content, as already noted in chapter 2, again emerged clearly in these experiments. While there was a marked difference in behaviour as a consequence of the acetate content, little difference could be detected between samples of different origin and molecular weight but the same acetate content. This holds for both low and high acetate contents.

Most striking is the irregular character of the time-dependence of the inter-

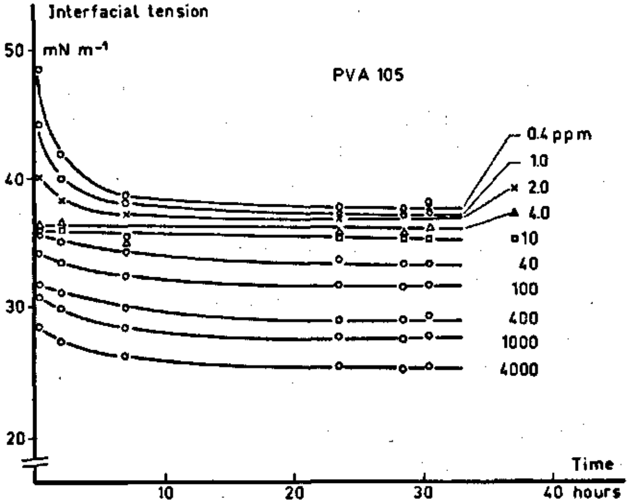


FIG. 3.1. Time-dependence of the interfacial tension of solutions of PVA 105 (ex Kurashiki) of different concentrations.

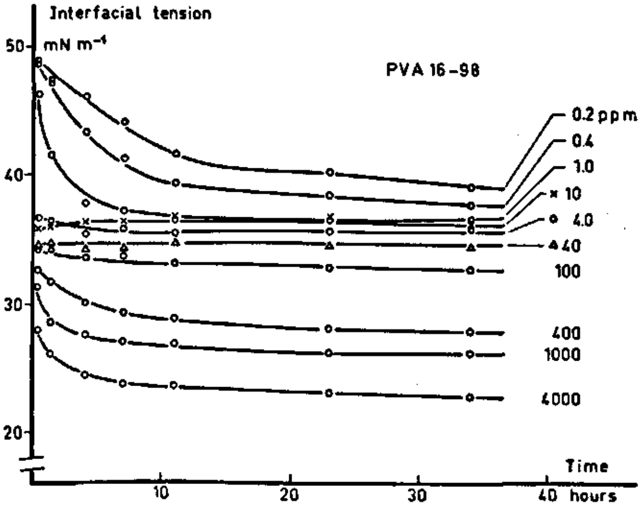


FIG. 3.2. Time-dependence of the interfacial tension of solutions of PVA 16–98 (ex Konam of different concentrations.

facial tension as a function of the PVA concentration at acetate contents of about 2%. At low concentrations ($\leqslant$ 2 ppm) the time-dependence can be explained by assuming diffusion to be the limiting factor (see 3.4.2.). In the concentration range between about 1 and 100 ppm the interfacial tension was

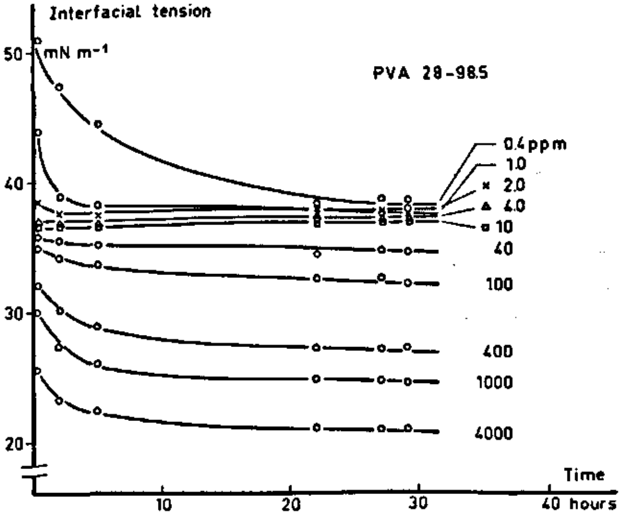


FIG. 3.3. Time-dependence of the interfacial tension of solutions of PVA 28–98.5 (ex Wacker) of different concentrations.

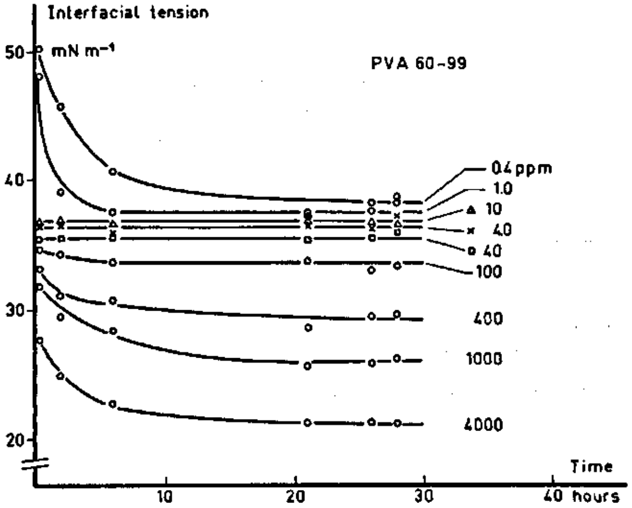


Fig. 3.4. Time-dependence of the interfacial tension of solutions of PVA 60–99 (ex Wacker) of different concentrations.

found to be hardly dependent on time, for which it can be concluded that diffusion can no longer be the limiting factor. The time required to form a complete monolayer by diffusion can be estimated from equation 3.1. For this we assume that the mechanism is that described in section 2.4.1., namely

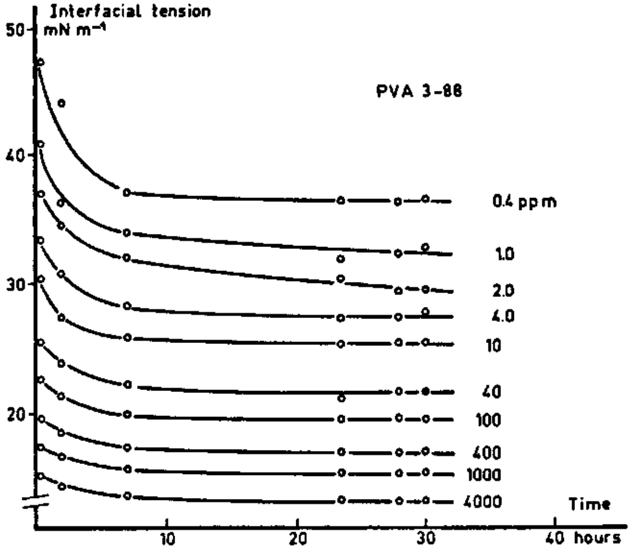


Fig. 3.5. Time-dependence of the interfacial tension of solutions of PVA 3–88 (ex Wacker) of different concentrations.

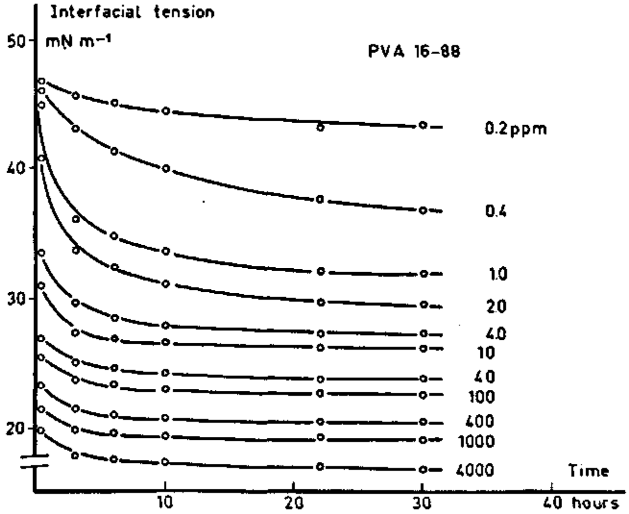


FIG. 3.6. Time-dependence of the interfacial tension of solutions of PVA 16–88 (ex Konam) of different concentrations.

that a molecule with a low acetate content can unfold quickly and extensively at the interface. About 0.4 mg m^{-2} of PVA can be spread in a monolayer (Chapter 4). Thus, if the diffusion coefficient of PVA is taken as 3×10^{-7} cm^2 s^{-1} (PVA 16–98) and its concentration as 4 ppm, supply by diffusion will be

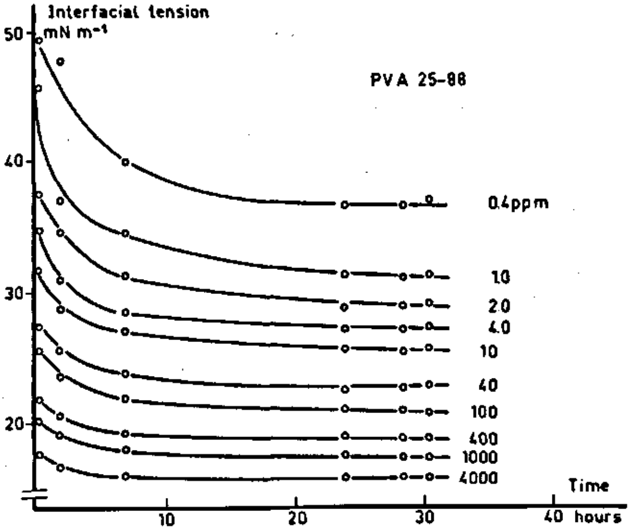


FIG. 3.7. Time-dependence of the interfacial tension of solutions of PVA 25–88 (ex Wacker) of different concentrations.

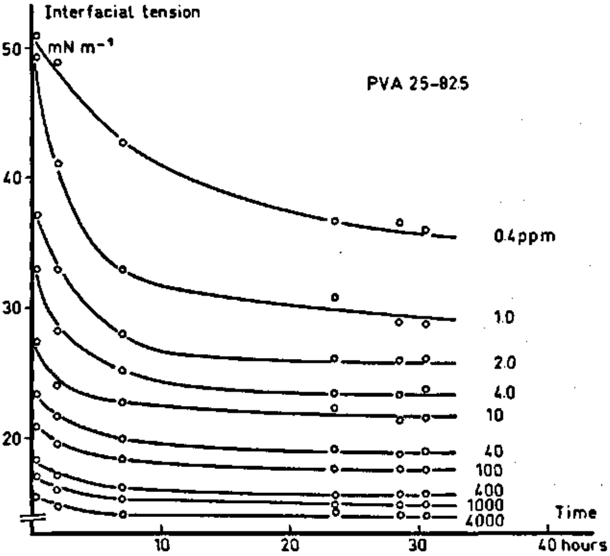


FIG. 3.8. Time-dependence of the interfacial tension of solutions of PVA 25–82.5 (ex Wacker) of different concentrations.

sufficient to completely form a monolayer within 2 or 3 minutes. The monolayer will therefore be completely occupied before the first measurement, which in all cases is made after 15 minutes. An estimate of the rate of unfolding can be made by calculating from equation 3.1. the time necessary for the interface to be occupied by diffusion at a concentration of about 60 ppm, which corresponds to the kink in the γ-log c_p curve. The calculated time of unfolding amounts to several seconds. The other mechanism which can cause the interfacial tension to be time-dependent, namely the reconformation of the polymer in the interface, will not take place because of the flat conformation of the polymer. Thus it is plausible that, for the concentration range in which the initial occupation of the interface is due to the unfolding of the polymer, the interfacial tension will not be time-dependent.

The marked time-dependence at higher concentrations (> 100 ppm) must then be ascribed to factors other than the limitation by diffusion, and may well be caused by reconformation of the polymer in the interface. For when the concentration is high, the supply by diffusion will ensure that the molecules arriving at the interface will have no room to unfold, and hence that the conformation of the polymer at the interface will be looped. Reconformation of a boundary layer built up in this way, which is a slow process, will in turn result in a slow reduction in γ. Thus the discontinuity in the γ-log c_p curves of figs.2.4. to 2.6. can be explained by kinetic factors, as is done in chapter 2.

Behaviour analogous to that of PVA 98 has been found for polymethyl methacrylate (M = 420,000) at the toluene-water interface by HUBER and THIES

(1970). For concentrations between 1 and 100 ppm, the interfacial tension measured by the du Nouy ring method showed hardly any time-dependence. For concentrations above 100 ppm there was a marked time-dependence, which was ascribed to a slow change in the structure of the polymer at the interface.

Such irregularity in the time-dependence is entirely absent for PVA samples with a higher acetate content (> 10%). The time-dependence at high concentrations cannot be explained by a limited supply by diffusion in this case either, since the diffusion coefficients for PVA 88 samples are comparable with those for PVA 98, for which it has already been shown that diffusion cannot be limiting. With PVA 88, there is probably a gradual transition from diffusion-determined time-dependence to reconformation-determined time-dependence with increasing concentration. The slight differences between samples of different molecular weight and from different sources may again be a consequence of the stereochemical structure of the polymer molecule not being identical in all cases.

3.4.2. *Continuous measurement at low concentrations*

To enable the diffusion mechanism at low concentrations to be studied quantitatively, the interfacial tension was measured continuously as function of time. The first measurement could be made after about one minute, whereafter the interfacial tension was measured at various intervals, the platinum plate remaining in the interface. The measured interfacial tension was plotted as a function of $t^{\frac{1}{2}}$, some of the curves being given in figs. 3.9. and 3.10. It appears that, at least after a certain initial period, the interfacial tension is proportional to $t^{\frac{1}{2}}$ over a long interval, which indicates that the diffusion

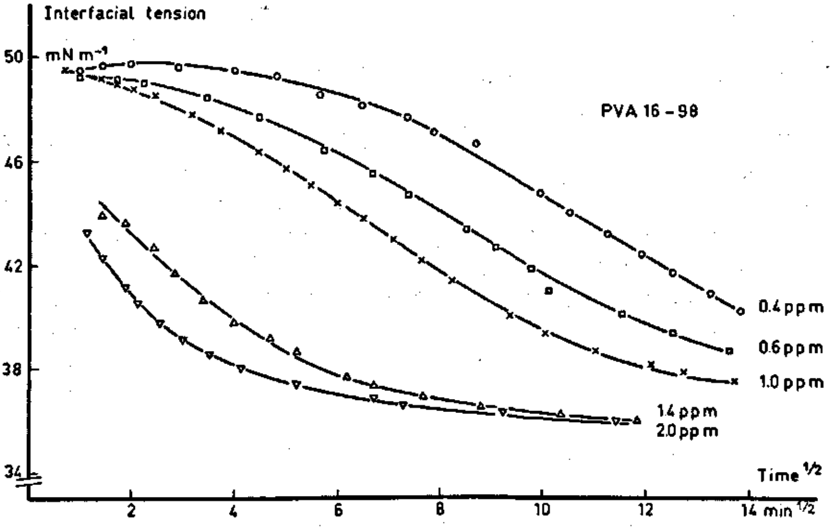


FIG. 3.9. Interfacial tension as a function of $t^{1/2}$ at very low PVA 16–98 concentrations.

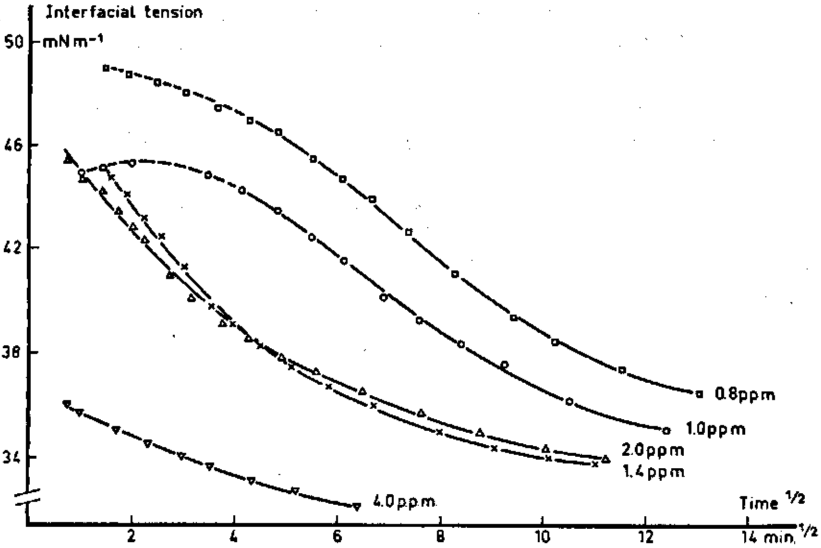


FIG. 3.10. Interfacial tension as a function of $t^{1/2}$ at very low PVA 16–88 concentrations.

mechanism may be playing a role. The relationship between γ and $t^{\frac{1}{2}}$ can only be linear if the slope β_1 is constant, which is the case if v is constant (equation 3.5.). The initial period of about 15 to 25 minutes before a linear relationship is established, which is found primarily at low concentrations can perhaps be ascribed to the slowness of unfolding since local gradients in the interfacial tension are still low. The time-dependence measured is the resultant effect of both diffusion and unfolding. The maximum slope, which corresponds to the linear part of the plot, is always taken for the quantitative interpretation- At this stage one can assume that the supply by diffusion, and not the rate of unfolding, is the limiting factor.

After the linear part of the $\gamma - t^{1/2}$ curve, the rate of decrease in the inter. facial tension with increasing $t^{\frac{1}{2}}$ falls off, probably as a result of the monolayer becoming saturated. The persisting time-dependence is probably due to reconformation at the interface of the polymer, which is not yet unfolded, or not completely so. For PVA 98 at high concentrations (fig. 3.9.) there is hardly any further decrease in interfacial tension about after 30 minutes. The drop of 1 mN m^{-1} in the subsequent 90 minutes is partially explained by the effect found with an interface free of polymer. The interfacial tension remains about 36 mN m^{-1}, the value which was also found with the discontinuous measuring technique (fig. 2.4.).

The slopes of the $\gamma - t^{\frac{1}{2}}$ curves for the various PVA samples are plotted as a function of the concentration in fig. 3.11.–3.13. It is striking that at a given concentration by weight, the slopes for PVA preparations of different molecular weight are almost the same. This supports the idea that the number of seg-

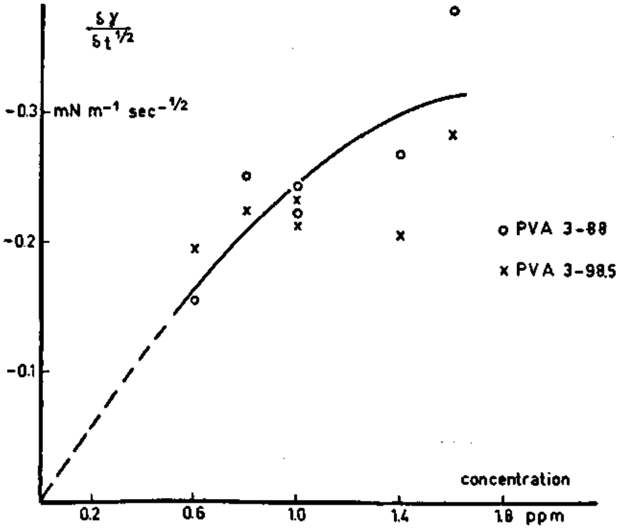


FIG. 3.11. Initial slope of the γ-$t^{1/2}$ plots ar very low PVA concentration.

ments, and not the number of molecules, determines the interfacial tension measured at these low concentrations. It can also be seen that the slope, except at very low concentrations, is not constant. If equation 3.2. were valid, one would indeed expect γ to be proportional to c. The diffusion coefficient could then in principle be calculated from the slope, as has been done by several

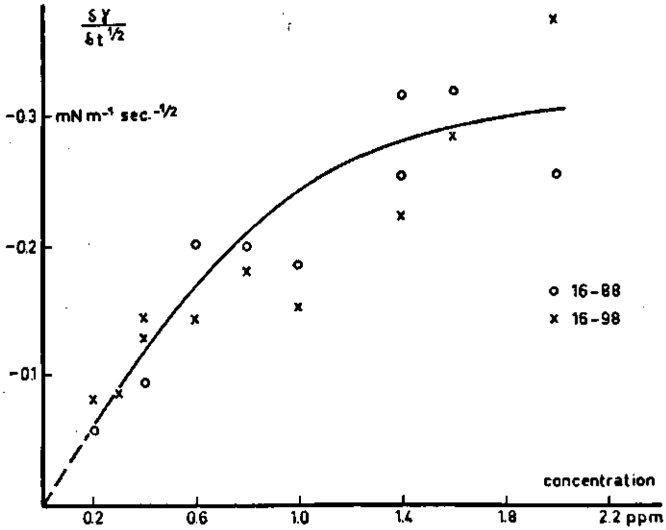


FIG. 3.12. Initial slope of the γ-$t^{1/2}$ plots at very low PVA concentration.

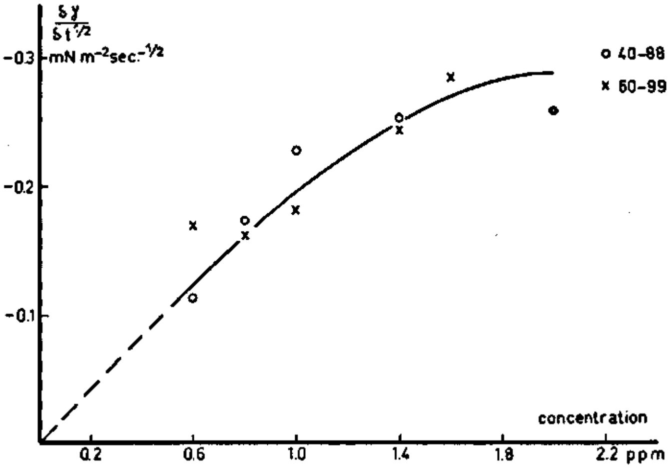


FIG. 3.13. Initial slope of the γ–$t^{1/2}$ plot at very low PVA concentration.

workers (e.g. GLASS, 1968) for much higher concentrations at which, however, diffusion can no longer be the limiting factor. For PVA 16–98 ($M = 55{,}000$) the slope at a concentration of 0.4 ppm is 0.129 mN m^{-1} sec$^{-1/2}$. According to equation 3.2., this corresponds to a diffusion coefficient of 0.6 cm^2 sec^{-1}, which is a factor of 10^5–10^6 too large. As mentioned earlier, this must be explained by assuming that the interfacial tension does not depend on the supply by diffusion of complete molecules, but that these molecules each bring a large number of surface-active units into the interface. This is taken into account in equation 3.3. by the introduction of the correction factor ν. Diffusion coefficients calculated from equation 3.2. are thus a factor ν^2 too high.

If, on the other hand, the diffusion coefficient is known, ν can be calculated. The diffusion coefficients for PVA preparations of different molecular weight can be calculated from the relationship $D = kM^{-\alpha}$. The constants k and α can be determined graphically from data of BRANDRUP and IMMERGUT (1965), who give diffusion coefficients of PVA at 20°C for different molecular weights. The values found were $k = 2.66 \times 10^{-4}$ and $\alpha = 0.625$. The diffusion coefficients of PVA 88 and PVA 98 samples were taken to be the same, which is justified in view of the experimental error, and the spread in molecular weight of the individual samples was not taken into account. The diffusion coefficients thus calculated vary from 6.90×10^{-7} cm^2 sec^{-1} for $M = 1.3 \times 10^4$ to 1.93×10^{-1} for $M = 10.5 \times 10^4$. The logarithm of the values of ν calculated from these diffusion coefficients with equation 3.5. is plotted as a function of concentration in fig. 3.14. It is found that, at low concentrations, the calculated value of ν tends to the total number of segments per molecule, P. Thus, at very low concentrations, all segments lie in the interface, the polymer molecules being completely unfolded. At higher concentrations ν decreases, as would be predicted from the decrease in gradient with increasing concentration in figs 3.11. to 3.13.

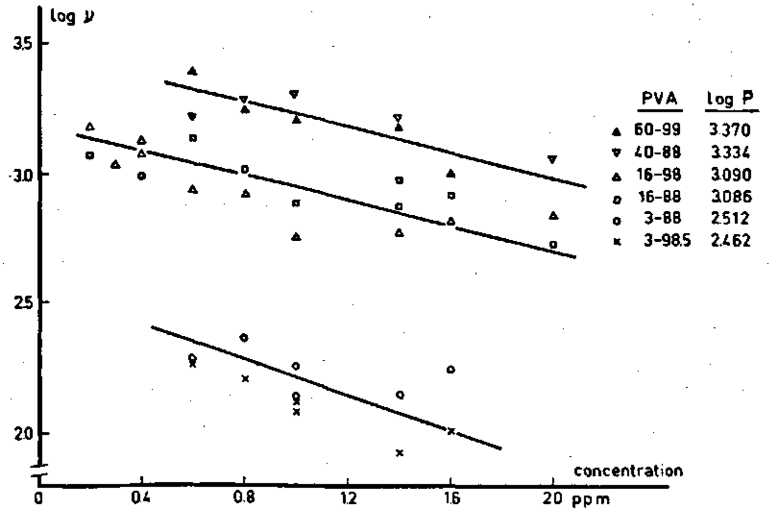


FIG. 3.14. The correction factor (ν) to be applied to the Ward and Tordai diffusion equation as a function of the concentration.

The relationship between γ and t at concentrations above 2 ppm cannot be interpreted so clearly, for two main reasons. Firstly, the technique followed *does not enable the interfacial tension to be measured sufficiently rapidly after* the formation of the interface. Secondly, the reconformation of the polymer molecules supplied by diffusion can also affect the time-dependence. The latter is not the case with the PVA 98 samples, for which there is hardly any time-

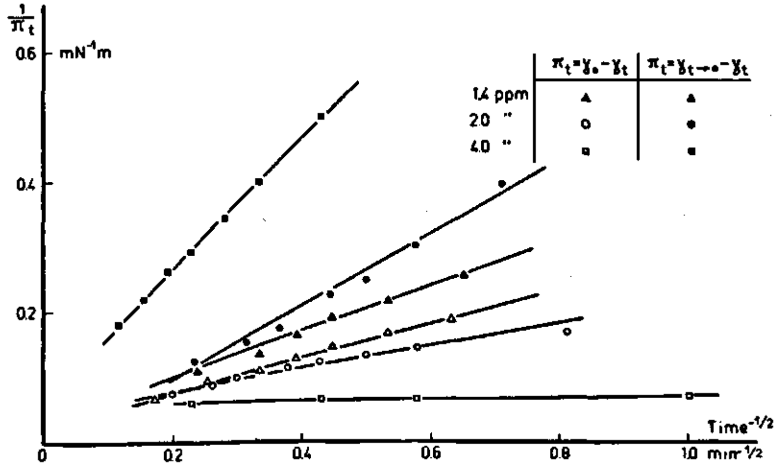


FIG. 3.15. The time-dependency of the interfacial tension according to the Bartholomé-Schäfer equation, both for $\Pi t = \gamma_o - \gamma_t$ and for $\Pi_t = \gamma_{t \to o} - \gamma_t$.

dependence found for concentrations between 4 and 40 ppm. This is an extra argument in favour of the model proposed to explain the discontinuous character of the γ-log c_p curves (figs. 2.4. to 2.6.): at a concentration of 4 ppm the supply by diffusion, compiled with subsequent unfolding, is sufficient to completely form a monolayer within a few minutes. The difference in behaviour between PVA 98 and PVA 88 at higher concentrations (4–100 ppm) must mean that PVA 88 unfolds less rapidly than PVA 98 at these concentrations. However, no evidence can be found for this at low concentrations.

In fig. 3.15. some measurements of the interfacial tension have been plotted against time in accordance with the BARTHOLOMÉ-SCHÄFER equation. The interfacial pressure, Π_t, has been expressed in two ways, namely as $\gamma_0 - \gamma_t$ (compare BARET, 1968a) and $\gamma_{t \to 0} - \gamma_t$. In both cases a linear relationship was found between Π_t^{-1} and $t^{-\frac{1}{2}}$, which indicates diffusion-dependence. The choice of γ_0 or $\gamma_{t \to 0}$, however, markedly influenced the slope of the plots. The choice of γ_0 seems unjustified since the interfacial tension at the moment when diffusion begins is not that between paraffin and distilled water but between paraffin and the PVA solution. The best agreement with the slopes determined from figs. 3.11. to 3.13. is indeed obtained when Π_t is taken as $\gamma_{t \to 0} - \gamma_t$. Nevertheless, it is difficult to calculate the correct value of $\gamma_{t \to 0}$ by extrapolation. Moreover, a small error in $\gamma_{t \to 0}$ causes a relatively large error in the slope; this shows that the method is less useful.

3.4.3. *Continuous measurement at higher concentrations and over longer periods*

For higher concentrations (> 4 ppm), at which the diffusion mechanism can no longer be held responsible for the time-dependence, the interfacial

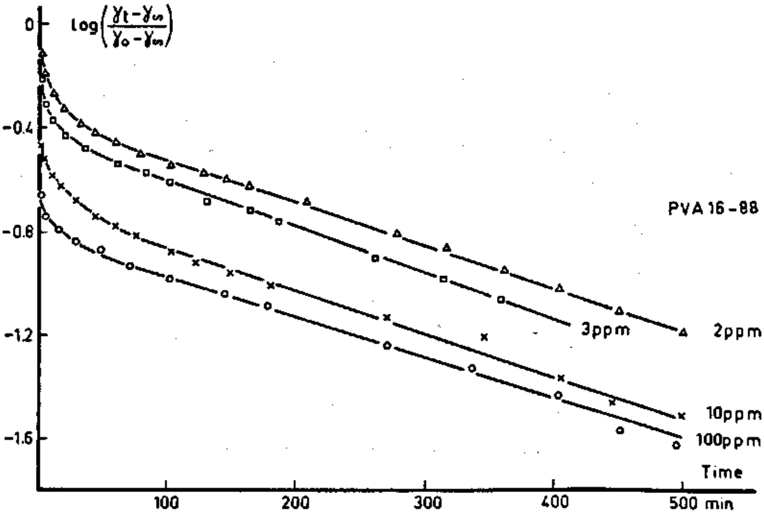


FIG. 3.16. The decrease of interfacial tension over longer periods and for higher PVA concentrations.

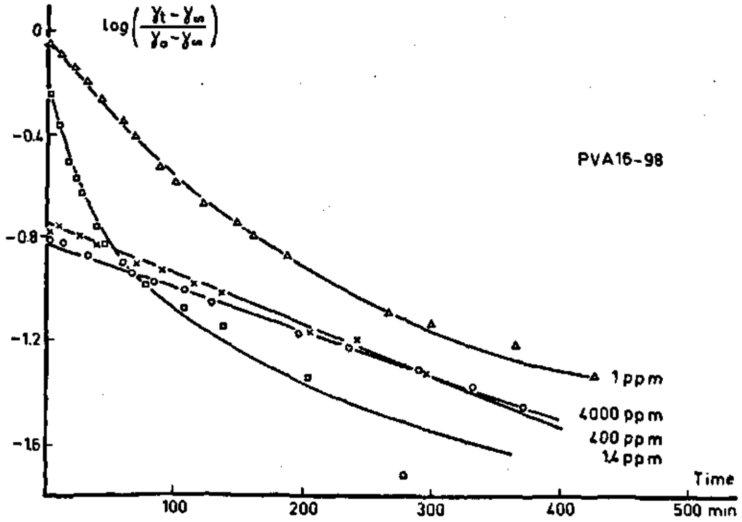


FIG. 3.17. The decrease of interfacial tension over longer periods and for higher PVA concentrations.

tension was again recorded continuously as a function of time for about 8 hours after the formation of the interface, just as in the experiments described in section 3.4.2. Log $\left(\frac{\gamma_t-\gamma_\infty}{\gamma_0-\gamma_\infty}\right)$ has been plotted as a function of time for some concentrations of PVA 16–88 and PVA 16–98 in figs. 3.16. and 3.17. respectively For PVA 16–88 a linear relationship was found for all concentrations between 1 and 4000 ppm after an initial period of about 40 minutes. The slope is approximately the same in all cases, indicating that the relaxation time is independent of the concentration. If follows therefore that diffusion cannot be a deciding factor and that the relaxation time is determined by the polymer layer at the interface. FAINERMAN (1969) also found the relaxation time for polymers adsorbed from solution to be independent of concentration. For PVA 16–98 (fig. 3.17.) an entirely different picture was found – one which agreed in fact with the discontinuous measurements described in section 3.4.1. and one which is not easy to interpret. At high concentrations the relaxation time was about the same as for PVA 16–88, which may indicate that the same mechanism is at work. For concentrations between 4 and 100 ppm, hardly any time-dependence was recorded. It should be mentioned that over longer periods the measured interfacial tension approaches its steady state value and the error in log $\left(\frac{\gamma_t-\gamma_\infty}{\gamma_0-\gamma_\infty}\right)$ can be rather large. According to equation 3.9. the curves in figs. 3.16. and 3.17. should intercept the y-axis at zero. The discrepancy is due to the incorrect choice of γ_0.

The exponential relationship found between γ and t at least demonstrates that supply by diffusion cannot be the limiting factor. One factor which probably does help to account for the exponential relationship is a certain degree of reconformation of the adsorbed polymer.

3.5. CONCLUSIONS

The time-dependence of the interfacial tension between paraffin and solutions of PVA-98 is of an irregular nature. This irregularity is not shared by PVA with a higher acetate content. At low concentrations of PVA, independent of acetate content, the time-dependence can be explained in terms of a limiting supply by diffusion. In the quantitative interpretation of the gradients of the γ–$t^{\frac{1}{2}}$ curves, one must remember that the supply of one diffusing molecule results in the introduction of many surface-active segments into the interface. At low concentrations the number of surface-active segments is almost equal to the total number of segments per polymer molecule. This means that all segments are then localised in the interface, if it is assumed that they all contribute to $\Delta\gamma$. At higher concentrations diffusion can no longer be the limiting factor, and another time-dependence mechanism must be assumed. In view of the exponential decrease of the interfacial tension with time at higher concentrations, a plausible alternative mechanism is the reconformation of the polymer in the interface. The change from diffusion-determined to reconformation-determined time-dependence is not abrupt. Extreme care should therefore be taken in the interpretation of the time-dependence of interfacial tension measurements.

4. SPREAD AND ADSORBED MONOLAYERS OF POLYVINYLALCOHOL AT PARAFFIN-WATER INTERFACES

4.1. INTRODUCTION

The monolayer technique is very suitable for estimation of the molecular dimensions of surface-active substances at an interface. Interpretation of the results is often easier however for simple amphipolar detergents than for polymers comprising a chain of surface-active segments. This chapter will be devoted to experiments with monolayers. It was hoped that the results of these experiments would supplement the picture outlined in chapters 2 and 3 for the adsorption of polymers at an interface. The irreversible nature of the adsorption of PVA (KUHLMAN, 1965; LANKVELD and LYKLEMA, 1968) enables it to be spread on the paraffin-water interface, despite its water-solubility.

In recent years much has been published about research on monolayers. The subject has been reviewed by GAINES (1960) and MINGINS (1966), of whom the latter deals extensively with experiments of biochemical importance. Both reviews include work on polymer monolayers, a field reviewed earlier by CRISP (1958). It appears that the interpretation of monolayer measurements is far from easy.

So far little research has been done on PVA monolayers. CRISP (1946) showed that monolayers of PVA were highly compressible and that the surface pressure remained very low (< 3 mN m^{-1}). This agrees with the small reduction in the surface tension which was measured upon the adsorption of PVA from aqueous solution. LLOPIS (1956) also found the surface pressure of PVA to be low, and independent of molecular weight, which confirmed the findings of CRISP. Compressibility proved to be high, while no hysteresis was observed upon compression and expansion.

More is known about the behaviour of polyvinylacetate (PVAc), the polymer from which PVA is obtained upon hydrolysis. ISEMURA (1953) found that PVAc forms a highly expanded monolayer, the surface pressure of which is hardly dependent on the molecular weight. The surface pressure is significantly higher than that for PVA, although in other respects the two monolayers are similar. The close resemblance between monolayers of PVA and PVAc emerged from the comparative experiments of LLOPIS (1956), although the higher interfacial pressure of PVAc was again evident. The finding that the interfacial pressure is independent of molecular weight would seem to invalidate the use of the monolayer technique for the determination of molecular weights, for instance done by BULL (1945) for proteins. RIES (1959) found that high-molecular-weight PVAc showed no hysteresis between compression and expansion and that the response to compression and expansion was unusually rapid. He assumed a flat orientation for the PVAc molecules at the water surface; the surface area per segment was found to be about 27 Å^2, while collapse of the monolayer always occurred at a surface pressure of about 25 mN m^{-1} (RIES et al., 1959, 1960, 1961).

In addition to the experiments with PVA and PVAc monolayers mentioned above, much research has been done recently into monolayers of other polymers, including many proteins. These investigations will not be referred to here, but will be mentioned when and where relevant in the discussion. One exception can be made for the work of YAMASHITA (1968), who describes a method for independently determining both the surface tension and the surface occupation of adsorbed lysozyme monolayers. By means of a special technique, the adsorbed monolayer was transferred to the clean surface of an aqueous potassium chloride solution and allowed to spread. Comparison of the surface tension measured with that recorded when known quantities of polymer were spread on the surface showed how much polymer had been adsorbed. By measurement of the surface tension in the original lysozyme solution, a relationship could be established between surface tension and the surface occupation of the adsorbed monolayer. YAMASHITA, however, measured the surface tension of the lysozyme solution by the drop weight method, a method which must be rejected for polymer solutions (2.1., 3.1.). An indication that this can have affected the results is that the adsorption measured in this way did not increase any more at lysozyme concentrations above 400 ppm, whereas the measured surface tension continued to decrease. Except for this objection this technique seems a good one for establishing an experimental relationship between the surface tension and the surface occupation as a result of adsorption.

4.2. THEORY

Monolayers can be broadly divided into two categories, namely expanded and condensed monolayers. Expanded monolayers have a less compact structure as a result of which the interfacial pressure does not rise steeply upon compression. At low interfacial pressures these monolayers behave like ideal two-dimensional gaseous films, which obey the simple equation of state, $\Pi A = kT$. With a condensed monolayer, however, the interfacial pressure increases sharply upon compression and there is a strong mutual interaction between the molecules. This distinction can be applied both to low-molecular-weight susstances and to polymers. PVAc and PVA monolayers belong more to the expanded type (ISEMURA, 1953; RIES, 1959).

The problem is now to find a general equation of state for polymer monolayers. The best known, and so far the most commonly used, equation of state is that of SINGER (1948), derived by a statistical-thermodynamic approach. The equation, which is a two-dimensional analogue of the Flory-Huggins theory for latices, is as follows:

$$\frac{\Pi}{\Pi_0} = \frac{(P-1)z}{2P} \ln\left(1 - \frac{2}{z}\frac{A_0}{A}\right) - \ln\left(1 - \frac{A_0}{A}\right) \qquad (4.1.)$$

in which:

Π = interfacial pressure $= \gamma_0 - \gamma$

Π_0 = interfacial pressure for a compact monolayer = kT/A_0
P = degree of polymerization
z = coordination number, to a close approximation, of the polymer at the interface
A = surface available per segment
A_0 = limiting surface area per segment
k = Boltzmann's constant
T = absolute temperature.

This equation of SINGER describes the behaviour of expanded monolayers reasonably well, because in this case the mutual interactions between the segments, which were neglected in Singer's derivation, are slight. The problem is how to measure or estimate the parameters z and A_0. In practice, values of z and A_0 are usually chosen by trial and error such that the calculated curve coincides with the experimental one. DAVIES (1954) interprets z as a measure of the flexibility of the polymer in the interface, but this hypothesis is contested by KAWAI (1959) on the grounds that theoretical support is lacking.

MOTOMURA and MATUURA (1963) have derived an equation of state for polymer monolayers, which takes into account the mutual interaction of the polymer segments and which constitutes an improvement of the SINGER equation. The equation of MOTOMURA and MATUURA reads as follows:

$$\frac{\Pi}{\Pi_0} = \frac{z}{2}\ln\left\{1-\frac{2}{z}\left(1-\frac{1}{P}\right)\frac{A}{A_0}\right\} - \ln\left(1-\frac{A_0}{A}\right) - \frac{z}{2}\ln\left[\frac{\left\{1-\frac{2}{z}\left(1-\frac{1}{P}\right)\frac{A_0}{A}\right\}\left(\chi+1\right)-2\left\{1-\frac{2}{z}\left(1-\frac{1}{P}\right)\frac{A_0}{A}\right\}}{\left(1-\frac{A_0}{A}\right)\left(\chi+1\right)}\right] \qquad (4.2.)$$

in which:

$$\chi = \left[\frac{4\left\{1-\frac{2}{z}\left(1-\frac{1}{P}\right)\right\}\left(1-\frac{A_0}{A}\right)\frac{A_0}{A}}{\left\{1-\frac{2}{z}\left(1-\frac{1}{P}\right)\frac{A_0}{A}\right\}^2}\left(e^{\frac{2\omega}{zkT}}-1\right)+1\right]^{\frac{1}{2}}$$

The energy of interaction between the segments is given by the term ω/kT, while the other symbols have the same meaning as in equation 4.1. Equation 4.2. becomes identical with the SINGER equation for $P \gg 1$ and $\omega/kT = 0$.

The theory of MOTOMURA and MATUURA has been used by JAFFE (1967a,b) for the interpretation of measurements with monolayers of polymethacrylates at both air-water and oil-water interfaces. The introduction of an extra term, the interaction energy (ω) between two segments, means that a combination

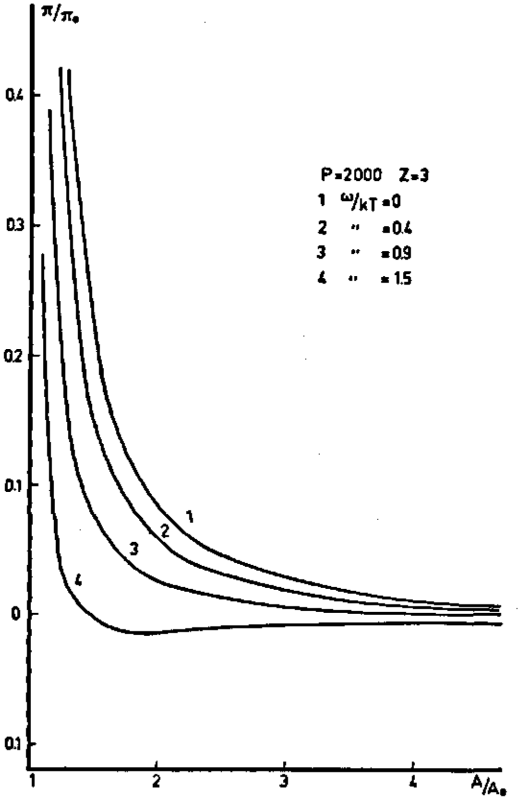


FIG. 4.1. Surface pressure-area isotherms for polymer monolayers according to the equation of state of MOTOMURA and MATUURA (1963) for $z = 3$ and various values of ω.

of ω, z and A_0 must be chosen which gives the best agreement between theory and experiment. Usually, z is taken to be 4 and a combination of values for ω and A_0 then remains to be chosen. As is clear from figs. 4.1. and 4.2., however, the choice of z is of very great importance. In these figures, Π/Π_0 has been calculated as a function of A/A_0 with the aid of equation 4.2. for $P=2000$ and for four values of ω, with $z=3$ (fig. 4.1.) and $z=6$ (fig. 4.2.). Comparison of fig. 4.1. and fig. 4.2. shows that the curve for $z=3$ and $\omega=0$ is almost identical to that for $z=6$ and $\omega=0.4$ kT. The choice of z thus markedly influences the value found for ω. This means that JAFFE's interpretation of his measurements with regard to the interaction between the segments should be treated with some reserve, since z can be different for the various interfaces. Interpretation according to the theory of MOTOMURA and MATUURA will therefore remain ambiguous until the unknown parameters can be verified independently.

We have already seen that, when $\omega=0$, equations 4.1. and 4.2. become identical. It therefore follows that the $\Pi-A$ curves for $\omega=0$ in figs. 4.1. and

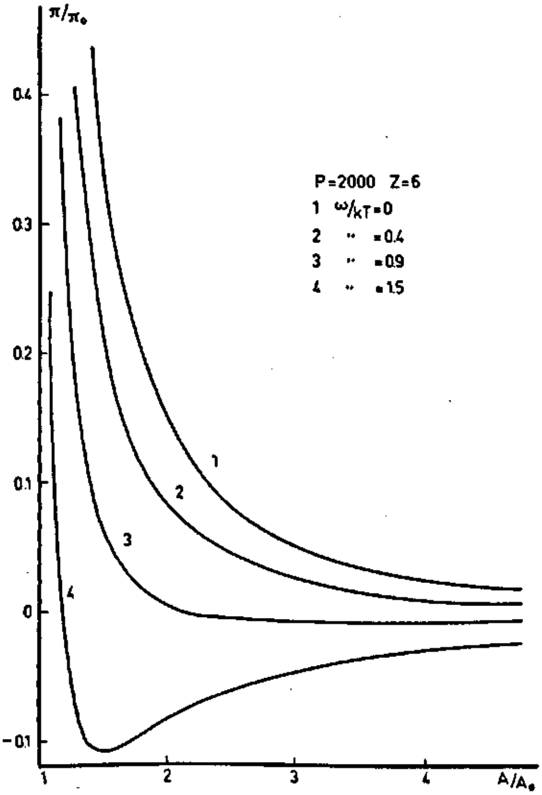


FIG. 4.2. Surface pressure-area isotherms for polymer monolayers according to the equation of state of MOTOMURA and MATUURA (1963) for $z = 6$ and various values of ω.

4.2. correspond to the SINGER equation for $z=3$ and $z=6$ respectively. Although the form of the $\Pi-A$ curves in figs. 4.1. and 4.2. corresponds with that found experimentally, it remains questionable whether the values of parameters determined by comparison of theoretical and experimental curves are of much real significance. In addition it must be assumed that all segments remain localized in the interface, which is possibly unjustifiable for hydrophilic polymers and for highly compressed polymer layers.

One interesting aspect is that the values of Π/Π_0 calculated from equation 4.2. can be negative for high interaction energies between the segments and/or high values of z (figs. 4.1. and 4.2.). The physical explanation of this is that, for negative values of Π/Π_0, phase separation occurs, which is conceivable when the segments interact strongly with one another.

FOWKES (1964) has derived an equation for the interfacial pressure which arises when solvent molecules penetrate a polymer monolayer. The equation can be written as follows:

$$\frac{\Pi}{\Pi_0} = -\ln\Theta - \left\{\frac{(z-2)m+2}{2}\right\}\ln\left\{\frac{(z-2)m+2\Theta}{(z-2)m+2}\right\} \tag{4.3.}$$

in which Θ is the fraction of the total interface which is occupied by solvent molecules and m the number of adsorption sites occupied by one solvent molecule. The meanings of other symbols are as defined in equation 4.1. In fig. 4.3. Π/Π_0 has been plotted as a function of the fraction of the interface occupied for two widely-differing values of $(z-2)m$. It can be seen how insensitive Π/Π_0 is to changes in z and m, which makes equation 4.3. seem of limited use for the description of polymer monolayers. It has again been assumed that all segments are lying in the interface, which will not always be the case.

The three theories discussed above are of little direct value in the interpretation of experimental $\Pi-A$ curves. The overall form of the $\Pi-A$ curve can be satisfactorily explained by the theories, but the parameters z, A_0, ω and m, which are needed for precise definition of the theoretical model, cannot be determined with sufficient accuracy by experiment. The interpretation of the experiments will therefore be primarily qualitative.

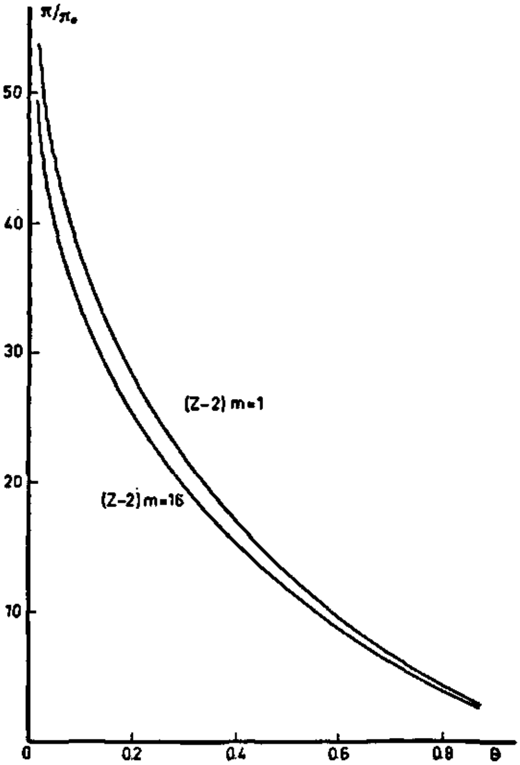


FIG. 4.3. Surface pressure-area isotherms for polymer monolayers according to the equation of state of FOWKES (1964) for two values of $(z-2)m$.

4.3. EXPERIMENTAL

4.3.1. *Spreading technique*

For the spreading of proteins on air/water interfaces, the well-known method of TRURNIT (1960) has often been applied with success. As far as I know, such a method has not yet been applied for the spreading of a polymer layer on liquid/liquid interfaces. If a polymer is to be spread on an air/water interface, it is usually dissolved in a volatile solvent which evaporates during spreading. This is, however, impossible for a liquid/liquid interface. In the latter case one has to spread the polymer from a solution, the solvent of which is completely miscible with one of the two liquid phases and has no effect on the interfacial tension. The PVA monolayer was therefore spread from an aqueous solution by a method similar to that of TRURNIT. A small glass rod was placed on the bottom of the measuring vessel containing distilled water and paraffin, with its roughened, tapered top just penetrating the paraffin layer (fig. 4.4.). The roughened top remains covered with a film of water. The point of the needle of an Agla micropipette containing aqueous PVA solution is placed on the top of the rod. The PVA solution is dispensed by operation of the micrometer screw of the pipette, and is spread in the direction shown by the arrows in fig. 4.4. Reproducibility was very poor when the needle of the micropipette was brought directly into the interface (i.e. without the glass rod) as done by HOTTA (1953), ZILVERSMIT (1963) and others. This is probably because it is difficult to place the needle precisely in the interface; in addition, the PVA is dispensed in the direction of the aqueous phase and one does not know whether and to what extent it disappears into the bulk. The spreading method illustrated in fig. 4.4. was used both for the experiments in the Langmuir trough and for the experiments in vessels at a constant surface area.

4.3.2. *Compression and expansion*

In recent years various techniques have been described for compressing a monolayer on a liquid/liquid interface in order to record $\Pi - A$ curves (ZILVERSMIT, 1963; BROOKS, 1964; BLIGHT, 1965; JAFFE, 1967b). In most cases a flexible tape is introduced into the interface so that the area enclosed by the tape can be

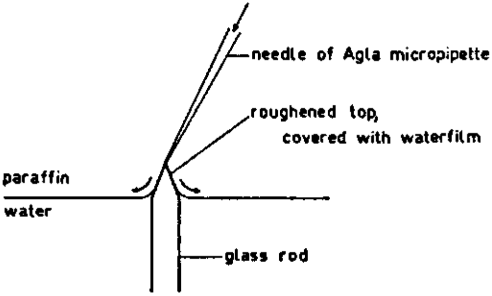


FIG. 4.4. Method of spreading PVA at the paraffin-water interface.

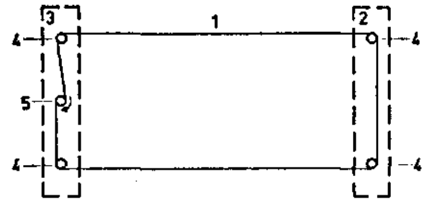


FIG. 4.5. Method of compressing monolayers at the paraffin-water interface. 1 = teflon tape; 2 = fixed bridge; 3 = movable bridge; 4 = glass rods; 5 = teflon rod.

reduced or increased. Reduction of the area can be achieved by moving the barriers supporting the band towards each other (BLIGHT, 1965; JAFFE, 1967b). The advantage of this technique is that the total bandlength remains constant, although a certain amount of dead space is created. Another method is that of ZILVERSMIT (1963) which involves the rolling-up of a teflon tape. This removes the drawback of the dead space, but the band-length no longer remains constant. Since adsorbed polymers can behave highly irreversibly, it was decided to avoid creating dead corners and to follow the method of ZILVERSMIT.

A glass trough measuring 60×20×8 cm was constructed by cementing together 1 cm thick glass plates with a two-component adhesive, which does not give off surface-active substances and which is resistant to alcoholic alkalis and chromic acid. A framework holding is fixed and a movable bridge was placed above the trough. Glass rods, around which the teflon tape was stretched, were mounted in these bridges. A teflon rod, with which the teflon tape can be rolled up in order to reduce the area of the enclosed interface, was also mounted in the movable bridge (fig. 4.5.). The teflon tape (2 cm wide, 0.15 mm thick) was type A 15 ex Huth, Bietigheim, Germany, and was specially reinforced to avoid stretching. The area enclosed can be readily calculated from the known distance between the two sections of teflon tape and from the distance between the fixed and the movable bridge. A correction was made for the cross-sectional area of the glass rods and the teflon rod. The area increase due to the curvature of the meniscus was not corrected for. The interfacial pressure measured was found to be independent of the position within the interface. The interfacial tension was in all cases measured at a distance of about 3 cm from the teflon tape near the fixed bridge by the Wilhelmy plate method described in section 2.3.1.

4.3.3. *Design of the experiments*

Three types of experiments were carried out, namely (1) spreading of PVA monolayers on an interface of constant area (45.4 cm^2), (2) spreading of monolayers in a Langmuir trough (surface area approximately 900 cm^2) with subsequent compression and expansion, and (3) compression and expansion of adsorbed monolayers. The experiments with a constant interfacial area were carried out in vessels of 250 ml, into which about 100 ml of distilled water and subsequently 50 ml of paraffin were introduced. The vessel was thermostated at 20 °C. The glass rod required for the spreading (fig. 4.4.) was placed on the bottom of the vessel. After about an hour, a capillary tube was brought into the interface and suction was applied to remove any impurities and to adjust the level of the interface so that the top of the glass rod just penetrated above it. After removal of the capillary, the platinum plate was positioned in the interface and the point of the Agla micropipette was placed on the top of the glass rod. PVA solution was dispensed in amounts of 0.004 to 0.01 ml at a time. Such an amount of PVA solution, accurate to 0.0002 ml, was brought into the interface with the aid of the micrometer screw of the pipette in the space of about a minute. Further PVA was added only when the interfacial tension altered by less than 0.2 mN m^{-1} within the space of 3 minutes. This normally took about 8 to 15 minutes, this interval thus determining the dispensing rate.

In the Langmuir trough experiments, spreading was performed in an analogous manner. The interface was cleaned by compressing it and sucking off the compressed interface several times. Upon compression of the spread layer, the interfacial tension was not measured until it altered by less than 0.2 mN m^{-1} in the space of 3 minutes. Solutions of 20–400 ppm were used for spreading, the concentration being found to have not noticeable effect on the $\Pi-A$ curves recorded.

Adsorbed monolayers were prepared by introducing 3 litres of PVA solution into the Langmuir trough with 1.5 litres of paraffin on top of it. It was found that the time between formation of the interface and compression markedly affected the Π-A curves. This will be returned to in the discussion of the results (section 4.4.3.). The experiments in the Langmuir trough were carried out at room temperature. Compression took about 40 minutes, while expansion was usually completed within about 25 minutes.

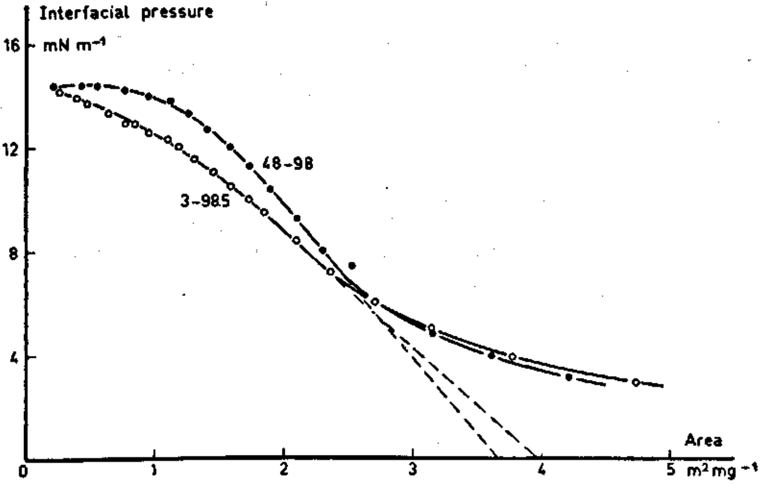


FIG 4.6. Interfacial pressure-area isotherms obtained by spreading PVA 3–98.5 ($\bar{P} = 290$) and PVA 48–98 ($\bar{P} = 2040$) on an interface of constant area.

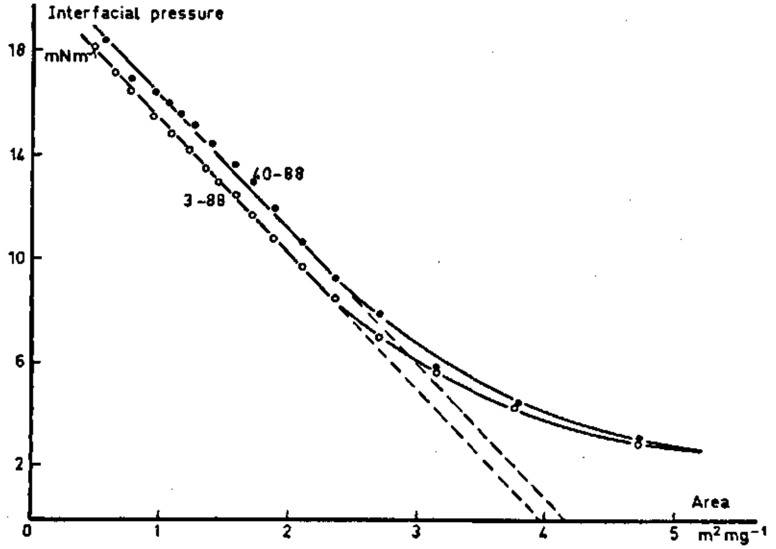


FIG. 4.7. Interfacial pressure-area isotherms obtained by spreading PVA 3–88 ($\bar{P} = 325$) and PVA 40–88 ($\bar{P} = 2160$) on an interface of constant area.

4.4. RESULTS AND DISCUSSION

4.4.1. *Monolayers spread on an interface of constant area*

Some Π-A curves obtained by spreading various amounts of PVA on an interface of 45.4 cm² are given in figs. 4.6. and 4.7. In these examples the PVA was spread from a 60 ppm solution. In fact no differences were found in the concentration range 20–80 ppm. The presence of 0.5 M KNO_3 in the aqueous phase likewise had no effect. The reproducibility of the measurements was within 0.5 mN m^{-1}. Comparison of figs. 4.6. and 4.7. again reveals the difference in interfacial activity between PVA samples of different acetate contents. Molecular weight, on the other hand, appears to have hardly any influence at all.

Extrapolation of the steep part of the Π-A curve to $\Pi = 0$ gives an intercept which is generally considered as corresponding to the area per segment for a close-packed monolayer (GAINES, 1966). For both PVA 88 and PVA 98 this intercept is between 3.6. and 4.2. m² mg^{-1} and is hardly dependent on molecular weight. This corresponds to an area per segment of about 26–31 Å², which agrees with the values quoted by RIES (1959) for vinyl acetate monomer. That no difference is found for different molecular weights implies that the total number of segments is the determining factor for the interfacial pressure. This is only possible if the molecule can unfold completely, or extensively, at the interface.

The maximum interfacial pressure attainable with PVA 98 samples is about 15 mN m^{-1} (fig. 4.6.) which agrees with the value derived from the γ-log c_p

curves in fig. 2.4. to 2.6. for concentrations below that at which the discontinuity occurred. At these concentrations it was assumed that the polymer had a flat conformation as a result of unfolding, as may also be assumed for the spread monolayers. Thus, for such flat conformations, the interfacial tensions measured in adsorbed and spread monolayers are comparable. The interfacial pressure of about 15 mN m^{-1} is attained at an area of 1.0 to 1.4 m^2 mg^{-1}, assuming that all the dispensed PVA is localized at the interface. Although this is 3 to 4 times lower than the value for a close-packed monolayer, it is of the same order of magnitude, which may well be indicative of a fairly flat polymer conformation. This experiment thus supports to some extent the model which was developed to explain the horizontal parts of the γ-log c_p curves for PVA 98 (section 2.4.1.).

4.4.2. *Spread monolayers on an interface of variable area*

In the experiments discussed in 4.4.1. a certain quantity of PVA is spread on the interface, but it is not known for certain whether all of the dispensed PVA is, and remains, adsorbed at the interface. It is conceivable that some of the water-soluble polymer will disappear into the aqueous phase when it is dispensed as a result of the compression incurred, particularly when the level of occupation of the surface is already high. The experiments were therefore repeated in the Langmuir trough. The PVA was spread to a level of about 1.4 m^2 mg^{-1}, and the monolayer was compressed and expanded.

The results are given in Figs. 4.8. to 4.11. for different samples of PVA. The insets show the effects on the interfacial pressure of two compression-expansion cycles. In comparison with the experiments described in section 4.4.1., the Π-A curves obtained upon spreading show a slight shift along the x

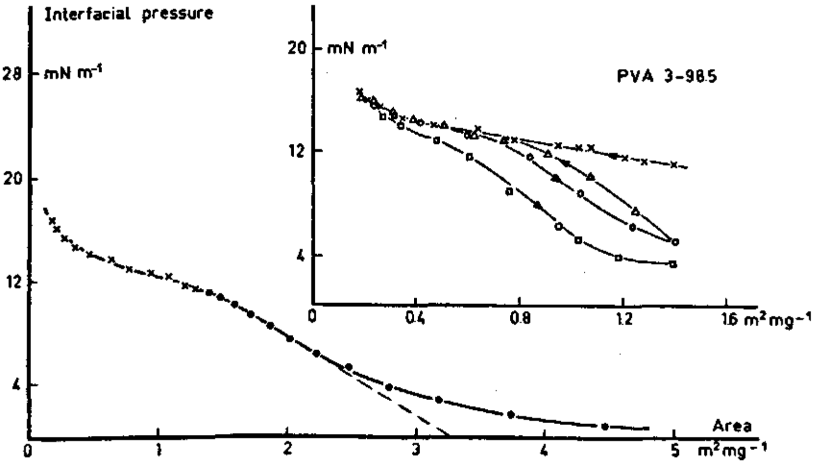


FIG. 4.8. Interfacial pressure-area isotherms of PVA 3-98.5 ($\bar{P}$ = 290) obtained by spreading it on an interface of constant area (●), and subjecting the interface successively to compression (×), expansion (○), compression (△) and, after 20 min, expansion (□).

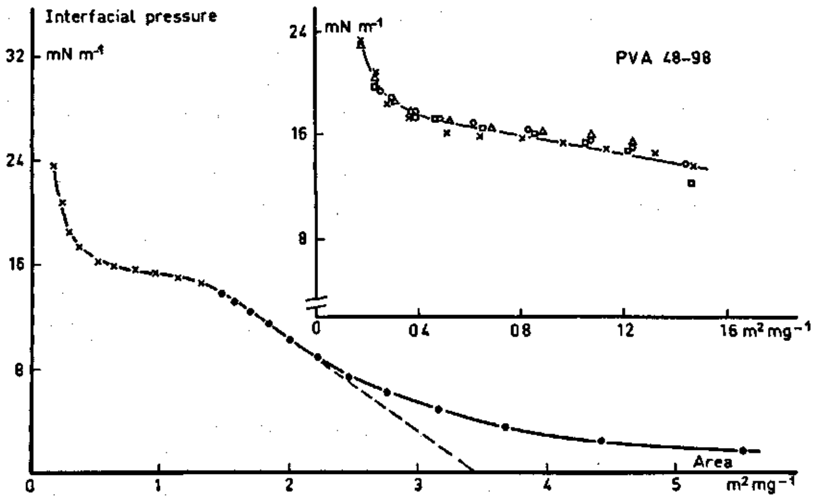


FIG. 4.9. Interfacial pressure-area isotherms of PVA 48–98 ($\bar{P}$ = 2040) obtained by spreading it on an interface of constant area (●), and subjecting the interface successively to compression (×), expansion (○) and, after one hour, compression (△) and expansion (□).

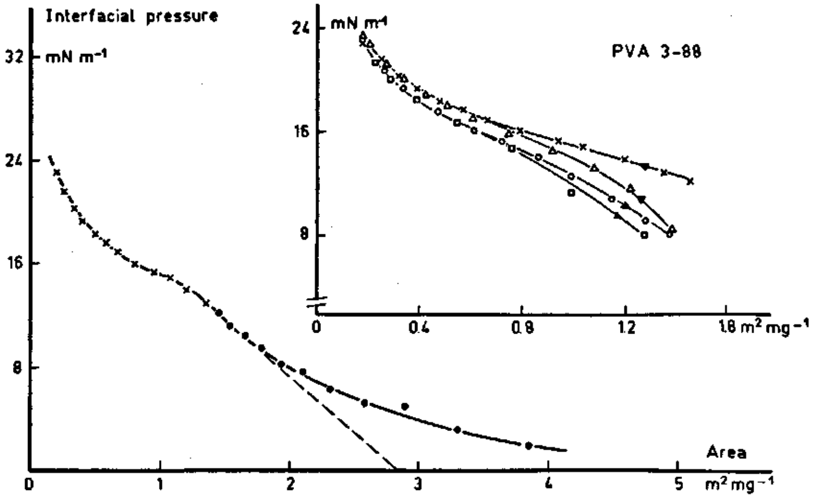


FIG. 4.10. Interfacial pressure-area isotherms of PVA 3–88 ($\bar{P}$ = 325) obtained by spreading it on an interface of constant area (●), and subjecting the interface successively to compression (×), expansions (○) and, after one hour, compression (△) and expansion (□).

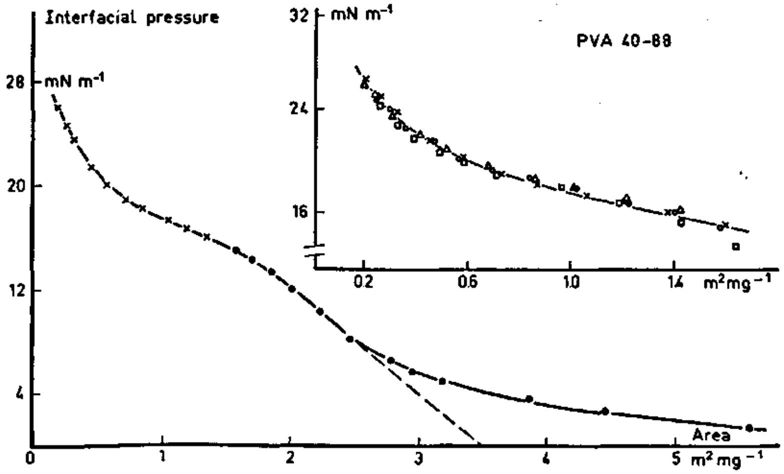


FIG. 4.11. Interfacial pressure-area isotherms of PVA 40–88 ($\bar{P}$ = 2160) obtained by spreading it on an interface of constant area (●), and subjecting the interface successively to compression (×), expansion (○) and, after one hour, compression (△) and expansion (□).

axis to lower values of the area per mg PVA. This is probably a result of the inaccuracy in the estimation of the size of the interface, which is partly due to the correction for the meniscus being neglected. This correction is relatively larger for small interfaces.

Definite signs of a horizontal section, or plateau, are evident in the Π-A curves for the PVA 98 samples (figs. 4.8. and 4.9.), as might be expected on the basis of the γ-log c_p curves. For the Π-A curves, though, such a plateau was also evident, though to a lesser extent, for the PVA 88 samples (figs. 4.10. and 4.11.). The occurence of a plateau in the Π-A curve of a polymer has been found many times before and is usually attributed to a conformational change of the polymer in the interface (LOEB, 1968a,b). A conformational change was also assumed to be responsible for the discontinuity in the γ-log c_p curves of PVA 98 (section 2.4.1.). As the interface is compressed and the interfacial pressure exceeds a certain value, some of the segments will be pushed out of the interface into the aqueous phase. This will cause a change in the conformation of the polymer at the interface. The same is possible for PVA 88, though the effect is smaller and more gradual.

To enable the occurrence of hysteresis upon compression and expansion to be investigated, the monolayers obtained by spreading were subjected to two successive compression-expansion cycles. High-molecular weight PVA showed no hysteresis upon compression and expansion (fig. 4.9. and 4.11.), whereas PVA of lower molecular weight did show hysteresis (figs. 4.8. and 4.10.). In monolayer experiments with high-molecular-weight polyvinyl acetate ($M \sim 10^6$)

Ries (1959) likewise found that no hysteresis occurred upon compression and expansion of the monolayer. He also found that the response to compression and expansion was unusually fast. Absence of hysteresis implies that all polymer segments, which are forced out of the interface into the aqueous phase upon compression, are readsorbed upon expansion. No polymer disappears into the aqueous phase, which again underlines the irreversible character of the adsorption.

The question still remains as to why lower-molecular-weight PVA shows hysteresis. A number of possible explanations can be mentioned. It is conceivable that low-molecular-weight PVA is in fact pushed out of the interface during compression and not readsorbed, thus leaving less PVA in the interface. This argument, however, is contradicted by the finding that the same interfacial tension can be obtained when compression is repeated after about an hour. This would not be feasible if some of the polymer had disappeared into the aqueous phase. If PVA disappears into the aqueous phase, it will not diffuse back again; this would involve diffusion against a concentration gradient, since the concentration of PVA in the aqueous phase is zero. As a check, the interfacial tension outside the teflon tape was always measured. Its value remained constant during compression and expansion, thus providing a further indication that no PVA is desorbed. It is not improbable that the explanation lies in the relatively large number of chain-ends per unit surface for low-molecular-weight polymers. When the monolayer is compressed to 0.2 m^2 mg^{-1}, about 90% of the segments are pushed out of the interface. This means that many molecule ends will stick out into the aqueous phase; these can on average be further removed from the interface than loops and will not contribute to Π. Upon expansion, it is possible therefore that the polymer requires more time to assume its original configuration. For we have already seen (section 3.4.3.) that the interfacial tension, albeit measured under different conditions, took several hours to reach its steady-state value when reconformation was the mechanism responsible for time-dependence. More experimental data would, however, be needed to substantiate this explanation of hysteresis. One could for instance spread the PVA on a small interface up to 1.4 m^2 mg^{-1}, and subject the interface first to expansion and then to compression. In this way no polymer should be pushed out of the interface and hysteresis should be absent.

The discontinuous character of the Π-A curves for spread monolayers on interfaces of variable area, which suggests a conformational transformation, is in accordance with the γ-log c_p curves for PVA 98 samples. On this basis, one would expect the discontinuity to be absent from the Π-A curves for PVA 88, but this is not entirely the case. This is probably due to differences in the methods of formation of the interfacial layer. In these experiments, increasing amounts of PVA were spread on an interface which was then made smaller. This possible explanation is supported by the observation that the discontinuity was absent when the area per milligram PVA was reduced only by spreading (fig. 4.7.).

4.4.3. *Adsorbed monolayers*

To enable comparison with spread monolayers, experiments have also been carried out on the compression and expansion of adsorbed monolayers. Some characteristic results are given in figs. 4.12. to 4.15.

With PVA 98 samples the age of the monolayer had a marked influence on its behaviour. Both hysteresis, and the interfacial pressure which can be achieved upon compression, increase with increasing age. This must be explained by assuming a high degree of structural order in the interface, as a result of the hydrogen bonds which the PVA can form (BAYER, 1968). Upon compression the adsorbed structure will be disturbed, the disturbance being greater for older interfaces. When a monolayer of PVA older than several hours was compressed, a visible film was formed. The interfacial pressure at which this occurred is indicated by an arrow in figs. 4.12. and 4.13. The marked hysteresis found upon subsequent expansion can be partially attributed to the fact that some of the PVA monolayer remained in the form of a clearly visible film at the interface thus causing a decrease in the surface occupation. This crystallization during the compression of older monolayers occurred always at an interfacial pressure of 30 to 32 mN m^{-1}. The formation of a visible film at the interface appears analogous to the recent finding of MACRITCHIE (1969) upon the compression of spread protein monolayers. He found that protein monolayers coagulated upon compression when there was a discontinuity in the *Π-A* curve. This is in fact the case for film formation with PVA 98 monolayers.

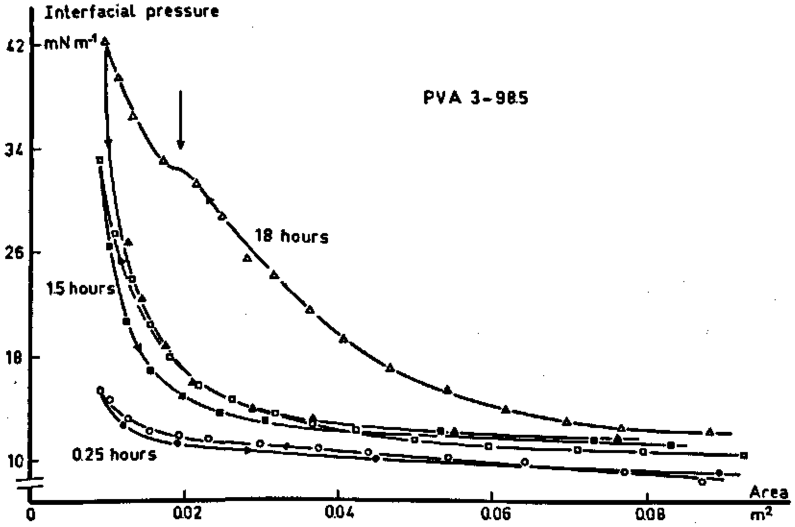


FIG. 4.12. Influence of ageing on the interfacial pressure-area isotherm of a monolayer of PVA 3-98.5 ($\bar{P}$ = 290) adsorbed from solution (4 ppm), The arrow denotes where crystallization of the PVA at the interface begins.

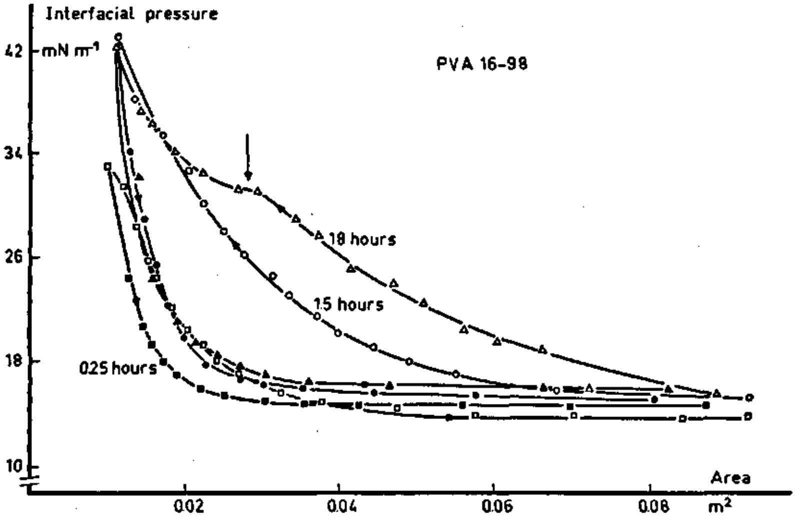


FIG. 4.13. Influence of ageing on the interfacial pressure-area isotherm of a monolayer of PVA 16–98 ($\bar{P}$ = 1230) adsorbed from solution (4 ppm). The arrow denotes where crystallization of the PVA at the interface begins.

With PVA 88 samples, the interfacial pressure rises less sharply upon compression and hysteresis is less marked. This probably because PVA 88, on account of its higher acetate content, forms less hydrogen bonds than PVA 98. One notable aspect is that the Π-A curve shifts to higher interfacial pressures with older films. This is in accordance, both qualitatively and quantita-

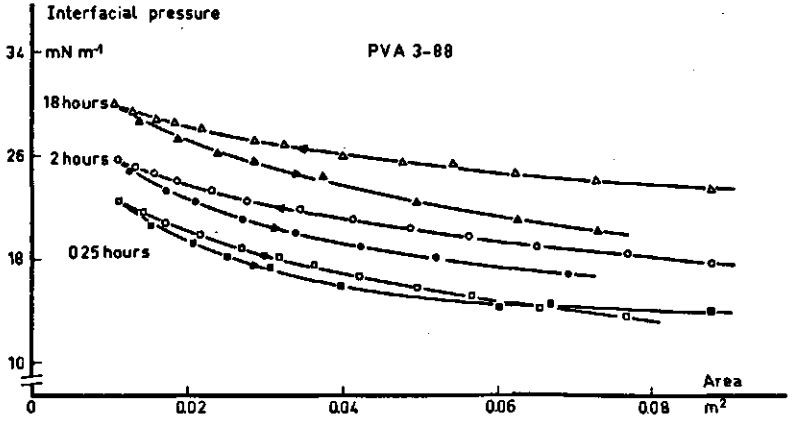


FIG. 4.14. Influence of ageing on the interfacial pressure area isotherm of a monolayer of PVA 3–88 ($\bar{P}$ = 325) adsorbed from solution (4 ppm).

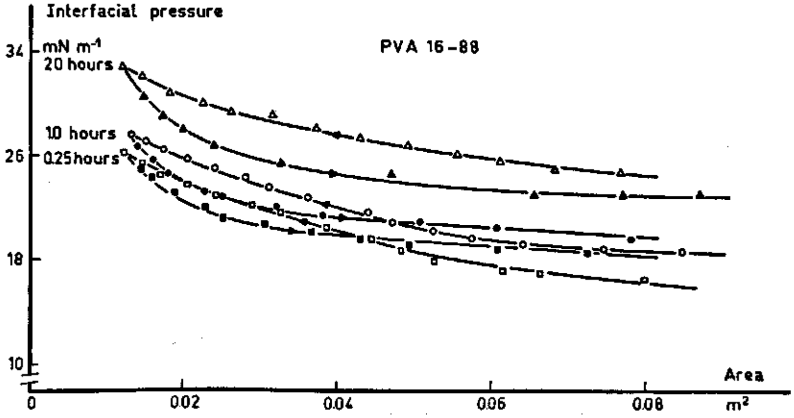


FIG. 4.15. Influence of ageing on the interfacial pressure-area isotherm of a monolayer of PVA 16-88 ($\bar{P} = 1220$) adsorbed form solution (4 ppm).

tively, with the time-dependence of the interfacial tension already discussed in section 3.4.3. The increase in hysteresis with increasing age is also in full agreement with this. For, the slowly established conformation of the polymer will be disturbed upon compression and the hysteresis, the result of this disturbance, will be larger for older interfaces. The structure of PVA 98 in the interface is completely destroyed upon compression. This can be concluded from the fact that the interfacial pressure reached after expansion is independent of the age of the interface and always equal to about 15 mN m^{-1}. This is not the case with PVA 88, which implies an essential difference in the ageing mechanism.

When an old interface is sucked off, the new Π-A curve is the same as that for a freshly interface, for all PVA samples. The ageing process then began again and all Π-A curves could be reproduced. It therefore seems unlikely that a component or PVA fraction, present in small quantities in the PVA solution, can be responsible for specific affects on the ageing process, since such components, which would accumulate in the interface, would be sucked off together with the interface.

4.4.4. *Comparison with the γ-log c_p measurements*

If the concentration (c_p) of polymer in the bulk is raised, the level of interfacial occupation will increase. For the interfacial tension measurements described in chapter 2, a linear relationship was found between γ and log c_p over a certain range of concentrations. The experiments dealt with in this chapter are all concerned with changes in the interfacial tension as a result of changes in the interfacial occupation, and it therefore seems useful to compare the results with those outlined in chapter 2.

In the experiments described in 4.4.1., the interfacial occupation was in-

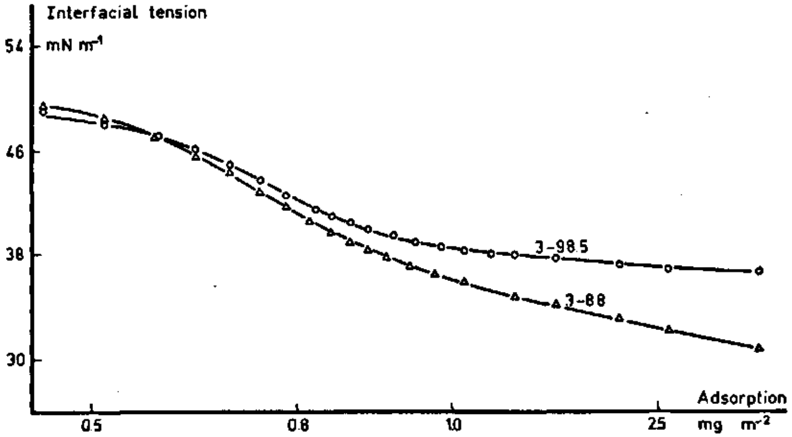


FIG. 4.16. Interfacial tension as a function of the interfacial concentration when PVA 3–98.5 ($\bar{P} = 290$) and PVA 3–88 ($\bar{P} = 325$) are spread on an interface of constant area.

creased by dispensing known amounts of PVA onto an interface of known area. In this way one can derive the relationship between interfacial tension (γ) and the logarithm of the interfacial occupation (log Γ_s). This relationship is shown in fig. 4.16. In an analogous way a relationship can be found between γ and log Γ_c (fig. 4.17.), where Γ_c is the interfacial occupation which is increased by compression of the monolayer (4.4.2.). Fig. 4.16. and 4.17. are almost identical, as would be expected for a flat monolayer. The slight difference is probably due to an error in Γ_c or Γ_s, as a result of the area of the interface

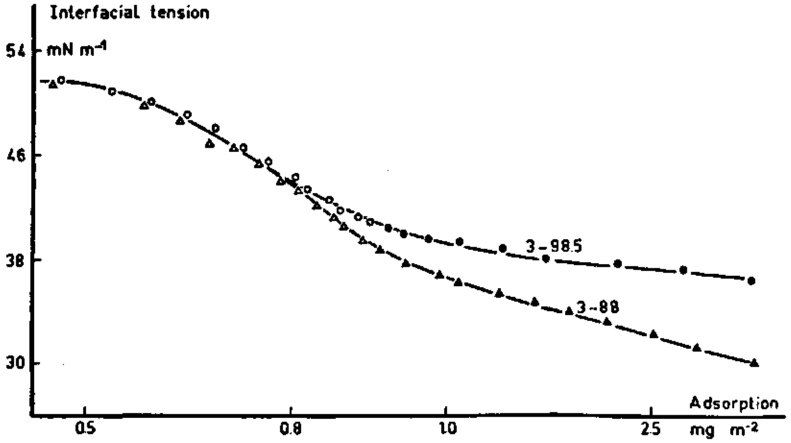


FIG. 4.17. Interfacial tension as a function of the interfacial concentration when PVA 3–98.5 ($\bar{P} = 290$) and PVA 3–88 ($p = 325$) are spread (○, △) on an interface which is subsequently compressed (●, ▲).

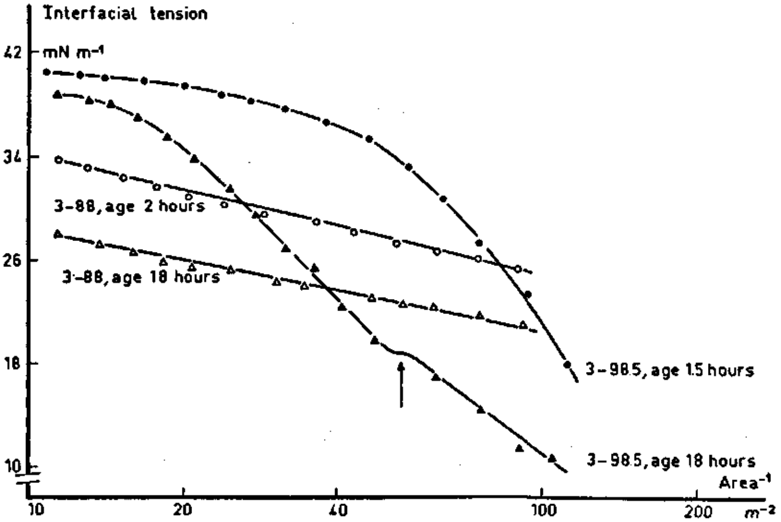


FIG. 4.18. Interfacial tension as a function of compression for monolayers of two ages for PVA 3-98.5 ($\bar{p} = 290$) and PVA 3-88 ($p = 325$) adsorbed from solution (4 ppm). The arrow denotes where crystallization of the PVA at the interface begins.

not being known accurately enough. The curves for PVA 3–98.5 clearly flattens off at an interfacial tension of about 37 mN m^{-1}, the same level as the 'plateau' of the corresponding γ-log c_p curve (fig. 2.5.).

With the adsorbed monolayers, it is not known exactly how much polymer is adsorbed at the interface. When, however, it may be assumed that, in view of the irreversible nature of the adsorption, the total interfacial occupation does not change, the relative increase in interfacial occupation can be calculated from the reduction in the area of the interface. In this case the interfacial occupation will increase proportionally to the compression. In fig. 4.18., therefore, γ has been plotted as a function of log A_i^{-1}, where A_i is the area of the interface. Plots are given for two ages of the interface. The two plots for PVA 3–88 have the same gradient, but this is not so for PVA 3–98.5 on account of the marked ageing of the interface (4.4.3.). The arrow in fig. 4.18. indicates the point at which crystallization at the interface becomes clearly visible. As with γ and log c_p, a linear relationship is found between the interfacial occupation over a certain concentration range.

Table 4.1. lists the gradients of the straight-line portions of figs. 4.16.–4.18. and that of the γ-log c_p curve (see table 2.1.) for both PVA 3–98.5 and PVA 3–88.

The reciprocal of the gradient of the γ-log Γ_s and γ-log Γ_c curves, which is termed the compressibility of the monolayer, is larger for PVA 98 than for PVA 88. For trypsine, AUGENSTINE (1958) found a marked difference in compressibility between monolayers of the polymer established by spreading

TABLE 4.1. Comparison of the changes in interfacial tension due to the interfacial occupation being altered in different ways

Plot	Gradient (mN m^{-1})	
	PVA 3–98.5	PVA 3–88
γ–log Γ_s	3.4	8.6
γ–log Γ_c	4.5	11.7
γ–log A_i^{-1}	40[a]	7.8
γ–log c_p[b]	1.15	4.25
	7.85	

[a] after 18 hours

[b] From Table 2.1. (values before and after discontinuity)

increasing amounts over a given area and monolayers obtained by compressing an interfacial layer containing a given amount of the polymer. No such marked difference was found for PVA.

No quantitative comparisons can be made between the interfacial tensions and their variations with the interfacial occupation, because the conformation of the polymer at the interface changes upon compression. Moreover the conformation is variable on account of the different ways in which the interfaces are formed. Comparison is, however, justified at low levels of surface occupation, when it can be assumed that the conformation of the polymer is flat.

4.5. CONCLUSIONS

The monolayer experiments demonstrated that the Π-A curves for PVA 98 are also characterized by a distinct kink, which suggests a change in the conformation of the polymer. This kink is found at an interfacial occupation of 1.0 to 1.4 m^2 mg^{-1}, which corresponds to a fairly flat conformation. This lends support to the model described earlier for the explanation of the kink in the γ-log c_p curves for PVA 98. In this model, the kink was likewise attributed to a conformational change in the polymer at the interface. The resulting 'plateau' in the γ-log c_p and Π-A curves was in both cases at about 15 mN m^{-1}. At higher interfacial pressures, the polymer is more likely to adopt a more looped conformation. In the monolayer experiments this conformation change is effected by compression; in adsorbed monolayers the conformation of the polymer will be partly determined by kinetic factors (2.4.1.).

For PVA 88, the time-dependance of the Π-A measurements is in accordance with the time-dependence found for the interfacial tension. The interfacial layer, slowly built up by reconformation, is disturbed by compression: this causes hysteresis to increase with time. Wit aged PVA 98 monolayers, compression causes some of the polymer to crystallize; thus, the surface occupation upon subsequent expansion is lower and hysteresis can be even more marked.

The behaviour of adsorbed monolayers is clearly different from that of spread monolayers; this must be due to the difference in conformation of the polymer. With adsorbed monolayers, age is an important parameter, since the polymer in the layer is subject to reconformation. The polymer in a spread layer, on the other hand, is flat at low interfacial pressures and hence less subject to reconformation.

More extensive experiments could have to be carried out if the measured effects were to be explained more precisely. In this study, however, the monolayer experiments served only to substantiate the qualitative interpretation of the γ-log c_p curves for interfaces on which polymer is adsorbed from the bulk.

5. ADSORPTION OF PVA ON PVA-STABILIZED EMULSIONS

5.1. Introduction

In the literature on interface chemistry, an emulsification technique is often referred to as a direct method of determining the adsorption of surface-active substances at liquid-liquid interfaces. The principle involves measurement of the drop in concentration of the surface-active substance in the continuous phase when the liquid-liquid system is emulsified in the presence of this susstance. In order to determine the adsorption per unit area of interface, one should simultaneously and independently measure the specific surface of the emulsion formed. As far as I know, however, the emulsification technique in this form, i.e. in combination with determination of the specific interfacial area has not yet been used for determining adsorption. The closest approach is the work of Cockbain (1954), who compared the adsorption at a liquid-liquid interface measured directly by the emulsification technique with the adsorption calculated from interfacial tension measurements with the Gibbs' equation. The specific interfacial area of the emulsion, though, was not measured by an independent method. Kundu et al. (1969) directly measured the adsorption of cetyltrimethylammonium bromide on paraffin-water emulsions, but assumed that the interfacial area is independent of the concentration of emulsifier.

The determination of the interfacial area of an emulsion is often difficult and too time-consuming to be done as a routine analysis. This is probably the main reason why the emulsification technique has not yet been applied for determining adsorption. In addition, the emulsions formed are often reasonably stable only at high concentrations of emulsifier. Thus, the amount of emulsifier remaining in the continuous phase is large compared with the amount adsorbed, which causes the error in the measured adsorption to be high.

There is, however, hardly any need for a direct method of determining adsorption in the case of low-molecular-weight surface-active substances, since the indirect method, i.e. measurement of the interfacial tension and application of Gibbs' law, gives the correct results. The validity of Gibbs' law for ionic detergents at water-air interfaces has been demonstrated by the foam method by Wilson et al. (1957) and van Voorst Vader (1960).

Applicability of Gibbs' law to polymers though is highly questionable (chapter 2). The emulsification technique was therefore chosen to enable the polymer adsorption to be determined directly and, by comparison of this value, with the value calculated from interfacial tension measurements (2.4.3.), to enable the applicability of the Gibbs equation for polymers to be tested. When comparing the adsorption measured directly by the emulsification method and that calculated from interfacial tension measurements, one should remember that the conformation of the polymer at the interface will not be the same in the two cases. With the interfacial tension measurements the polymer was allowed to assume its conformation at an undisturbed interface, whereas emulsification forcefully increases the interfacial area. Thus the conformation of the polymer, and hence the amount of polymer adsorbed per unit area, can be different in the two cases.

The information obtained about the adsorption of polyvinylalcohol on the paraffin-water emulsion interface is described in this chapter. The experiments also yielded information on the emulsifying capacity of the polymer, since the specific are (m^2 ml^{-1} paraffin) of the emulsion, which was measured in all cases, can be considered as a measure of the emulsifying capacity. The properties of polyvinyl alcohol as an emulsifier will be returned to in detail in chapter 6, since they are highly interesting and, in several respects, unexpected. Some insight could be gained into the mode of action of a polymer as an emulsion stabilizer, a subject on which little fundamental research has been done to date.

5.2. PREPARATION OF THE EMULSIONS

The properties of emulsions can depend markedly on the way in which the emulsification process is carried out (BECHER, 1965), so a standard method had to be chosen for preparing reproducible emulsions. The method chosen was as follows. To a glass beaker of 250 ml (diameter about 7.0 cm) was added exactly 80 ml of a PVA solution of known concentration; paraffin was then added and the beaker weighed continuously until exactly 20 ml of paraffin had been introduced. The contents of the beaker were emulsified with a type T45 Ultra Turrax, ex Janke and Kunkel K.G., Germany. The emulsifier head (external diameter 4.5 cm) contained 6 concentric rings, three of which revolve at about 13,000 rev/min at 220 V. The distance between the rotating and the stationary rings is between 0.10 and 0.12 cm; the Reynolds number is thus about 10^4. The time of emulsion was exactly 2 minutes. This time was chosen because emulsifying for more than 1.5 or 2 minutes had little or no further effect on the specific surface of the emulsion obtained. During emulsification, the temperature of the emulsion rose to between 50° and 57°C, the exact level depending on the PVA concentration, and the initial temperature. After preparation of the emulsion the temperature was always recorded because it had a slight, but noticeable, effect on the specific area obtained (6.4.3.). The emulsion was then cooled to 20°C.

With this standard procedure, the specific area of the emulsions was reproducible within 5%. Both the adsorption and the specific area were always determined between 14 and 20 hours after preparation of the emulsions. The emulsion should be highly diluted before determination of the area. The emulsions were always diluted with an aqueous solution of about 0.1% polyoxyethylene lauryl ether (Brij 35, ex Atlas Chemicals) to keep them stabilized. The Brij 35 also played an important role in avoiding flocculation, which sometimes occurred during the dilution of emulsions prepared at low concentrations of PVA.

5.3. DETERMINATION OF THE SPECIFIC AREA OF THE EMULSIONS

Since the interfacial area of emulsion created is dependent on the concentration of the emulsifier, it has to be determined for each emulsion for which the adsorption is measured to enable the amount absorbed per unit area to be calculated. There are several suitable techniques for determining the specific area (SHERMAN, 1968), though the turbidity method seems the best one in our case for routine determination. The turbidity measurements of specific area have been checked against Coulter counter measurements.

5.3.1. *Coulter counter measurements*

Principle. The principle of the Coulter counter lies in the registration of voltage pulses arising when small particles flow through a narrow opening across which an electric field is established. The size of the voltage pulse is proportional to the volume of the particle (ALLEN, 1966). By electronically counting the number of pulses above a certain level and by reducing this level step by step, one obtains a cumulative distribution of particle size. The theory of the Coulter counter method for characterizing dispersions is described by ALLEN (1966). Some aspects of Coulter counter measurements of particular relevance to emulsions have been recently discussed by WALSTRA and OORTWIJN (1969). The method proves to be a good one for characterizing emulsions provided these aspects are taken into account. The many precautions which have to be taken, however, make the Coulter counter method time-consuming and less suitable for routine purposes. The measurements therefore served only as a

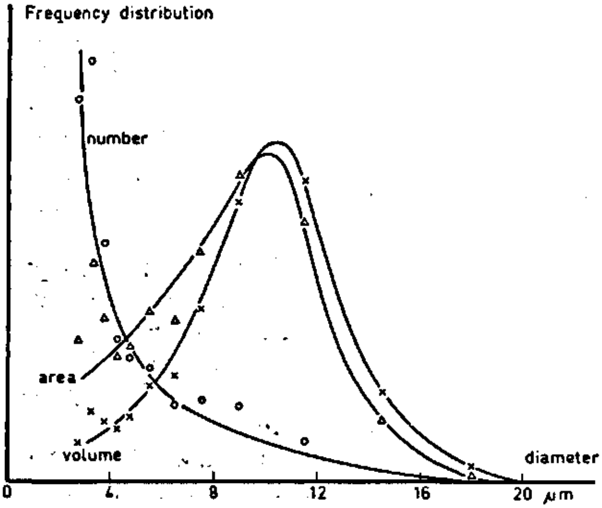


FIG. 5.1. Frequency distribution of droplet diameter in a PVA-stabilized emulsion as measured with the Coulter counter, and the relative contribution of the different-sized droplets to the area and volume of the emulsion.

check on the turbidity measurements and as a means of determining the nature of the particle size distribution function for the emulsions.

Experimental. A model A Coulter counter with a tube opening of 70 or 100 μm was used for counting. The emulsions were diluted 100-fold to a volume fraction of the oil, Φ, of 2×10^{-3} with Brij 35 solution (see 5.2.) which had been filtered through a micropore filter (0.22 μm). The dilute emulsion was further diluted 50-, 100- and 200-fold with 0.9% NaCl solution which had likewise been filtered. For these three dilutions, the number of emulsion droplets were counted with volumes above certain different values. Counting at three dilutions enable coincidence to be corrected for. Figure 5.1. gives the frequency distribution according to droplets and of the the area and volume of the emulsion in the case of an emulsion stabilized by PVA 16-98 (10 mg ml^{-1} paraffin) The general form of the distribution curve was the same for all types of PVA at all concentrations tested. The distribution of droplets in the diameter range accounting for the major part of the interfacial area of the emulsion is invariably exponential. It is important to know this particle size distribution in the turbidity method. The average droplet diameter of emulsions calculated from Coulter counts, will be compared with those determined from turbidity measurements later on (5.3.3.).

5.3.2. *Turbidity measurements*

Measurement of turbidity to characterize emulsions has been applied in milk research (GOULDEN, 1958; WALSTRA, 1965b, 1968) and has also been found suitable for paraffin-water emulsions (WALSTRA, 1968). The speed of the method, once it has been adapted for a certain system, makes it suitable for routine determinations.

Principle. The attenuation of a light beam incident on a diluted, colourless emulsion is due to scattering. The measured optical density obeys Lambert-Beer's law and for a homodisperse system, can be expressed as follows

$$O = \log \frac{I_0}{I} = \frac{\log e}{4} \pi x^2 KNl \tag{5.1.}$$

in which

O = the measured optical density
I_0 = intensity of incident light
I = intensity of transmitted light
x = diameter of the droplets
K = the light scattering coefficient
N = number of emulsion droplets per unit volume
l = optical pathlength

The light scattering coefficient K depends on the droplet diameter (x) and the difference in refractive index between the disperse phase (n_d) and the continuous phase (n_c) at the wavelength in question (λ). The theory of MIE (1908) provides a relationship between K and the dimensionless parameter of droplet size, ρ, which is defined by:

$$\rho = \frac{2\pi x\,(n_d - n_c)}{\lambda} \tag{5.2.}$$

This relationship is highly complicated, although WALSTRA (1964) has derived an approximation valid for $\rho \ll 2.5$ and $1 < n_d/n_c < 1.25$. The value of the light scattering coefficient for $\rho < 2.5$ is given by HELLER (1959). A correction to K for forward scattering has been worked out by WALSTRA (1965a). The scattering coefficient K, and the scattering coefficient K^* corrected for the forward scattering (angle of acceptance 1.5°), are plotted as a function of ρ in fig. 5.2. for $n_d/n_c = 1.05$. A similar plot is given by WALSTRA (1965b) for $n_d/n_c = 1.10$.

Determination of the droplet diameter x is based on the dependence of the scattering coefficient on the dimensionless parameter of droplet size ρ, which includes x. It can be seen from fig. 5.2. that the method can only be applied successfully if ρ is not too large. The smaller the difference in refractive indices and the higher the wavelength, the larger the values of x for which the method can be used.

For simple comparison of the theoretical with the measured turbidity, it is useful to introduce the reduced tubidity Z, which is defined by $Z = K^*/\rho$ (dimensionless). Combination of equations 5.1. and 5.2. yields:

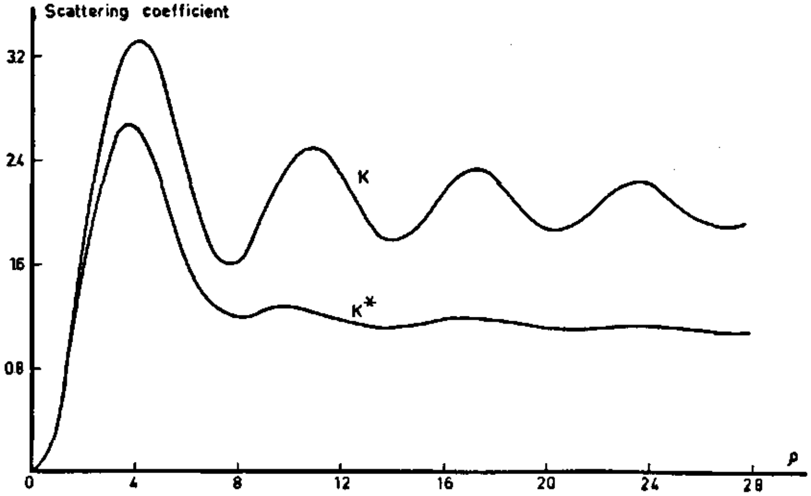


FIG. 5.2. Light scattering coefficient K, and the coefficient K^* corrected for forward scattering, as functions of the particle size parameter $\rho = \frac{2\pi x(n_d - n_c)}{\lambda}$ for $n_d/n_c = 1.05$.

$$Z = \overline{K^*/\rho} = \frac{O\lambda}{1.30\,\pi\, l\, \Phi\, (n_d - n_c)} \tag{5.3.}$$

in which Φ is the volume fraction of the disperse phase of the emulsion in which the optical density is measured. For a given emulsion, the parameters on the right-hand side of equation 5.3. either are known or can be determined. Since, however, the emulsions are always polydisperse, the average droplet diameter ought to be used in equations 5.1. and 5.2. In this case, equation 5.3. then becomes (WALSTRA 1965b):

$$\overline{K^*/\rho_{32}} = \frac{\lambda}{2\,\pi\,(n_d - n_c)} \cdot \frac{\sum\limits_i K^*\, N_i\, x_i^2}{\sum\limits_i N_i\, x_i^3} \tag{5.4.}$$

or, if the droplet diameter distribution, f (x), is known:

$$\overline{K^*/\rho_{32}} = \frac{\lambda}{2\,\pi\,(n_d - n_c)} \cdot \frac{\int_0^\infty K^*\, x^2\, \mathrm{f}(x)\cdot \mathrm{d}x}{\int_0^\infty x^3 f(x)\cdot \mathrm{d}x} \tag{5.5).}$$

It follows from this that the average diameter which is found by the turbidity method is the 'volume-surface' diameter ($\bar{x}_{32}$). Thus, if the dispersed volume is known, the specific interfacial area can be calculated directly, which is one of the reasons why the method is so suitable for our purposes.

Calculated turbidity spectra. In order to calculate the theoretical turbidity spectra, one must know the light scattering coefficient (fig. 5.2.), the ratio of the refractive indices of the dispersed and continuous phases, the angle of acceptence (α) of the turbidimeter used, and the droplet size distribution function of the emulsion. The ratio of the refractive indices of paraffin and water is 1.10 ± 0.01 for the range of wavelengths used. When $\bar{x}_{32}$ is large, the measured optical density is low. The value of Z, however, can be increased by reduction of the difference in refractive indices (equation 5.3.); when the continuous phase is mixed 1:1 by volume with glycerol, the difference in refractive indices is halved, and n_d/n_c becomes 1.05. The theoretical tubidity was in fact calculated for both $n_d/n_c = 1.10$ and $n_d/n_c = 1.05$.

The angle of acceptance of the turbidimeter was set to 1.5° (=0.0262 radians) in water. At such a small angle of acceptance, the forward scattering can be corrected for by applying the correction to K. Moreover, for small α, multiple scattering can be neglected (WALSTRA, 1965a). The corrected scattering coefficient was calculated for an angle of acceptance of 1.5°.

From the Coulter counter measurements (5.3.1.), it was found that the droplet diameter distribution of emulsions stabilized by PVA was described by an exponential function:

$$f(x) = \exp(-\,x^{1/p}) \tag{5.6.}$$

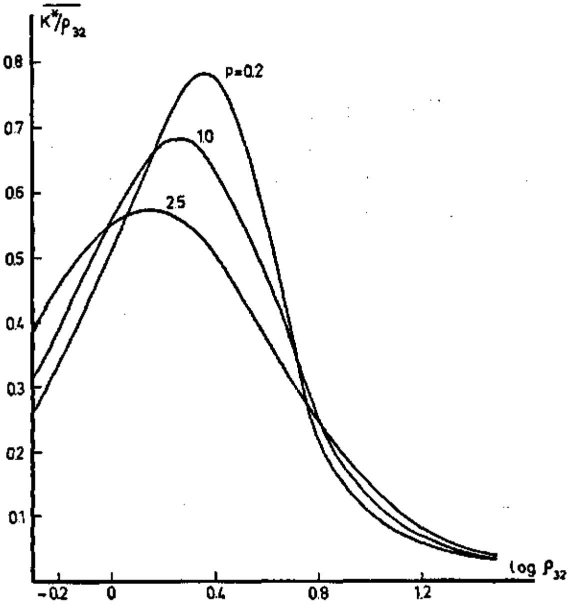


FIG. 5.3. Theoretical turbidity spectra for an exponential particle size distributions, f (x) = exp. $(-x^{1/p})$, and a refractive index ratio, n_d/n_c, of 1.05.

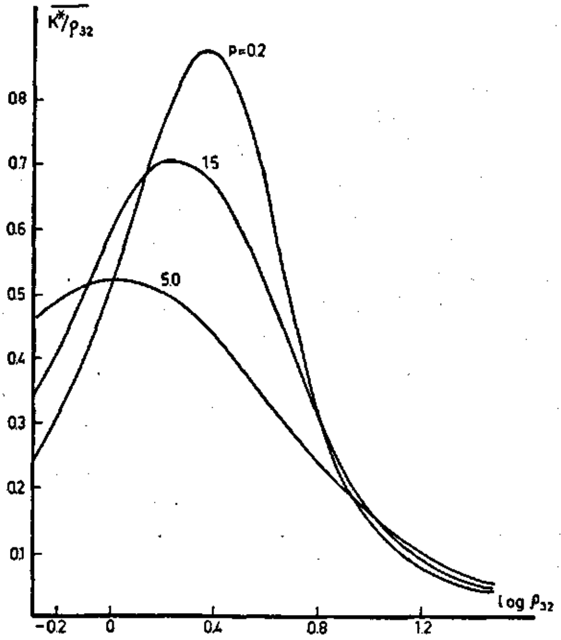
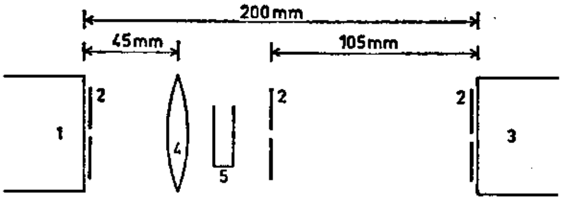


FIG. 5.4. Theoretical turbidity spectra for an exponential particle size distribution, f (x) = exp. $(-x^{1/p})$, and a refractive index ratio, n_d/n_c, of 1.10.

FIG. 5.5. Modification of the Beckman DU spectrophotometer for turbidimetry. 1 = Monochromator; 2 = diaphragm; 3 = photocell; 4 = lens (+ 20 d); 5 = cuvette.



in which p indicates the spread in droplet size. Substitution of this distribution function in equation 5.5. enables the theoretical turbidity spectrum to be calculated for different values of p. These calculations were mostly carried out with a computer. The turbidity spectra calculated from equation 5.5. for several different values of p are shown in fig. 5.3. (for $n_d/n_c = 1.05$) and fig. 5.4. (for $n_d/n_c = 1.10$).

Turbidity measurements and calculation of the specific area. The turbidity measurements were made with a Beckman DU spectrophotometer, which is readily adapted for this purpose and which has been used as such by for instance BATEMAN et al. (1959). The standard cuvette holder is replaced by one in which several diaphragms and a lens are placed, as shown in fig. 5.5., whereby the angle of acceptance is set at 1.5°.

Before measurement of their optical density the emulsions were diluted with an aqueous solution of about 0.1% non-ionic detergent (Brij 35) so that the optical density measured at 380 nm in a 0.5 cm cuvette was between 0.2 and 0.6. The optical density of emulsions diluted in this way was measured at 380, 420, 470, 530, 615, 725, 890 and 1150 nm. The refractive indices at these wavelengths were determined by the method described by WALSTRA (1965c) for the determination of the refractive indices of milk fat. For the 1:1 mixture of glycerol and water, the algebraic mean of the refractive indices was taken, with a small correction based on the difference between the refractive index at 589 nm calculated in this way and that measured at 589 nm. Emulsions were only diluted with glycerol when $\bar{x}_{32}$ was larger than about 10 µm. When dilution was applied, 25 ml of the emulsion already diluted with Brij solution was introduced into a 50 ml measuring flask and brought up to the mark with glycerol.

It is important that no flocculation should occur upon measurement of the optical density. This was checked with a microscope. Flocculation was always absent provided the emulsions were diluted with Brij 35. In fig. 5.6. the measured optical density has been plotted against the volume fraction Φ of the dispersed phase of a diluted emulsion. It can be seen that there is a linear relationship between optical density and Φ at a given wavelength, which implies that multiple scattering is absent and that no aggregation or dispersion occurs upon dilution.

The average droplet diameter $\bar{x}_{32}$ is determined graphically as follows.

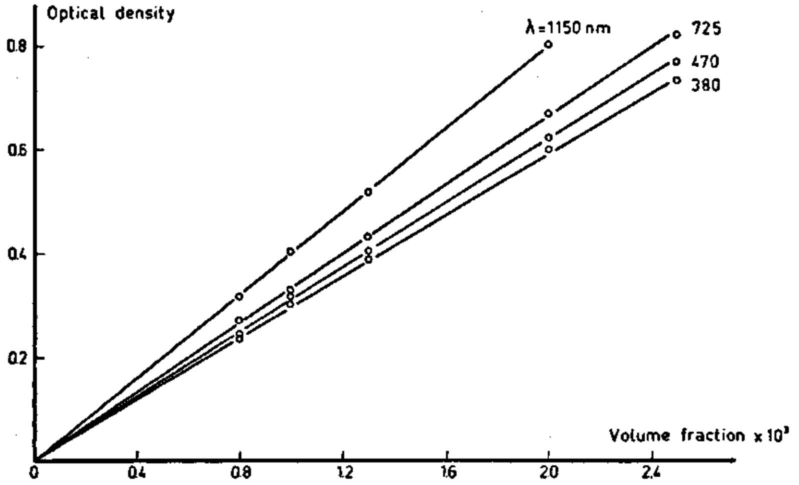


Fig. 5.6. Optical densities of dilute emulsions measured at different wavelengths in the modified Beckman DU spectrophotometer as a function of the volume fraction of the dispersed phase.

The value of Z is calculated from the measured optical density at each wavelength with equation 5.3. and plotted against log y, where y is defined by:

$$y = \frac{\bar{p}_{32}}{\bar{x}_{32}} = \frac{2\,\pi\,(n_d - n_c)}{\lambda} \qquad (5.7).$$

In fact, y is the conversion factor between the real average droplet diameter and the dimensionless droplet size parameter used throughout the calculation. One can now find $\bar{x}_{32}$ by shifting the experimental Z/log y curve until it coincides with one of the calculated theoretical Z/log $\bar{p}_{32}$ curves. The distance which the curve must be shifted then corresponds to log $\bar{x}_{32}$. Two experimental turbidity spectra are given in fig. 5.7., together with the three theoretical curves from fig. 5.3. Once log $\bar{x}_{32}$ has been read off, the specific interfacial area can be calculated from the relationship:

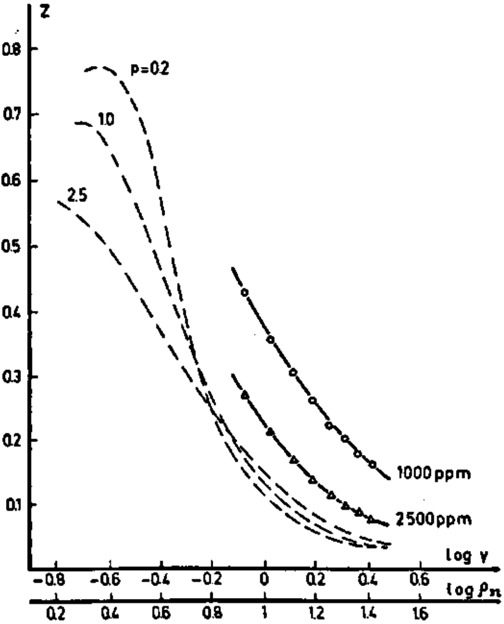
$$S = \frac{6\,V}{\bar{x}_{32}} \qquad (5.8.)$$

in which V is the known volume of the dispersed paraffin. The areas calculated in this way were found to be always reproducible within 3% for a given emulsion.

5.3.3. *Comparison between turbidity and Coulter counter measurements*

The average diameter $\bar{x}_{32}$ determined for different emulsions by the turbidity method has been compared with the value obtained by the Coulter counter measurements in fig. 5.8. There is close agreement between the two, although the

FIG. 5.7. Comparison between experimental turbidity spectra (Z against log y) for emulsions stabilized with PVA 16–88 and the theoretical spectra (Z against log ρ_{32}) for $n_d/n_c = 1.05$ (dashed lines).



average diameter found with the Coulter counter tends to be slightly higher. This is because droplets smaller than 2 μm cannot be counted with the Coulter counter. Thus, the estimated area and volume of the dispersed phase will be too low, the

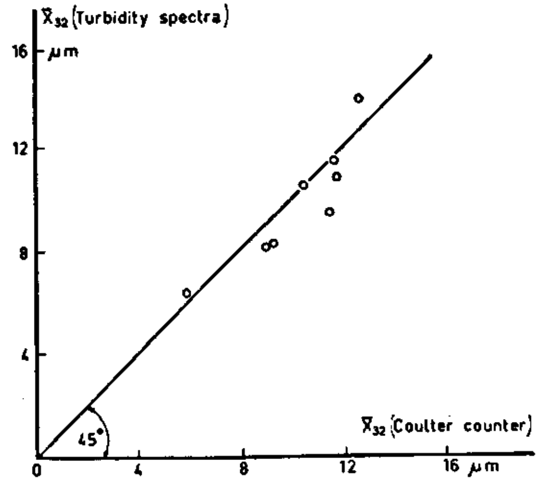


FIG. 5.8. Comparison of the mean droplet diameter $\bar{x}_{32}$ determined from (i) turbidity spectra and (ii) Coulter counter measurements.

error in the area being reltively larger than that in the volume (fig. 5.1.), hence causing

$$\bar{x}_{32} = \frac{\sum_i n_i x_i^3}{\sum_i n_i x_i^2}$$

to be too high.

WALSTRA et al. (1968, 1969a) also found goo agreement between the two methods both for milk fat emulsions and for paraffin-water emulsions. The turbidity method thus seems suitable for the determination of the specific area of an emulsion. Due to the rapidity with which the specific area can be determined, the method is ideally suited for routine analysis.

5.4. DETERMINATION OF THE ADSORPTION

The amount of PVA adsorbed at the interface of the emulsion was calculated from the amount added initially and the amount recovered in the aqueous phase. For the determination of PVA in the aqueous phase by the method described in 1.3.2., the paraffin must first be removed. The emulsion was therefore centrifuged for 30 minutes at about 3500 rev/min in a Homef table centrifuge. Samples were taken from the aqueous phase with a syringe. When the specific area of the emulsion was large, the aqueous phase was seldom sufficiently clear and it was therefore centrifuged again, this time for 30 minutes at about 20.000 rev/min in a Christ Universal ks III centrifuge.

From each emulsion two samples were centrifuged and the PVA concentration in the clear aqueous phase of each sample was determined three times. The reproducibility of the concentration determinations was found to be within 2%. To check whether centrifuging influenced the PVA concentration found, the concentration was also determined after creaming of the emulsion. No differences could be detected. This check was made on emulsions with low concentrations of PVA, for which the specific area is low and which settle out sufficiently quickly (within 24 hours). At high PVA concentrations the specific area was measured before and after centrifuging, whereby no difference could be found. It may therefore be concluded that centrifuging does not influence the adsorption determined, or at least does not cause noticable coalescence.

5.5. RESULTS AND DISCUSSION

With the knowledge of the specific area and the amount of PVA adsorbed, the amount adsorbed per unit area of interface can be calculated. An adsorption isotherm can now be generated by emulsifying at different PVA concentrations. One should however bear in mind that this adsorption isotherm may not be literally interpreted as such, for the interfacial area adapts itself during emulsification to the amount of PVA initially added. Moreover, the interface created depends on the manner of emulsification (6.3.3. and 6.4.1.). Besides, the adsorption is irreversible and one cannot therefore talk of an adsorption equilibrium, as is assumed for adsorption isotherm equations. The fact that the temperature rise during emulsification can differ by several degrees for the various emulsions did not effect the adsorption recorded per unit area, but it did have a marked influence on the specific interfacial area (6.4.3.). Thus the word isotherm in the literal sense is not wholly justifiable here.

Since for each emulsion the interfacial concentration is measured as a function of the steady-state concentration in the aqueous phase, we will continue to talk about an adsorption isotherm. Nevertheless, one should bear in mind what has been mentioned above. The steady-state concentration is in fact not the only independent variable determing the adsorption; the latter is also dependent on the conditions under which the emulsion is prepared, such as the volume fraction of paraffin and the way in which the PVA is added (6.3.3. and 6.4.1.). When however the emulsification conditions remain the same, the emulsions are highly reproducible, the same adsorption per unit area being found at a given steady-state concentration.

5.5.1. *Effect of the acetate content*

The adsorption isotherms for different types of PVA are given in figs. 5.9.–5.11. The adsorption was not found to increase with increasing acetate content, i.e. increasing hydrophobicity of the PVA. This is in contrast to what would be expected. However the more hydrophobic character of PVA 88 is manifest by a greater emulsifying capacity (figs. 5.12. and 5.13)., although the higher acetate content of PVA 25–76.5 with respect to PVA 25–88 appears to have no additional effect (fig. 5.11.). The degree of adsorption is found to be determined more by the molecular weight than by the acetate content.

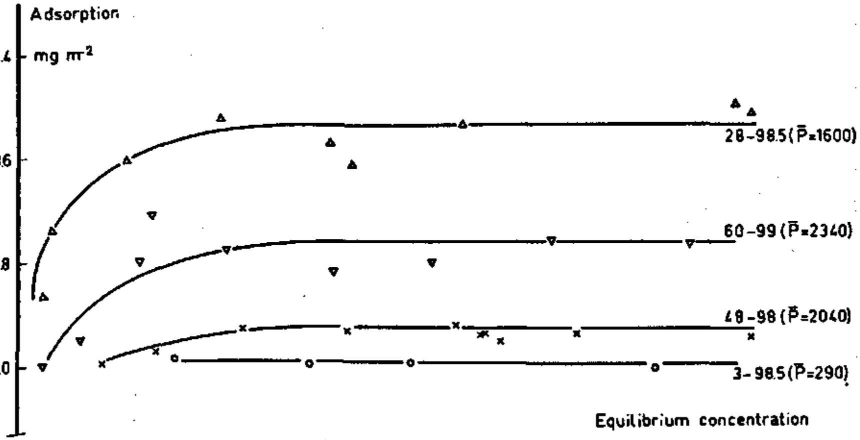


FIG. 5.9. Isotherms for the adsorption of PVA containing about 2% acetate groups at the interface of paraffin-water emulsions.

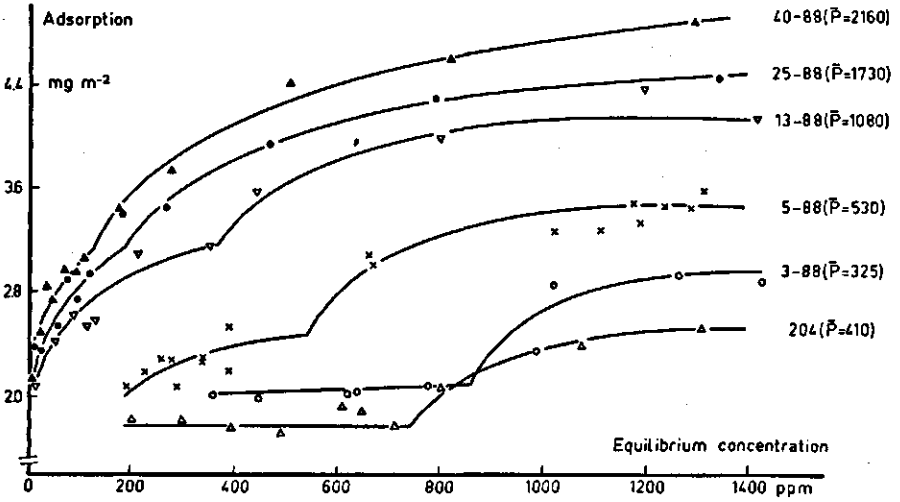


FIG. 5.10. Isotherms for the adsorption of PVA containing about 12% acetate groups at the interface of paraffin-water emulsions.

At an acetate content of ≥ 12%, the adsorption isotherms are of a clearly discontinuous character. At low acetate contents (fig. 5.9.), there is no discontinuity and in all cases adsorption tends to a plateau value at low concentrations. These isotherms thus have a high-affinity character. It should be mentioned that no measurements could be made at very low concentrations because stable emulsions can seldom be prepared. The discontinuities in the adsorption iso-

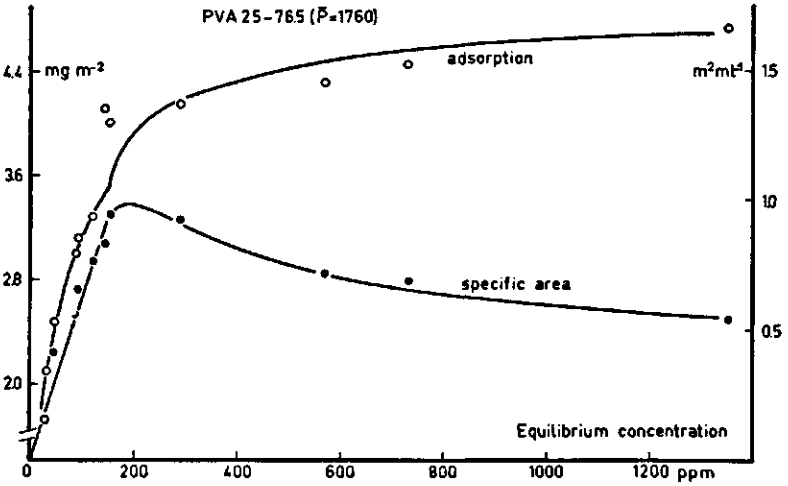


Fig. 5.11. Isotherm for the adsorption of PVA 25-76.5 at the interface of paraffin-water emulsions and the specific areas of these emulsions.

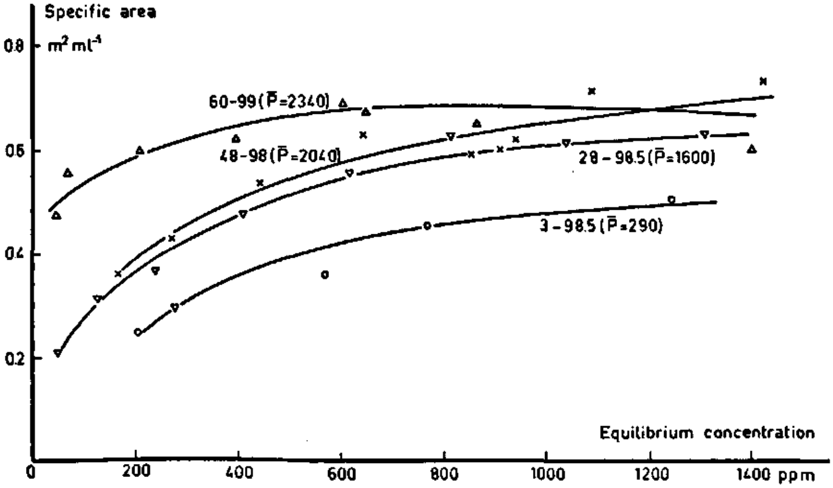


FIG. 5.12. Specific areas of emulsions stabilized by PVA containing about 2% acetate groups.

therms for acetate contents $\geqslant$ 12% (figs. 5.10. and 5.11.) correspond to the discontinuities in the plots of specific area against concentration. These plots are shown in fig. 5.13. for PVA 88 samples and in fig. 5.11. for PVA 25–76.5. It is noteworthly that, above a certain critical PVA concentration, the interfacial area created decreases with increasing concentration, contrast to what would be expected. This irregularity is not found for PVA 98 samples (fig. 5.12.)

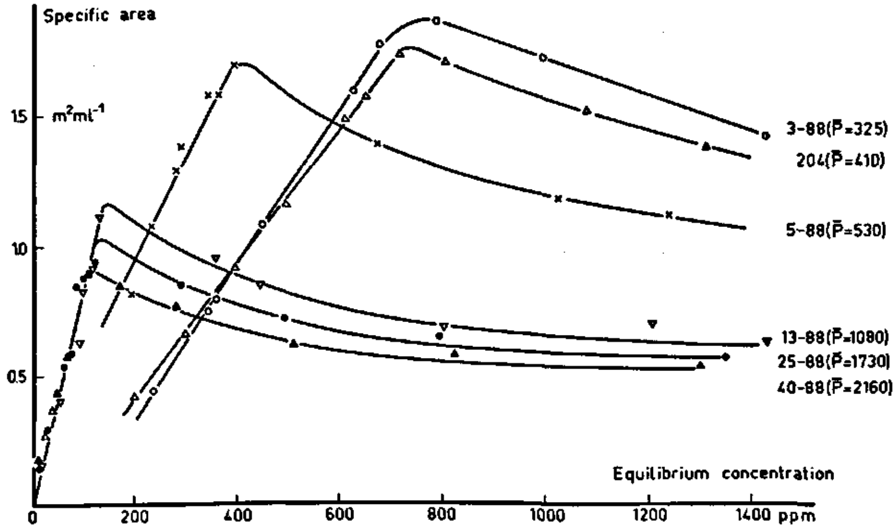


FIG. 5.13. Specific areas of emulsions stabilized by PVA containing about 12% acetate groups.

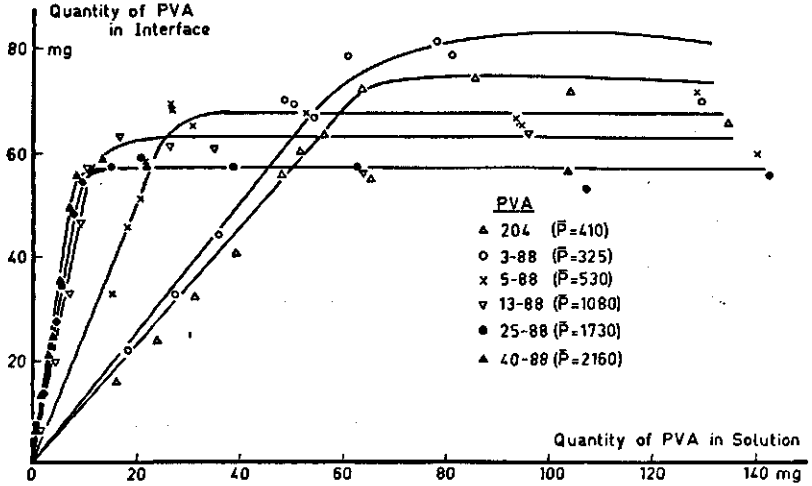


FIG. 5.14. Distribution of PVA containing about 12% acetate groups between the interface and the continuous phase in emulsions of 20 ml paraffin in 80 ml water.

for which the specific area tends to a plateau value with increasing concentration.

The distribution of PVA between the interface and the 80 ml of aqueous phase, which is plotted in fig. 5.14. for the different PVA 88 samples, shows that above the same critical concentration, at which the area began to decrease, the amount of PVA in the interface remains approximately constant. A constant amount of PVA in the interface and a decreasing specific area imply that the amount adsorbed per unit area increases. The additional increase in the adsorption per unit area above a certain critical concentration is therefore correlated with a drop in the specific area created. The question remains as to whether the decrease in area with increasing c_p is the cause, of or a consequence of the discontinuity in the adsorption isotherm. This question, which concerns the emulsifying capacity of PVA, will be returned to in chapter 6.

5.5.2. *Effect of molecular weight*

For both PVA 88 and PVA 98 samples, with the exception of PVA 28–98.5, the adsorption was found to increase with increasing molecular weight. This can be explained by a thicker layer in the interface for the polymers of higher molecular weight, as a result of the polymer loops being longer. According to the theory of HOEVE (1966), the adsorption should increase proportionally to $M^{1/2}$ at least in a Θ-solvent; this has been found experimentally for polystyrene on a solid metal surface by STROMBERG (1965). For the PVA 88 series, maximum adsorption is also approximately proportional to $M^{1/2}$ (fig. 5.10.), in accordance with HOEVE's theory. For the PVA 98 series, the dependence of the adsorption on the molecular weight is less regular. This is probably caused by slight variations in acetate content, and/or a non-random distribution of the acetate groups, which can have a relatively large effect at an acetate content of about 2%.

That PVA 88 samples of higher molecular weight have more affinity for the paraffin-water interface is apparent from figs. 5.10. and 5.14. The distribution of the polymer between the interface and the aqueous phase shifts in favour of the interface at higher molecular weight. The ability of high-molecular-weight PVA 88 to form stable emulsions at lower concentrations is related to this. The discontinuity in the adsorption isotherms for PVA 88 shifts to lower steady-state concentrations with increasing molecular weight. At high molecular weights the kink in the adsorption isotherms is less prominent, but nevertheless present (6.3.3.).

When the adsorption data are plotted according to the linearized Langmuir equation, two straight-line sections are obtained with a kink corresponding to the discontinuity in the adsorption isotherm. Even though the premises valid for Langmuir adsorption are not met by polymer adsorption, the latter often fits the Langmuir isotherm closely (PATAT, 1964), as is the case here.

5.5.3. *Quantitative comparison with interfacial tension measurements*

When comparing the adsorption of PVA on the emulsion interface with its adsorption on the paraffin-water interface in the interfacial tension experiments, one should bear in mind the difference in the way in which the interface is formed. This may account for differences in both the amount of polymer adsorbed and the conformation of the adsorbed polymer. The order of magnitude of the measured plateau value of the adsorption, i.e. about 2.0–4.5 mg m^{-2}, suggests, however, that the adsorption is not markedly influenced by the emulsification process. The same order of magnitude of adsorption was recorded for PVA on silver iodide (FLEER and LYKLEMA, 1968).

The adsorption data determined by the emulsification technique, and the

TABLE 5.1. Summary of adsorption data determined with the emulsification technique and of the values of some parameter calculated from the data.

1	2	3	4	5	6	7	8	9	10
PVA sample	$\bar{P}$	adsorption (mg m^{-2})	a_0 (Å^2)	ν	$\nu/P \times 100$ (%)	$z_{0\cdot1}$ (Å)	$\bar{h}$ (Å)	πh^2 (Å^2)	$\frac{\pi h^2}{a_0}$
3 – 98.5	290	2.1	1030	34	11.7	79	29	2640	2.6
28 – 98.5	1600	3.9	3070	102	6.4	147	67	14100	4.6
48 – 98	2040	2.3	6550	218	11.7	87	75	17700	2.7
60 – 99	2340	3.0	5800	194	8.3	113	81	20600	3.6
240	410	2.5	1330	44	10.8	85	34	3630	2.7
3 – 88	325	2.9	920	31	9.5	98	30	2830	3.1
5 – 88	530	3.5	1230	41	7.7	118	38	4540	3.7
13 – 88	1080	4.1	2150	72	6.7	138	55	9500	4.3
25 – 88	1730	4.5	3140	105	6.1	152	69	15000	4.8
40 – 88	2160	4.9	3600	120	5.6	166	78	19100	5.3
25 – 76.5	1760	4.7	3360	112	6.4	159	70	15400	4.6

values of some parameters derived from these data, are summarized in table 5.1. The maximum adsorption of the PVA samples listed in column 1 are given in column 3. Column 2 gives the average degree of polymerization for each sample. From the adsorption one can calculate the area, a_0, occupied by one polymer molecule at the interface. When a_0 is compared with the area per polymer molecule calculated from the interfacial tension measurements with the GIBBS equation (table 2.1., column 5), it is found to be a factor of about 10 to 20 higher. If, however, the area calculated with the GIBBS equation is taken as being that occupied by a statistical chain element, this would suggest that about 10 to 20 statistical chain elements per molecule are adsorbed on the emulsion interface.

From the area per segment, about 30 Å², calculated from the monolayer experiments (4.4.1.), one can calculate the maximum number of segments (v) per molecule which can be adsorbed in the interface. This number is given in column 5 of table 5.1., and the percentage of adsorbed segments in column 6. The low proportion of adsorbed segments, usually < 10%, agrees with the results of the interfacial tension measurements for high c_p. If we compare the values in column 5 with the number of adsorbed segments calculated from the interfacial tension measurements with the aid of the FRISCH-SIMHA equation (table 2.1., column 7) there is fairly close agreement for PVA samples of low molecular weight. At higher molecular weights, as the percentage of adsorbed segments decreases, the value of v in column 5, which is calculated from the direct measurement of adsorption, becomes a factor of 5 higher. Molecular weight was in fact found to have hardly influence on the lowering of the interfacial tension. The increasing adsorption with increasing molecular weight is primarily due to the longer loops of the polymer. It seems likely that the reduction in interfacial tension is hardly influenced by segments far removed from the interface, which explains the lack of effect of the molecular weight on γ. The reduction in γ will be primarily determined by the segments in, or in the direct neighbourhood of, the interface, which possibly accounts for the fact that γ decreases linearly with log c_p over a large concentration range. With increasing concentration the polymer layer will become thicker as a result of conformational changes, but the number of segments in the immediate neighbourhood of the interface, which primarily determines $\Delta\gamma$, will hardly change any more. This probably explains why the agreement between the direct and indirect adsorption measurements at high c_p is better for low molucular weight than for high molecular weight.

The exponential distribution of the segments in terms of their distance from the interface, a consequence of the theory of HOEVE (1965), and the measured adsorption, enable the thickness of the polymer layer to be estimated. In fact the exponential distribution is valid only beyond the initial layer, but the distribution of segments over the whole layer is assumed to be exponential for the purpose of this estimation. Thus,

$$n_z = n_0 \exp(-qz) \tag{5.9.}$$

in which:

n_z = number of segments at distance z

n_0 = number of segments in the interface

q = a constant.

Integration of equation 5.9. from 0 to ∞ gives the total number of segments adsorbed per unit area of interface in terms of n_0 and q. From the measured adsorption and the known average weight of monomer, one can calculate the total number of segments in the layer, n_{total}, and hence q. For the thickness ($z_{0\cdot 1}$) at which the number of segments is 0.1 of that at the interface itself, the following is found to be valid:

$$z_{0\cdot 1} = 2.3\,\frac{n_{\text{total}}}{n_0} \qquad (5.10).$$

If we assume the initial layer to be 4 Å thick and the area per segment to be 30 Å^2, we can calculate $z_{0\cdot 1}$. The results are given in column 7 of table 5.1. The order of magnitude of the calculated thickness is in agreement with thickness of a PVA layer adsorbed on silver iodide determined by viscometry (FLEER, 1970). The value calculated from equation 5.10. depends in fact on the assumptions made and is proportional to the assumed thickness and area of the segments in the inital layer. By way of comparison the radius of gyration, $\bar{h}$, of the polymer molecule in solution is given in column 8. This has been calculated from the relationship (TANFORD, 1961):

$$\bar{h} = c\sqrt{6\,\bar{P}}$$

in which c = a polymer constant. The value of c is quoted as 4.09 by MATSUO and INAGAKI (1962) and is assumed to be independent of the acetate content. From the radius of gyration one can calculate the projected area, $\pi\bar{h}^2$, of the polymer in solution (column 9), which is always larger than a_0 (see column 10). From this it follows that the polymer at the interface is compressed laterally, the more so the higher the molecular weight.

From the dimensions of the adsorbed polymer molecule calculated from adsorption data, one can conclude that the percentage of segments adsorbed per molecule is only small and that the major part is found in the loops penetrating the aqueous phase. This picture is in agreement, at least qualitatively, with that derived from the interfacial tension measurements.

5.6. CONCLUSIONS

For the determination of the adsorption of PVA on the paraffin-water interface, the direct technique of emulsification proved to be well suited. For each emulsion, both the adsorption and the specific interfacial area were measured, since the latter is dependent on the concentration of emulsifier. The turbidity method is particularly suitable for the routine determination of the specific area. This method has been adapted to PVA-stabilized paraffin-water emulsions, and found to give results in agreement with Coulter counter measurements.

The measured amounts of adsorbed polymer per unit area proved to be little dependent on the acetate content but markedly dependent on the molecular weight of the polymer. A higher level of adsorption for the higher molecular weights suggests a thicker layer of polymer at the interface. This is realised by the polymer loops, sticking out further into the aqueous phase.

The acetate content does, however, clearly influence the specific area of the emulsion, which is larger for an acetate content of $\geqslant 12\%$ than for one of about 2%. At a low acetate content the specific area gradually increases with increasing polymer concentration until a plateau level is reached. At acetate contents $\geqslant 12\%$ the specific area first rises sharply with increasing concentration, but then, above a certain critical concentration, starts to decrease. This critical concentration increases with decreasing molecular weight. The adsorption isotherms are characterized by a discontinuity at the same concentration.

6. CHARACTERISTICS OF PVA-STABILIZED EMULSIONS AND INVESTIGATIONS INTO THE MECHANISM OF THEIR FORMATION

6.1. INTRODUCTION

Emulsion stability has been the subject of many investigations, which are extensively reviewed by BECHER (1965) and SHERMAN (1968). Most of the investigations, however, have concerned emulsions stabilized by low-molecular-weight ionic or non-ionic emulsifiers. Little fundamental research has been done on the emulsifying capacities of polymers and the properties of polymer-stabilized emulsions. The irreversible nature of polymer adsorption makes the system much more complicated than emulsions stabilized by low-molecular weight emulsifiers, and consequently the experimental results lend themselves less readily to theoretical interpretation. A short review of the research, much of it applied, into the properties of polymers as stabilizers has been compiled by KITCHENER and MUSSELWHITE (1968); it appears that emulsions stabilized by polymers are usually very stable to coalescene. This high stability is attributed by many workers to the mechanical properties of the polymer film at the interface.

The measurements, described in the previous chapter, on the specific area of emulsions and the corresponding interfacial occupation stimulated a closer study of the emulsifying capacity of PVA, particularly since it was found that under certain circumstances the degree of dispersion decreased with increasing polymer concentration. It was hoped that such a study would provide more insight into the mode of operation of polymers as emulsifiers.

Little can be found in the literature about the emulsifying capacity of PVA, although it is often applied as a stabilizer in emulsion-polymerization (TSUNEMITSU and SHOHATA, 1968; REYNOLDS and GULBEKIAN, 1968). BIEHN and ERNSBERGER (1948) studied the stability to coalscence of PVA-stabilized emulsions of various oils and concluded that a high molecular weight and a low degree of hydrolysis increased the effectiveness of PVA as a stabilizer. The PVA concentration in this case was always $> 0.4\%$. MAHROUS and LEMBERGER (1968) compared the stabilizing effects of various water-soluble polymers on emulsions of 2% hexadecane in water, stabilized by 0.09% Aerosol OT. PVA was found to have a marked stabilizing effect, which was ascribed to the formation of a strongly hydrated film around the droplets. The degree of hydrolysis and molecular weight of the PVA, however, were not specified.

More work has been done on the effect of PVA as an emulsifier in emulsion-polymerization, although this work is mostly in the applied field (COKER, 1957; O'DONNELL et al., 1958; DUNN and TAYLOR, 1965; GROMOV et al., 1967; ALBRAMZON et al., 1969). Of particular interest is the comparison by REYNOLDS and GULBEKIAN (1968) of the results of O'DONNELL's group and DUNN's group, both of whom measured the rate of polymerization of vinyl acetate as a function of the concentration of PVA-88, which served as an emulsifier of the monomer. DUNN and TAYLOR found that the rate of polymerisation decreased with increasing PVA concentration, whereas O'DONNELL's group found just the reverse. The two groups, however, worked with different concentration ranges, which may explain the apparent disagreement. A high degree of dispersion increases the rate of polymerization (COKER, 1957). The decrease in the rate of polymerization with increasing PVA concentrations up to 0.36%, as found by DUNN and TAYLOR, thus suggest a corresponding decrease in the degree of dispersion of the monomer. This is in accordance with the results for PVA-stabilized emulsion of paraffin in water (fig. 5.13.). O'DONNELL, on the other hand, worked with PVA concentrations of > 0.75%, at which concentrations the area of paraffin-water emulsions also began to increase again.

ABRAMZON (1969) found that the stability of PVA-stabilized styrene droplets, as a function of the concentration of sulphate ions added to the PVA solution, went through a maximum at a given PVA concentration. On account of the strong salting-out effect which sulphate has on PVA, the effective concentration of the latter drops as the sulphate concentration rises. Thus, in this case, the anomalous stability characteristics can also be attributed to the anomalous behaviour of the dispersing power of PVA as a function of concentration. In agreement with the above, the specific area of PVA-stabilized paraffin-water emulsions also goes through a maximum as the amount of sulphate added to the PVA solution increases.

As far as I know, the only reported case of a reduction in the degree of dispersion of an emulsion with increasing polymer concentration is that of mineral oil emulsions stabilized by Xanthan gum (ARAUJO, 1967). No explanation was offered for this behaviour. We found that the specific area of emulsions stabilized with casein also went through a maximum as the casein concentration increased. In fact, the emulsifying capacity of casein closely resembled that of the more hydrophobic PVA.

Since PVA-stabilized emulsions are extremely stable to coalescence and since the degree of dispersion does not noticably vary with time, it seems likely that the mode of formation of the emulsion is the determining factor for the degree of dispersion. It is therefore important to study the mechanism of emulsifion formation.

6.2. KINETIC MODEL FOR THE FORMATION OF EMULSIONS AND THEIR STABILIZATION BY PVA

The different factors which are of importance in the emulsification process have been summarized recently by GOPAL (1968). Little attention appears to have been paid to the rôle of the emulsifier which is assumed to influence the dispersion of the emulsion droplets only on account of its effect on the interfacial tension. VAN DEN TEMPEL (1960) has shown, however, that it is not so much the absolute value of γ which is important, but rather gradients in γ which arise during the emulsification process. For it is these gradients which determine the flow pattern during emulsification and which thus help to determine the degree of dispersion. VAN DEN TEMPEL (1965) has discussed the dynamic properties of the interface in relation to the stability of the interfacial film. It turns out that, in the stretching of the film, its elasticity and the interfacial dilational viscosity should be taken into account, particularly at high rates of shear and low levels of interfacial occupation. These are just the conditions which prevail during emulsification. The dispersion of the emulsion droplets is therefore not simply correlated with the interfacial tension, to which the created area of emulsion was previously considered as being inversely proportional (GOPAL, 1968). With the paraffin-water-PVA system an increase in c_p always causes a decrease in γ, but, in the case of PVA 88, this is not necessarily accompanied by an increase in emulsion area. This shows that the interfacial tension is not or at least not the only determining factor for dispersion. In addition, the molecular weight was found to have hardly any effect on γ (2.4.2.), but had a marked effect on the emulsifying capacity (5.5.2.). In trying to find an explanation of the anomalous behaviour of the emulsion area with respect to the concentration of emulsifier, the following experimental facts should be taken into account (5.5.):

1. The maximum in the plot of the specific area of the emulsion against c_p is present only for acetate contents of $\geqslant 12\%$, and not for an acetate content of about 2% (fig. 5.12. and 5.13.).
2. The steady-state value of c_p at which the specific area begins to drop is lower for samples of higher molecular weight (fig. 5.13.).
3. The maxima in the specific areas correspond to discontinuities in the adsorption isotherms (fig. 5.10.); beyond the maxima, the total amount of polymer adsorbed at the interface remains approximately constant (fig. 5.14.).
4. Up to the polymer concentration corresponding to the maximum in surface area there is a linear relation between the amount in the interface and that in the aqueous phase. This resembles a distribution equilibrium. For high molecular weights, the distribution shifts in favour of the interface (fig. 5.14.).
5. With PVA 88, the maximum degree of dispersion is larger for low-molecular-weight polymer, while for PVA 98 the reverse is true.
6. The emulsions are very stable to coalescence.

The points listed here can provide more insight into the problem as to which factors are important during emulsion formation. It may be noted that points 2 to 5 inclusive are closely interrelated.

The fact that PVA with a low acetate content (about 2%) behaves differently from PVA with a higher acetate content ($\geqslant 12\%$) can be due to at least two factors. The first of these is the difference in flexibility of the polymer molecule, which is partly determined by the nature of the solvent. In this context the rise in temperature to between 50° and 57°C during emulsification may be important. As the temperature rises, water becomes a relatively poorer solvent for PVA 88 (which flocculates above 65°C), whereas PVA 98 becomes more soluble. The second factor is the higher affinity for the paraffin interface of PVA 88, which, on account of its higher acetate content, is more hydrophobic. Both factors will influence the rheological behaviour of the interface and hence the formation of the emulsion.

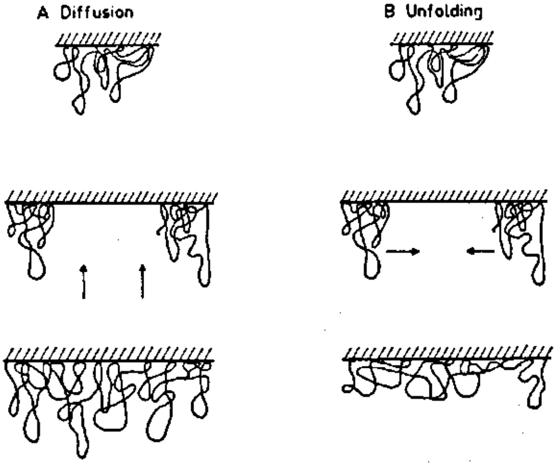
It is worth noting that anomalous behaviour in the interfacial tension measurements (chapter 2 to 4) was associated with a low acetate content, whereas in emulsion formation anomalous behaviour is the hall-mark of the higher acetate contents. The discontinuous nature of the γ-log c_p curves was explained by the kinetics governing the establishment of the interface. Kinetics may also be important in the formation of the interfacial film during emulsification, although the time-scale will be much shorter (shear rate $\geqslant 10^4 \text{ s}^{-1}$). Comparison with the γ-log c_p measurements, however, is difficult because the concentration range of PVA with the emulsions is always higher than that at which the discontinuity was found in the γ-log c_p curve for the PVA 98 samples. At lower concentrations no stable emulsions could be formed.

That the explanation for the measured drop in specific area at higher concentrations should be sought in the mechanism of formation of the emulsion can also be deduced from the fact that the emulsions, once prepared, are extremely stable to coalescence, as illustrated by the following observations. (a) The interfacial area measured after several days was the same as that measured a few minutes after emulsification. (b) A sample of emulsion between a microscopic slide and a cover glass was dried so that the individual droplets were forced together to give a foam-like structure in which the individual films were preserved; when water was added the droplets segregated again without any coalescence. (c) The paraffin in emulsions ($\Phi = 0.20$) stabilized with 0.1 or 0.2% PVA did not separate out at all in the course of 2½ years, irrespective of the acetate content of the PVA.

If points 2 to 5 are to be explained, a closer look will have to be taken at the mechanism of emulsion formation since the processes occuring during emulsification apparently determine the properties of the emulsion obtained. During emulsification new droplets, and hence new interfaces, are continually being formed. If a newly formed droplet is to survive as an individual droplet, it has to be stabilized against coalescence. Each newly formed interface will therefore have to be occupied sufficiently rapidly by the stabilizer, in this case the polymer. Dynamic equilibrium is reached when the rates of formation and coalescence are equal. The interfacial area eventually obtained will therefore depend, amongst other things, on how quickly and how well the newly created interface can be occupied so that coalescence is prevented.

From point 3 it follows that the adsorption per unit area must rise quite abruptly at concentrations above that at which the maximum area is found. There are tow possible explanations for this. The first is that coalescence is enhanced at increasing concentrations, and that the same amount of polymer (fig. 5.14.), which is irreversibly adsorbed at the interface, has to be distributed over a smaller area. The second is that the mechanism of occupying newly created interface changes with increasing concentration, such that the adsorption increases while the specific area remains low. In the first case, coalescence is the cause of a higher adsorption per unit area, while in the second case the increased adsorption, as a consequence of the change in mechanism, is the cause of lower dispersion and/or increased coalescence during emulsification,

FIG. 6.1. Two possible mechanisms of by which a polymer can occupy a newly created interface.



and hence of a lower area. It is clear that the correct choice between the two alternative explanations depends on a distinction being made between cause and effect.

An argument in favour of the first explanation is that the increase in adsorption can be completely accounted for by the decrease in the area, since the total amount in the interface remains constant (fig. 5.14). The question remains, though, why coalescence should increase above a certain concentration. It seems unlikely that a higher concentration in the aqueous phase should be the direct determining factor in the breaking of the film.

If the mechanism of occupation of the interface is the determining factor, the rate at which occupation occurs is important.Two mechanisms are possible, namely diffusion and unfolding, both of which are represented highly schematically in fig. 6.1. With supply by diffusion (fig. 6.1. A) the concentration in the aqueous phase should be sufficiently high for the interface to be occupied in the short time before coalescence can occur. It is not only the polymer concentration which is important, but also the amount of polymer which is situated between two newly-formed, still uncovered droplets (VAN DEN TEMPEL, 1960). When the concentration, or amount, is too low for the interface to be covered sufficiently quickly, unfolding of the polymer constitutes an alternative possible means of achieving this (fig. 6.1.B). The readiness of the polymer molecule to unfold will depend on its flexibility. When an interface is stretched, an interfacial tension gradient is established which causes adsorbed molecules to be pulled into a flatter conformation. This flatter conformation must then be responsible for reducing the change of coalescence and hence for preserving the enlarged interfacial area. This increased stability to coalescence is possibly the result of a stronger interaction in the interface (more segments per molecule adsorbed). If, during emulsification, the supply by diffusion becomes insufficient on account of the drop in polymer concentration, the unfolding mechanism can play an important role.

The time required for the interface to be occupied by diffusion at the bulk concentration corresponding to the kink in the adsorption isotherm can be estimated from equation 3.1. The estimated time is in order-of-magnitude agreement with the shear rate during emulsification. This time is determined not only by the diffusion rate but probably also by the amount of PVA between two newly formed droplets. For sufficient PVA to be supplied at the given concentration, the diffusion distance must be approximately equal to the average distance between the droplets at $\Phi = 0.20$.

Points 2 to 5 may thus be attributable to the rheological properties of the interface, which in turn will depend on the level of interfacial occupation and the molecular weight. These properties include the speed of unfolding as compared to rate of diffusion which will influence the point of transformation from the one adsorption mechanism to the other. The apparent distribution equilibrium between the interface and the liquid (point 4) is possibly a result of the capture of the PVA in the freshly created interface, the chance of which will increase with increases in the interfacial area, the concentration in the aqueous phase, and the degree of polymerization.

The picture outlined for the mechanism of interfacial occupation can broadly explain the emulsification behaviour and the corresponding measured adsorption (5.5.). For more insight to be gained into the mechanism of emulsion formation, various tentative experiments have been done both on emulsions and on the dynamic properties of the interface.

6.3. EMULSIONS WITH DIFFERENT VOLUME FRACTIONS OF PARAFFIN

If the mechanism described above is a true representation of emulsion formation, the volume fraction of the paraffin may influence the degree of dispersion, for increasing the volume fraction of paraffin increases the chance of coalescence during emulsification and hence reduces the time in which diffusion can occur. This will cause a shift in the concentration at which the occupation of the newly created interface reverts from one mechanism to the other, i.e. from unfolding to diffusion.

6.3.1. *Experimental*

Emulsions were prepared as described in 5.2. except that the volume fraction of paraffin was now varied between 0.025 and 0.40. To $(100-x)$ ml of PVA solution was added x ml paraffin, so that the total volume in all cases was 100 ml. The amount of PVA in the aqueous phase was always chosen so that the amount per ml paraffin was constant with variable Φ. The specific areas of the emulsions were determined by the turbidity method (5.3.2.), while the adsorption was determined by the method described in 5.4.

6.3.2. *Specific area as a function of the volume fraction*

The degree of dispersion as a function of the volume fraction Φ for different amounts of polymer per ml paraffin is shown in figs. 6.2. and 6.3. for PVA 3–88

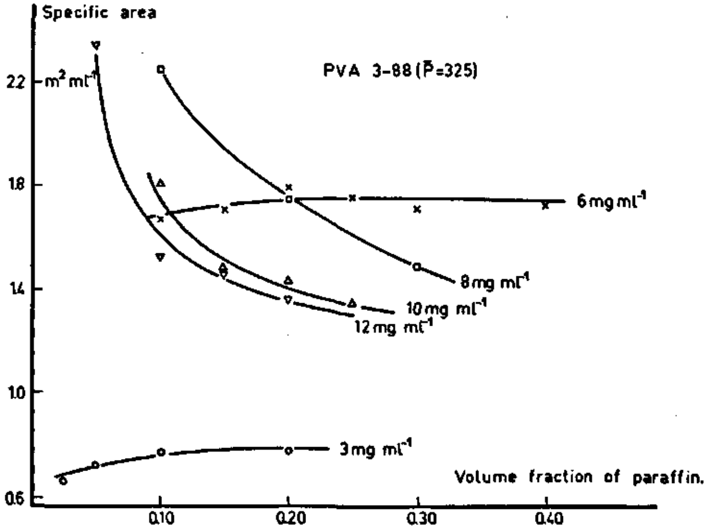


FIG. 6.2. Specific areas of emulsions stabilized by PVA 3-88 as a function of the volume fraction of paraffin for different amounts of PVA per ml paraffin.

and 40–88 respectively. The degree of dispersion achieved is almost independent of Φ at low levels of polymer supply, but at higher levels of polymer supply it decreases markedly as Φ increases, particularly for small Φ. This means that, when the supply is low, the polymer film has time to form itself in such a way

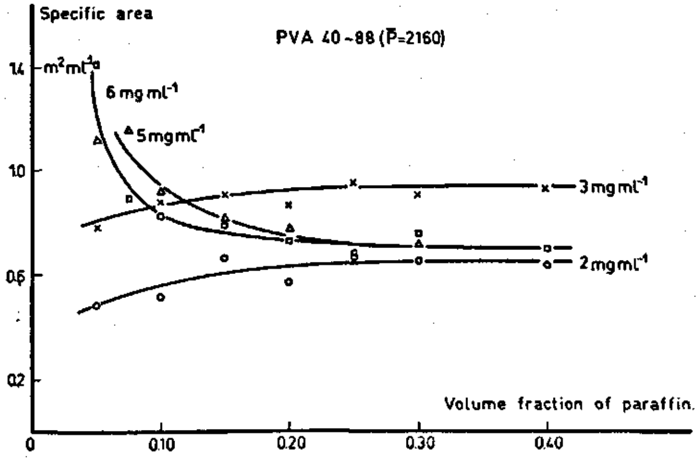


FIG. 6.3. Specific areas of emulsions stabilized by PVA 40-88 as a function of the volume fraction by paraffin for different amounts of PVA per ml paraffin.

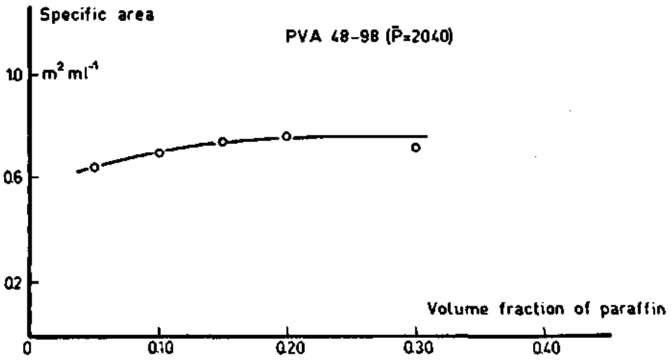


FIG. 6.4. Specific areas of emulsions stabilized by PVA 48-98 as a function of the volume fraction of paraffin for a PVA level of 10 mg per ml paraffin.

that an increased chance of collision does not result in increased coalescence. From the model outlined in 6.2. it follows that at a low level of supply the newly formed interface can be occupied by unfolding (fig. 6.1.B). The conformation of the polymer will then be flat, irrespective of Φ, which probably explains why the degree of dispersion is independent of Φ.

The unfolding mechanism was assumed to apply to the region in which the area increased proportionally to the steady-state concentration, in other words prior to the maximum in the area (fig. 5.13.). The emulsions for $\Phi = 0.20$ at low levels of polymer (3 and 6 mg ml^{-1} paraffin for PVA 3–88 and 2 and 3 mg ml^{-1} paraffin for PVA 40–88) are indeed found to lie in this region. For higher levels of polymer per ml paraffin, the steady-state concentration is higher than that at which the maximum in the area occurs. If, at such high concentrations, diffusion is responsible for the interfacial occupation, the degree of dispersion may be expected to decrease with increasing Φ. For, on account of the increased change of collision, the time available for the occupation of the interface will be the limiting factor. The behaviour of the degree of dispersion as a function of Φ at different levels of polymer availability is thus in complete agreement with the picture outlined in 6.2. By way of comparison, the degree of dispersion of an emulsion stabilized with PVA 48–98 is shown in fig. 6.4. as a function of Φ for a high level of polymer availability. It appears that at this level of polymer the degree of dispersion is almost independent of Φ, which suggests an unfolding mechanism. This shows that PVA 98 can unfold more quickly at the interface than PVA 88, which was already deduced from the interfacial tension measurements (2.4.1.). The question remains though as to why the area of emulsions stabilized with PVA 48–98 does not increase proportionally to the concentration as was the case with PVA 88. The difference may well be due to the difference in affinity for the interface. This affinity helps to determine the rheological behaviour of the interface and may be responsible for the total emulsion area remaining low. Once prepared, the emulsions stabilized with PVA 98 are very stable to coalescence; this is possibly a consequence of the marked ageing of the film (4.4.3.) whereby a stiff film is formed.

Little has been published about the effect of the size of the volume fraction on the average droplet diameter. SHOTTON and DAVIS (1968) found that the average droplet diameter of paraffin emulsions was almost independent of Φ when lauric acid was the stabilizer but decreased markedly with increasing Φ when potassium arabinate, a macro-molecule, was the stabilizer. Also interesting in this context is the investigation by INKLAAR and FORTUIN (1969) of the emulsifying capacities of proteins. Separation of the oil was taken as a measure of the emulsifier capacity. The amount of oil separated was found to decrease as the volume fraction of the oil increased, for a given level of protein. Thus, here as well, it appears that a lower level of emulsifier per ml oil gives a more stable emulsion. No explanation was given for this, although the results are in accordance with the emulsifying behaviour of PVA with a high acetate content. We carried out a number of tentative experiments with casein as stabilizer and found that the specific area of the paraffin-water emulsions, which was also dependent on pH and electrolyte concentration, showed the same dependence on Φ as did emulsions stabilized with PVA 88. At low amounts of stabilizer per ml paraffin the specific area was independent of Φ, but it decreased with increasing Φ at higher levels of stabilizer.

6.3.3. *Adsorption isotherms for different volume fractions*

If the adsorption mechanism, as described above, depends on the volume fraction, it is likely that the amount adsorbed at the interface will also depend on Φ. Adsorption isotherms were therefore determined at two volume fractions for both PVA 3–88 and PVA 40–88. These are shown in figs. 6.5. and 6.6. respectively.

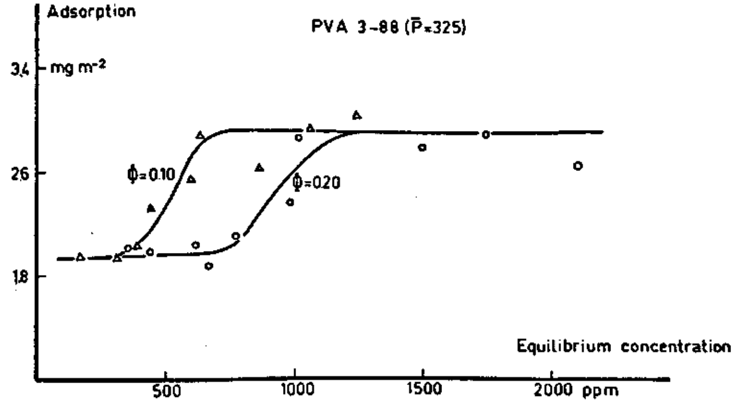


FIG. 6.5. Influence of the volume fraction Φ of paraffin on the adsorption isotherm of PVA 3–88.

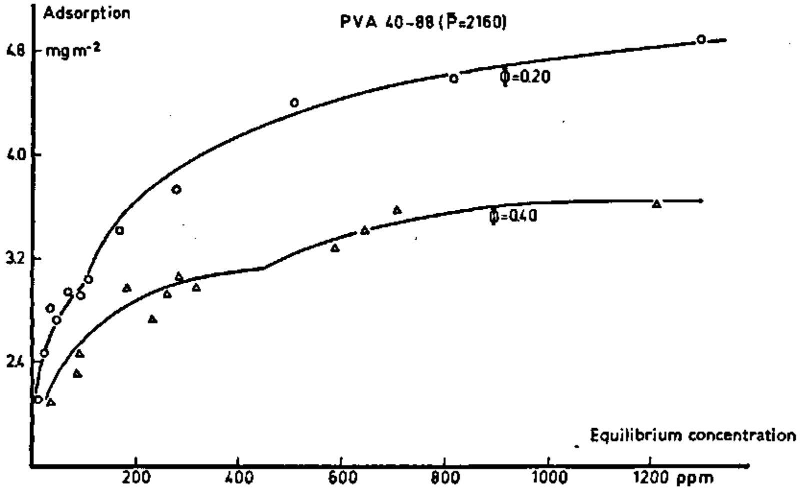


FIG. 6.6. Influence of the volume fraction Φ of paraffin on the adsorption isotherm of PVA 40–88.

It is clear from these isotherms that the adsorption also depends on Φ. The discontinuity in the isotherms shifts to lower steady-state concentrations for lower values of Φ. The occurrence of the discontinuity is again found to be correlated with the maximum in specific area. At the concentration at which the adsorption starts to increase after the discontinuity, the specific area starts to decrease, as is shown in figs. 6.7. and 6.8. The shift of the discontinuity to lower steady-sate concentrations for lower Φ indicates that diffusion is the determining factor down to a smaller concentration. This may be a consequence

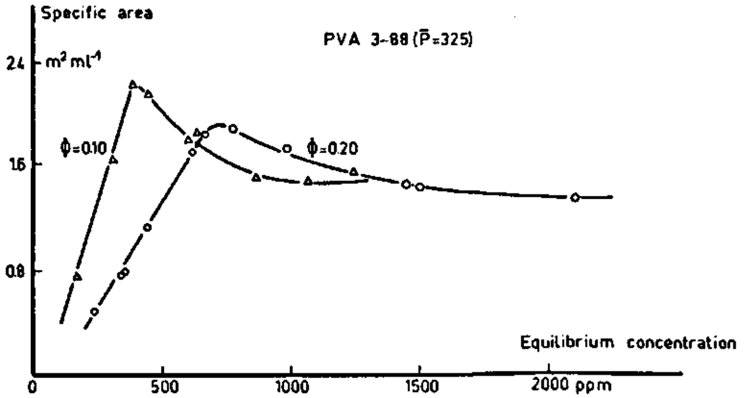


FIG. 6.7. Influence of the volume fraction Φ of paraffin on the specific areas of emulsions stabilized by PVA 3–88 at different concentrations of the latter.

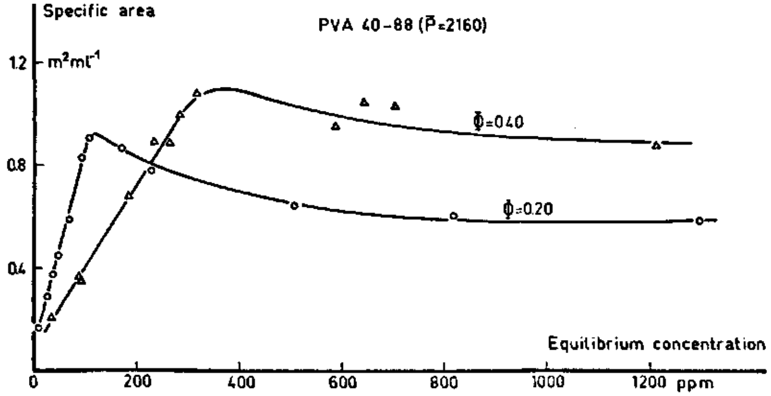


FIG. 6.8. Influence of the volume fraction Φ of paraffin on the specific area of emulsions stabilized by PVA 40–88 at different concentrations of the latter.

of the smaller change of collison, which means that more time is available for adsorption by diffusion. It is, however, also possible that the amount of PVA between the emulsion droplets is the determining factor at high Φ; this amount will decrease as Φ is increased, because the average distance between the droplets then decreases. These experiments again underline the importance of the kinetics of interfacial occupation in emulsification.

If one compares the effect of Φ on the adsorption and degree of dispersion for PVA 3–88 and PVA 40–88, it is clear that the molecular weight plays a role. With PVA 3–88 the maximum adsorption before and after the discontinuity is the same for both volume fractions; this is not the case with PVA 40–88. The maximum degree of dispersion as a function of Φ is also different for emulsions stabilized with the two types of PVA. For PVA 3–88 maximum dispersion is larger for lower Φ, while for PVA 40–88 this is just the opposite. This may be because of the different regions of Φ for which the experiments were performed (compare figs. 6.2. and 6.3.).

6.4. SOME FACTORS INFLUENCING THE DEGREE OF DISPERSION

6.4.1. *Renewed emulsification after addition of extra PVA*

Since, with PVA 88, the emulsion area decreases above a certain polymer concentration, the question arises as to whether the area of an emulsion can be reduced by renewed emulsification after addition of extra PVA. If the degree of dispersion is determined solely by the steady-state concentration of PVA, then emulsions with an area just before the maximum should show a decrease in area.

Two standard emulsions (Φ=0.20) were prepared in portions of 100 ml with PVA 3–88 as stabilizer at levels of 6.0 mg ml^{-1} paraffin (emulsion A)

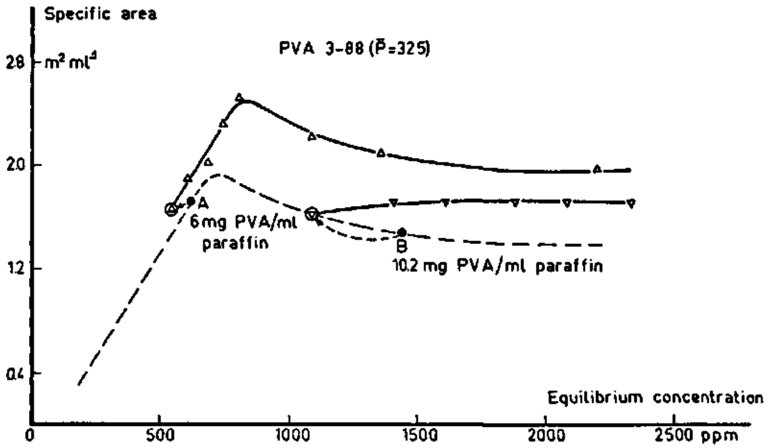


FIG. 6.9. Influence of a second emulsification on the specific area. To 90 ml of emulsions A and B ($\Phi = 0.20$), 10 ml of PVA solution of various concentrations was added and the mixture was emulsified again for one minute.

and 10.2 mg ml^{-1} paraffin (emulsion B). After 18 hours, 10 ml amounts of PVA solutions of different concentrations were added to 90 ml portions of the standard emulsions, and the mixtures were emulsified for 1 minute. The specific areas and the adsorptions were determined for the new emulsions. The age of the standard emulsions had no influence on the area of the new emulsions. The degree of dispersion after the second emulsification is shown in fig. 6.9. as a function of the steady-state PVA concentration. The dashed line indicates the specific area obtained after a single emulsification at $\Phi = 0.20$ (fig. 6.7.), and includes the areas for the standard emulsions A and B. The circled points on the new curves are the values for the blanks, i.e. the specific areas obtained by emulsifying 90 ml of the standard emulsions with 10 ml of water for 1 minute. The shift of these points relative to the original values after just one emulsification is partially due to the dilution which lowers the volume of the paraffin fraction.

The effect on the specific areas of the second emulsification after addition of extra polymer is markedly different for emulsions A and B. The curve for emulsion A is similar to that for the standard emulsion, whereas the specific area of emulsion B is almost independent of the extra amount of PVA added. This means that not only the supply mechanism, as described in 6.2., but also the structure of the polymer film already present (which is different for emulsions A and B), influences the degree of dispersion. For emulsion A the maximum specific area achieved when the polymer is added in two portions in 30% higher than when it is added in one go. This implies that the level of polymer per ml paraffin should be kept low if a large specific area is to be obtained by emulsification. The adsorption before the maximum in specific area, even when emulsion A was re-emulsified with extra PVA, was 2.0 mg m^{-2}, while after the maximum an adsorption of 2.8 mg m^{-2} was measured. The maximum in area corresponded to a polymer level of 6–7 mg ml^{-1} paraffin for the standard emulsion A but to a level of between 9.6 and 10.0 mg ml^{-1} paraffin when the PVA was added in two lots. This increase of about 30% corresponds with the increase in the maximum specific area. Since the area of emulsion A does not decrease when extra polymer is added, it seems that the degree of dispersion is dependent not only on the steady-state concentration but also on the order of addition. This again stresses the irreversible nature of the polymer adsorption.

6.4.2. *Polydispersity of the PVA*

The question remains as to whether the rate of diffusion or the total amount of polymer between two newly formed interfaces becomes the determining factor at decreasing polymer concentrations. To investigate this, emulsions ($\Phi = 0.20$) were prepared with mixtures of PVA 3–88 and PVA 40–88 as emulsifier. The PVA 3–88 and PVA 40–88 were mixed either in equal proportions by weight (50/50 w/w) or in approximately equal gram molecular proportions (10/90 w/w). The specific areas of the resulting emulsions are plotted in fig. 6.10. as a function of the total steady-state concentration of PVA. The figure also includes the curves of 100% PVA 3–88 and 100% PVA 40–88 (dashed lines). For the determination of PVA in the aqueous phase, the relative proportions of the two PVA types after emulsification have been taken to equal those before emulsification. This assumption is necessary because the calibration curve for PVA (1.3.2.) is dependent on molecular weight. If one of the PVA types has been preferentially adsorbed, then the error in the determined steady-state concentration will be no more than about 5%.

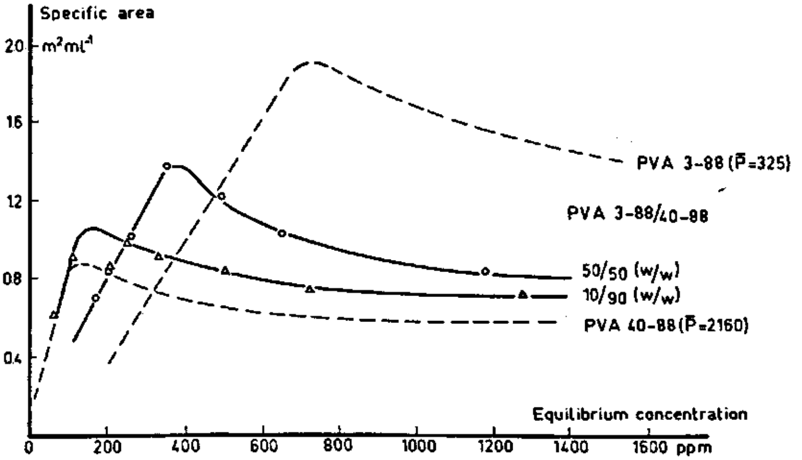


FIG. 6.10. The specific area of emulsions stabilized by high- and low-molecular weight PVA 88 and by mixtures of the two.

Fig. 6.10. clearly illustrates that the specific area generated is determined not by the number of gram molecules but by the weight of PVA, i.e. by the concentration of segments. This may well mean that the occupation by diffusion, at concentrations above that corresponding to the maximum area, is determined by the amount of polymer situated between two newly formed interfaces rather than by the rate of diffusion.

6.4.3. *Temperature reached during emulsification*

When the reproducibility of the emulsification method was being tested, it was found that the higher the temperature reached after emulsification (usually between 50 and 57 °C) the higher the specific area was. For this effect to be studied in more detail, a number of otherwise identical paraffin-water-PVA systems were cooled to different extents before emulsification, so that their initial temperatures, and hence their final temperatures, differed considerably. This was done for an emulsion ($\Phi = 0.20$) stabilized with PVA 3–88 at two concentrations, one each side of the area maximum. The specific area of the resulting emulsions is plotted as a function of the final temperature in fig. 6.11. The area was found to be proportional to the final temperature. The rate of increase in specific area with increasing temperature was the same for both concentrations, namely $3 \times 10^{-2} \mathrm{m}^2 \mathrm{ml}^{-1} {}^{\circ}\mathrm{C}^{-1}$. The temperature dependence is therefore independent of the way in which the interface is occupied, which is different for the two concentrations.

The temperature dependence of the specific area can be explained by the temperature dependence of the ratio of the viscosity in the continuous phase (η_c) to the viscosity in the disperse phase (η_d). The relationship between viscosity

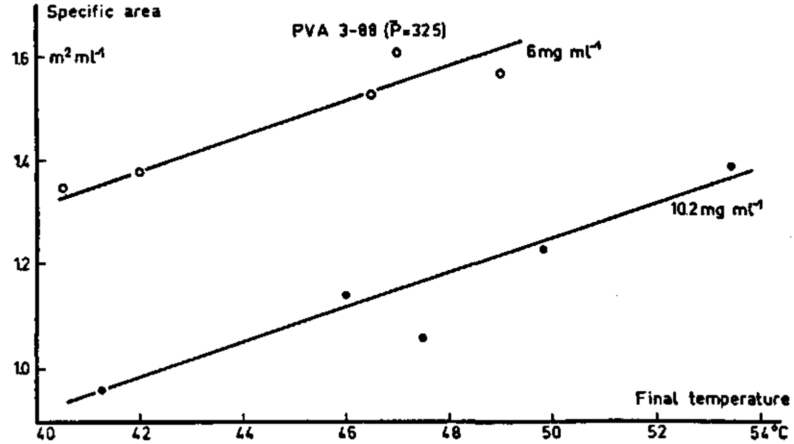


FIG. 6.11. Influence of the temperature reached at the end on the emulsification on the specific area of the emulsions for two different amounts of PVA per ml paraffin.

(η) and the temperature (T) can be expressed by the Andrade equation (EIRICH, 1956):

$$\eta = A \exp\left(\frac{B}{T}\right) \tag{6.1.}$$

in which A and B are constant for a certain substance. For the ratio of the viscosities in the continuous and disperse phases, therefore, the following relationship is valid:

$$\frac{\eta_c}{\eta_d} = \frac{A_c}{A_d} \exp\left(\frac{B_c - B_d}{T}\right) \tag{6.2.}$$

which, for low values of $\left(\frac{B_c - B_d}{T}\right)$, reduces to:

$$\eta_c/\eta_d = \frac{A_c}{A_d}\left(1 + \frac{B_c - B_d}{T}\right) \tag{6.3.}$$

The viscosity of the continuous phase can be taken as being equal to that of water at these low concentrations ($< 0.2\%$) and for low molecular weight. The viscosity of water as a function of the temperature was taken from the International Critical tables. The viscosity of paraffin was measured as a function of the temperature with a Haake Rotovisko rotation viscometer. This enabled the specific area to be plotted as a function of the viscosity ratio η_c/η_d, with temperature as the variable parameter (fig. 6.12.). The ratio η_c/η_d increases

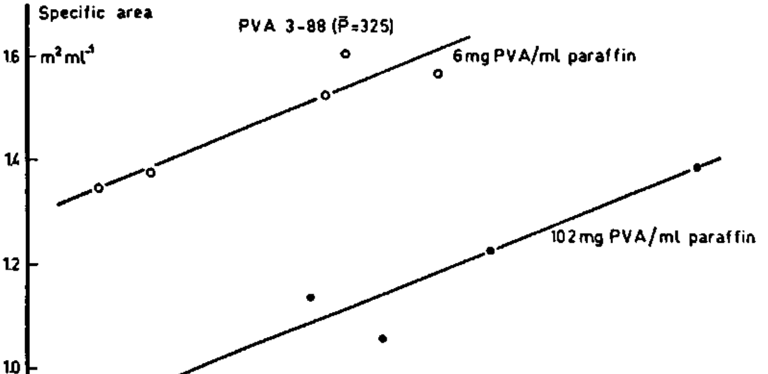


FIG. 6.12. Dependence of the specific emulsion area on the viscosity ratio η_c/η_d, changes of which were due to temperature changes.

with increasing temperature because $B_d > B_c$ (equation 6.3.). We see therefore that a possible increase in the viscosity of the PVA solution at higher PVA concentrations cannot explain the reduction in the specific area, since the area increases with increasing η_c/η_d. In the literature, the specific area has been quoted as both increasing and decreasing with increasing η_c/η_d (GOPAL, 1968).

6.5. STABILITY CHARACTERISTICS OF EMULSIONS PREPARED BY SHAKING

In order to check whether the emulsification technique could be responsible for the anomalous emulsifying behaviour of PVA 88 at higher concentrations, the following experiment was carried out. To each of a series of cylinders, 25 ml of PVA solution was added, the concentration of which increased from one cylinder to the next. A number of glass beads were put on the bottom of each cylinder. The cylinders were topped up with heptane and the stoppers were inserted so that no air was enclosed. The cylinders were shaken vigorously by hand, and the amount of heptane which separated out was assessed. Since no air was enclosed, the glass beads were required to ensure good mixing. On account of its much lower viscosity, heptane was used rather than paraffin, in order to facilitate mixing. The results are shown in fig. 6.13. and 6.14. for PVA 3–88 and PVA 40–88 respectively. The concentrations of PVA 3–88 (fig. 6.13.) were, from left to right, 10, 40, 70, 100, 250, 500, 750, 1000, 1250, 1500, 2000, 2500, 4000 and 6000 ppm. The concentrations of PVA 40–88

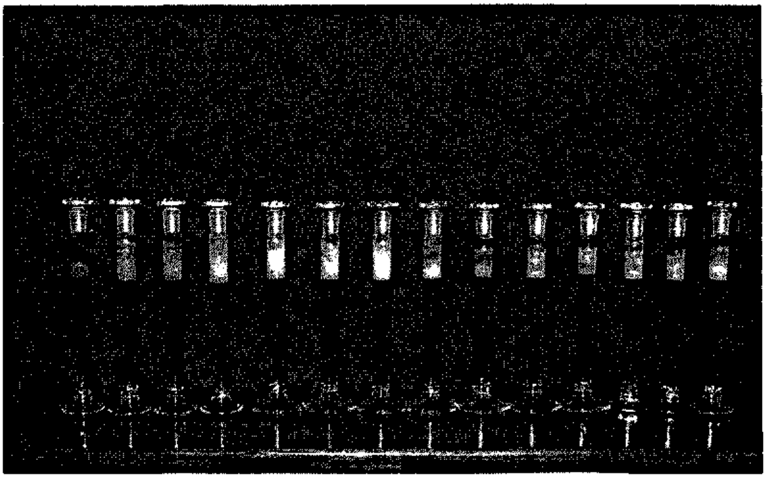


FIG. 6.13. Effect of PVA 3–88 concentration on the stability of heptane-water emulsions prepared by shaking. Above the aqueous phase is the creamed emulsion layer, from which the oil phase has partially separated out. PVA concentrations from left to right: 10, 40, 70, 100, 250, 500, 750, 1000, 1250, 1500, 2000, 2500, 4000 and 6000 ppm.

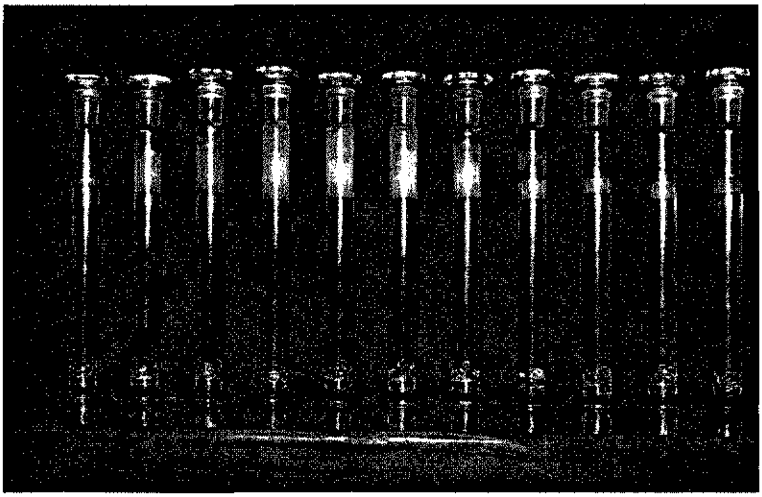


FIG. 6.14. Effect of PVA 40–88 concentration on the stability of heptane-water emulsions prepared by shaking. Above the aqueous phase is the creamed emulsion layer, from which the oil phase has partially separated out. PVA concentrations from left to right: 10, 40, 70, 100, 250, 500, 750, 1000, 1250, 1500 and 2000.

(fig. 6.14.) were identical with the first 11 of the 3–88 series. The photographs were taken about 16 hours after preparation of the emulsions. The vapour bubble which can be seen under the stopper was not present upon emulsification and is due to slight evaporation of heptane during standing.

The variation of the emulsification capacity with concentration agrees qualitatively with that observed on emulsions prepared with the Ultra Turrax (fig. 5.13.). As before, the emulsifying capacity decreases above a certain concentration. This decrease is less clear for PVA 3–88 than for PVA 40–88, probably because a lower molecular weight gives a greater specific area (fig. 5.13.). The concentration at which the separating out of heptane is a minimum is not noticably different, which is in contrast to what might be expected in view of the positions of the maxima in the emulsion area plots in fig. 5.13. The experiment clearly shows, however, that the decrease in emulsifying capacity of the polymer with increasing concentration is independent of the emulsification method, and is a property of the polymer used as emulsifier. Shake experiments carried out in the presence of air gave the same result, showing that this has no effect on the outcome.

6.6. DYNAMIC SURFACE AND INTERFACIAL TENSION MEASUREMENTS

A few tentative experiments have been carried out to see whether the degree of dispersion was correlated with the dynamic properties of the interface, for both the interfacial dilational viscosity (η_s) and the elasticity modulus (ε) can influence the stability of thin films (VAN DEN TEMPEL, 1965; KITCHENER and MUSSELWHITE, 1968) and hence of the emulsion. The elasticity modulus of the interface is defined by:

$$\varepsilon = \frac{\mathrm{d}\gamma}{\mathrm{d}\ln A} \tag{6.4.}$$

and the interfacial dilational viscosity by

$$\eta_s = \frac{\triangle\gamma}{\mathrm{d}\ln A\mathrm{d}/t} \tag{6.5.}$$

in which $\triangle\gamma$ is the increase in interfacial tension for a relative increase, d ln A, of the interface and d ln A/dt gives the speed at which the interface is expanded. A high elasticity and a high dilational viscosity usually enhance the film stability and hence the foaming and emulsifying capacity.

6.6.1. MEASUREMENT OF THE DIFFERENCE IN SURFACE TENSION BETWEEN AN EXPANDED AND A COMPRESSED SURFACE

Since the emulsifying capacity of PVA 88 as a function of concentration goes through a maximum, it is worthwhile measuring the difference in surface tension ($\triangle\gamma$) between the expanded and compressed surface of a PVA solution. For this difference gives an indication of the interfacial dilational viscosity and should go through a minimum with increasing concentration if a low dilational viscosity is indeed correlated with a higher emulsifying capacity.

PVA solution (about 1600 ml) was pumped round in the apparatus sketched in fig. 6.15. in the direction shown with a constant velocity of 26 ml sec.$^{-1}$ The apparatus is analogous to that used by PADDAY (1957) to measure dynamic surface tensions. At 1 (area about 25 cm^2) the surface is continually expanded, while at 2 (area about 115 cm^2) the surface is continually compressed. The surface tension at both 1 and 2 was measured as a function of concentration

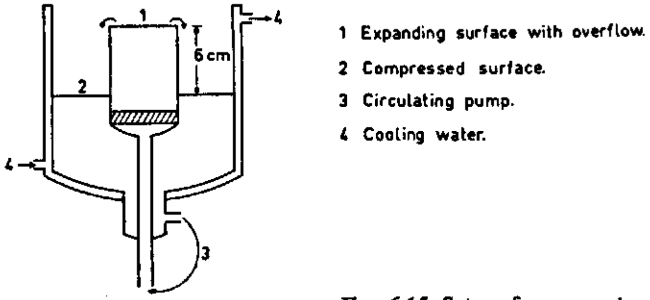


FIG. 6.15. Set-up for measuring dynamic surface tensions.

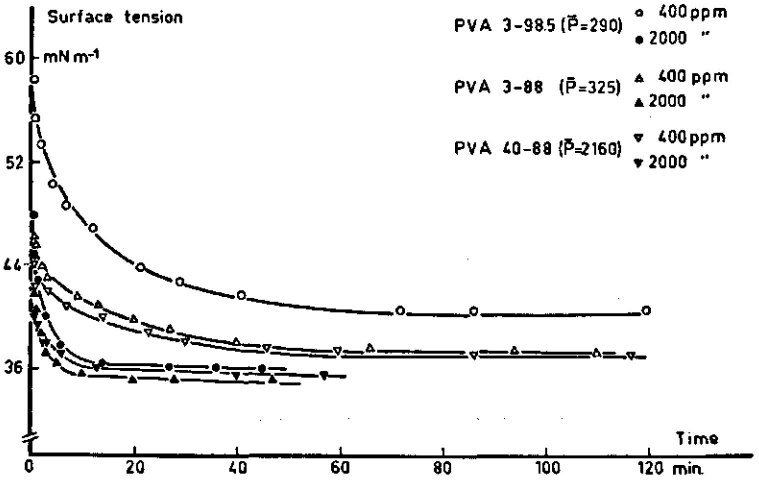


FIG. 6.16. Time-dependence of the surface tension of different PVA solutions, the surfaces of which were subject to continual compression.

at 20°C for PVA 3–98.5, PVA 3–88 and PVA 40–88. The reproducibility of a duplicate measurement was about 0.3 mN m^{-1} at 1 and about 1.0 mN m^{-1} at 2. Sucking off the compressed surface several times had hardly any effect on the result.

The surface tension of the compressed surface was, in contrast to that of the expanded surface, dependent on time, as is shown in fig. 6.16. for the three

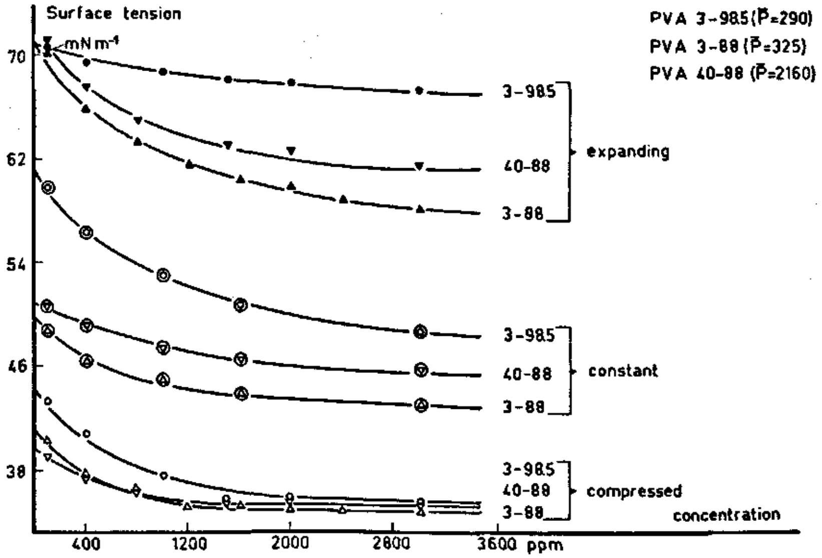


FIG. 6.17. A comparison between the surface tensions of expanding, compressed and constant surfaces for different PVA solutions.

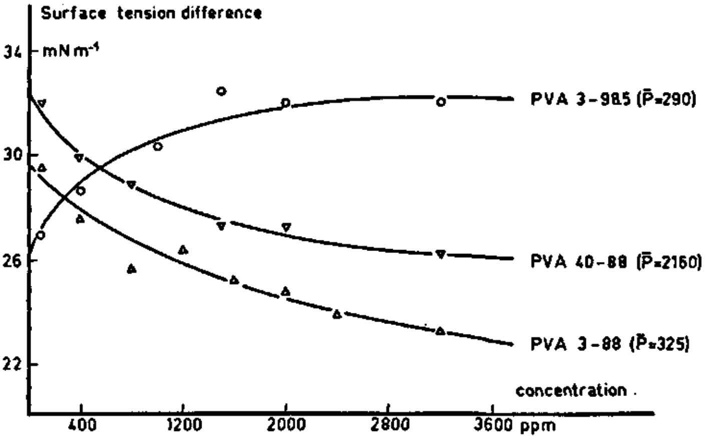


Fig. 6.18. Difference in surface tension between compressed and expanding surfaces for different PVA solutions.

types of PVA. Fig. 6.17. shows the steady-state values of the surface tension of the expanded and compressed surfaces as a function of concentration and, in addition, the surface tension of the same solutions in the steady state. In fig. 6.18. the difference between the surface tension of the compressed and expanded surfaces is plotted as a function of the concentration. As may be seen, there is no minimum. At the concentrations at which emulsions were prepared, though, $\Delta\gamma$ increases in the order 3–88, 40–88 and 3–98.5, which is also the order of decreasing emulsifying capacity. Here again, a marked difference is found between the surface acttvity of the PVA 88 and PVA 98 samples. The differences in $\Delta\gamma$ appear to be determined primarily by the surface tension measured on the expanded surface. It is, however, difficult to interpret the data, particularly their relation to emulsifying capacity, because the frequency with which the surface is expanded and compressed is very much lower than that of the emulsification process.

6.6.2. LONGITUDINAL WAVE MEASUREMENTS WITH PVA MONOLAYERS

To get an idea about the size of the elasticity modulus of the interface, and the effect of the acetate content of the PVA on it, some measurements were made with longitudinal waves (LUCASSEN, 1968) at the Unilever Research Laboratory, Vlaardingen. The elasticity modulus is plotted as a function of the wave frequency in fig. 6.19. It is found that the elasticity modulus of PVA 3–98.5 in the frequency range studied is higher than that of PVA 3–88 but, unlike the latter, is independent of the frequency. It is thus quite possible that at the higher frequencies prevalent during emulsification, the elasticity of 3–88 is higher than that of 3–98.5, which would indeed be expected in view of the higher emulsifying capacity of PVA 3–88. It is interesting to note that there is hardly

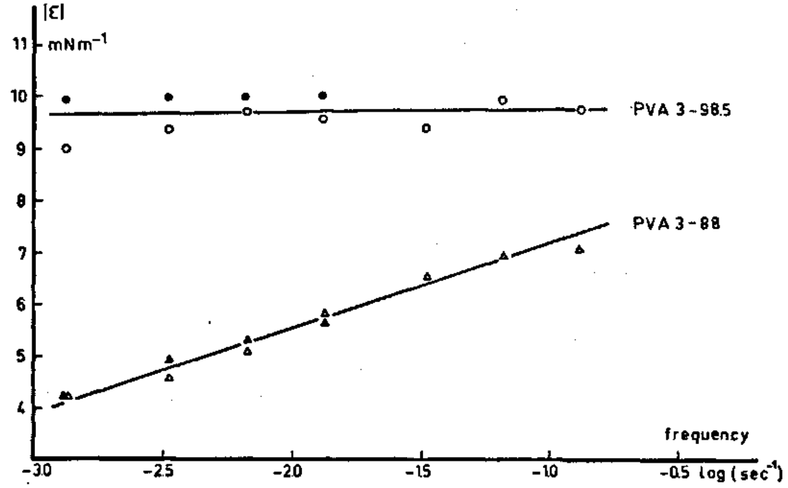


FIG. 6.19. *Surface dilational modulus determined from longitudinal wave measurements as a* function of frequency for PVA 3–98.5 and PVA 3–88, adsorbed from solution (400 ppm) at air-water (○, △) and paraffin-water (▲, ●) interfaces.

any difference between the elasticity of the polymer monolayer at the air/water interface and that at the paraffin/water interface, which shows that the dynamic interfacial properties of the polymer are independent of the upper phase.

The measured elasticity of the adsorbed polymer layers is surprisingly low compared with that measured for low-molecular-weight monolayers (LUCASSEN, 1968), which may well be an indication of the flexible nature of the polymer at the interface. For the flexibility of the polymer permits those segments, which are situated in loops close to the interface, to be adsorbed upon expansion of the interface and desorbed upon compression. Thus $\Delta\gamma$ will be low upon compression and expansion, and hence ε will be low as well. It seems likely that such dynamic interfacial measurements can give more insight into the emulsifying mechanism of PVA, and it may be advisable to extend the investigation in this direction.

6.7. CONCLUSIONS

Measurement of the degree of dispersion of PVA-stabilized emulsions as a function of the volume fraction Φ showed that, for PVA 88, the properties of the adsorbed polymer layer at high concentrations are markedly different from those at low concentrations. A model is described with which the discontinuity of the plots of degree of dispersion against concentration for the PVA 88 samples can be explained in terms of the kinetics of the formation of the interface. When the availability of polymer is low the newly created interface can be occupied by unfolding, which gives a relative flat polymer conformation at the interface. At high concentrations the supply by diffusion will be sufficiently rapid to affect occupation, with the result that the adsorbed polymer layer will be thicker and of a different structure. A flatter conformation corresponds with a greater stability to coalescence. A greater emulsion area can therefore be generated if the concentration of the emulsifier is kept low. This can be achieved by stepwise addition of the emulsifier to the oil and not the other way round. Experiments in which emulsions were prepared by vigorous manual shaking showed that the anomalous emulsifying behaviour of PVA 88 was not affected by the emulsification technique. It is not yet entirely clear what is the reason behind the difference in emulsifying behaviour of PVA 88 and PVA 98.

The increase in the specific area with an increase in the temperature reached during emulsification can be explained by the increase in the ratio of the viscosity of the continuous phase to that of the disperse phase. The tentative dynamic interfacial experiments show that there is a marked difference between the interfacial activity of the PVA 88 and that of PVA 98. It is, however, difficult to correlate the results with the emulsifying capacity, because the frequency during the emulsification process is very much higher.

SUMMARY

The adsorption of polyvinylalcohol (PVA) on the paraffin-water interface has been studied by interfacial tension measurements and by direct measurement of the adsorption with emulsions. The aim of the study was to provide more insight into the factors which influence the adsorption of polymers at phase interfaces. The interfacial properties of polymers, some of which find application as adhesives, flocculating agents and emulsion stabilizers, are of great practical importance. This helps to explain why much fundamental research, both theoretical and experimental, has been performed in recent years on polymer adsorption. Only a small proportion of this research, however, has been devoted to the adsorption of polymers at liquid-liquid interfaces, and so this was chosen as the subject for our investigation. To this end, the interface of a well defined model system has been studied by several different techniques.

The interfacial tension was measured with the static Wilhelmy plate method as a function of the concentration of PVA (0.1–4000 ppm) and time (up to 30 h) for PVA samples differing in degree of hydrolysis, molecular weight and origin. Experiments were also done in a Langmuir trough with spread and adsorbed PVA monolayers at the paraffin-water interface. Interpretation of the interfacial tension measurements in terms of polymer adsorption is complicated by the irreversible nature of the latter. The irreversibility of polymer adsorption can be deduced from the fact that the measured interfacial tension depends not only on the concentration of PVA in the aqueous phase but also on the history of the interface. As a result, the Gibbs law of adsorption cannot be applied without further preface to polymers.

Characteristic differences were noted between the interfacial activities of PVA of different degrees of hydrolysis. The discontinuity found in the plots of interfacial tension (γ) against the logarithm of polymer concentration (c_p) for PVA with a low content of acetate groups (about 2%) was absent from the corresponding plots for PVA with a higher acetate content ($\geqslant$ 12%). The discontinuous nature of the former γ-log c_p curves was explained in terms of kinetic factors, namely the relative rates of diffusion and unfolding of the polymer, which determine how the interface is occupied. Differences in the mechanism of interfacial occupation will be reflected by differences in the configuration of the adsorbed polymer molecules. This picture was confirmed by the time-dependence measurements.

The molecular weight of the PVA was found to have no obvious effect on the interfacial tension, whereas the adsorption measured directly on the emulsion interface clearly increased with increasing molecular weight. One may conclude therefore that there is no well-defined relationship between the reduction in interfacial tension and the amount of polymer adsorbed. In this respect, the behaviour of polymer contrasts with that of low-molecular-weight surfactants.

In the adsorption experiments with emulsions, the specific area of each emulsion was determined by measurement of the turbidity. The degree of dispersion went through a maximum with increasing PVA concentration when the acetate content of the latter was $\geqslant 12\%$. This maximum corresponded to a discontinuity in the adsorption isotherm. The concentration at which the maximum was situated decreased with increasing molecular weight and with decreasing volume fractions of paraffin. An explanation for this was again sought in terms of kinetic factors influencing the formation of the stabilizing polymer layer during emulsification.

The properties of the polymer layer of the emulsions were markedly different, depending on whether the emulsion had been prepared with a polymer concentration below or above that corresponding to the maximum specific area. The emulsion area was large when the amount of polymer per ml paraffin was kept low. A number of tentative experiments were done to enable the mechanism of emulsion formation to be studied more closely.

All emulsions obtained were found to be extremely stable to coalescence right down to low polymer concentrations.

Comparison of the results of the different measurements with the same system shows that the way in which the interface is formed has a great influence on its properties. This underlines the irreversible nature of the adsorption, which is one of the reasons why none of the existing theories is adequate to explain the measured effects quantitatively. By virtue of the many different measurements, however, this tudy serves as a basis for further theoretical and experimental work on the surface-active properties of polymers. In addition this investigation helped to show which factors determine the emulsifying capacity of polymers.

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SAMENVATTING

De adsorptie van polyvinylalcohol (PVA) aan het paraffine-water grensvlak is bestudeerd via grensvlakspanningsmetingen en via directe adsorptiemetingen aan emulsies. Het doel van het onderzoek was om meer inzicht te krijgen in de factoren van invloed op de polymeeradsorptie aan grensvlakken. De grensvlakchemische eigenschappen van polymeren zijn immers van groot praktisch belang zoals b.v. bij het gebruik als hechtmiddel, vlokmiddel en als emulsiestabilisator. Dit verklaart waarom de laatste jaren, zowel theoretisch als experimenteel, veel fundamenteel onderzoek wordt gedaan over de adsorptie van polymeren. Slechts een gering deel van dit onderzoek heeft betrekking op vloeistof-vloeistof grensvlakken en is daarom nader onderzocht. Hiervoor werd een goed gedefinieerd modelsysteem genomen waarbij verschillende technieken zijn gebruikt om het grensvlak te bestuderen.

De grensvlakspanningen zijn gemeten m.b.v. de statische Wilhelmyplaat methode als functie van PVA concentratie (0,1–4000 ppm) en tijd (tot 30 uur) voor verschillende PVA monsters; verschillend in hydrolysegraad, moleculair gewicht en herkomst. Daarnaast zijn tevens experimenten uitgevoerd aan gespreide en geadsorbeerde monolagen aan het paraffine-water grensvlak in een Langmuirtrog. De interpretatie van de grensvlakspanningsmetingen in termen van polymeeradsorptie is door het irreversibel karakter van de polymeeradsorptie moeilijk. Het irreversibel karakter van de polymeeradsorptie volgt direct uit het feit dat de PVA concentratie in de waterfase niet de enige bepalende grootheid is voor de gemeten grensvlakspanning doch dat ook de voorgeschiedenis van het grensvlak van invloed is. Dit houdt in dat de adsorptiewet van Gibbs niet zonder meer gebruikt mag worden.

Karakteristieke verschillen in grensvlakactiviteit werden gevonden tussen polymeren met verschillende hydrolysegraden. De discontinuïteit welke werd gevonden in de γ-log c_p curven bij PVA met een laag acetaatgehalte (ca 2%) was afwezig bij een hoger acetaatgehalte ($\geqslant$ 12%). Het discontinue karakter van γ-log c_p curven werd verklaard met kinetische factoren, namelijk de relatieve snelheden van ontvouwing en diffusie van het polymeer die de opbouw van het grensvlak bepalen. Verschil in mechanisme van grensvlakbezetting zal een andere conformatie van het geadsorbeerde polymeer tot gevolg hebben. Dit beeld werd bevestigd door tijdsafhankelijkheidsmetingen.

Er werd geen duidelijk effect gevonden van het molecuulgewicht op de gemeten grensvlakspanning, terwijl daarentegen de adsorptie gemeten aan het emulsieoppervlak duidelijk toenam met toenemend molecuulgewicht. Hieruit kan geconcludeerd worden dat – in tegenstelling tot het geval bij laagmoleculaire grensvlakaktieve stoffen – er voor polymeren geen eenduidig verband bestaat tussen grensvlakspanningsdaling en geadsorbeerde hoeveelheid.

Bij de adsorptiemetingen aan emulsies werd steeds van elke emulsie via turbiditeitsmetingen het specifiek oppervlak bepaald. Hieruit bleek dat bij een acetaatgehalte $\geqslant$ 12% de dispersiegraad een maximum vertoonde als functie van de PVA concentratie. Dit maximum correspondeerde met een discontinuiteit gevonden in de adsorptie isotherm. De concentratie waarbij dit maximum werd gevonden nam af met toenemend molecuulgewicht en afnemende volumefractie van de paraffine. De verklaring hiervoor werd ook hier gezocht via kinetische factoren die van invloed zijn bij de opbouw van de film tijdens het emulgeerproces.

De eigenschappen van de polymeerlaag van de emulsies vóór en ná het maximum in oppervlak bleken duidelijk verschillend. Een groot emulsieoppervlak werd gevonden wanneer het polymeeraanbod per ml olie laag werd gehouden. Enkele orienterende proeven werden uitgevoerd om het mechanisme van emulsievorming nader te bestuderen.

Al de verkregen emulsies bleken reeds bij lage concentraties uiterst stabiel tegen coalsescentie.

Door vergelijking van de uitkomsten van de verschillende metingen aan hetzelfde systeem blijkt dat de manier waarop het grensvlak is gevormd, van groot belang is voor de eigenschappen ervan. Dit onderstreept het irreversibel karakter van de adsorptie. Mede hierdoor is het ook niet goed mogelijk de gemeten effecten met de bestaande theorieën kwantitatief te verklaren. Door de vele verschillende metingen kan dit onderzoek echter dienen als uitgangspunt voor verder experimenteel en theoretische onderzoek naar de grensvlakaktieve eigenschappen van polymeren. Tevens biedt dit werk informatie over de factoren die van belang zijn voor het emulgerend vermogen van polymeren.

REFERENCES

ABRAMZON, A. A., GROMOV, E. V., DERYAGINA, G. M., DOKUKINA, L. F., EGOROVA, E. I and OSTROVSKII, M. V. (1969). Kolloidn. Zh. 31, 3–7.

ABRAMZON, A. A. and GROMOV, E. V. (1969). Kolloidn. Zh. 31, 163–168.

ALLEN, T. (1967). Proc. Conf. Particle Size Analysis Loughborough, sept. 1966. Publ. 1967, page 110–127.

AL-MADFAI, S. and FRISCH, H. L. (1958). J. Am. Chem. Soc. 80, 3613–14.

ARAUJO, O. E., (1967). J. Pharm. Sci. 56. 1141–45.

AUGENSTINE, L. G., GHIRON, C. A. and NIMS, L. F. (1958). J. Phys. Chem. 62, 1231–39.

BARET, J. F. and ROUX, R. A., (1968). Kolloid Z. Z. Polymere 225, 139–147.

BARET, J. F. (1968). J. Phys. Chem. 72, 2755–58.

BARTHOLOMÉ, E. and SCHAFER, K. (1950). Melliand Textilber. 31, 487–491.

BATEMAN, J. B., WENECK, E. J. and ESHLER, D. C. (1959). J. Colloid Sci. 14, 308–329.

BAYER, O. (1968). Chem. Unserer Zeit 2, 61–2.

BECHER, P. (1965). 'Emulsions, theory and paractice' A.C.S. Monograph Reinhold Publ. Co New York.

BIEHN, G. F. and ERNSBERGER, M. L. (1948). Ind. Eng. Chem. 40, 1449–53.

BLIGHT, L., CUMPER, C. W. N. and KYTE, V. (1965) J. Colloid Sci. 20, 393–99.

BLOCK, L. H. and LAMY, P. P. (1968). Kolloid Z. Z. Polymere 225, 164–66 .

BRANDRUP, J. and IMMERGUT, E. H. (1965). 'Polymer Handbook' Intersc. Publ. New York.

BROOKS, J. H. and PETHICA, B. A. (1964). Trans. Faraday Soc. 60, 208–15.

BULL, H. B. (1945). J. Am. Chem. Soc. 67, 4–12.

CHENE, M., MARTIN-BORRET, O. and CLERY, M. (1966). La Papeterie 3, 273–76.

CLAYFIELD, E. J. and LUMB, E. C. (1966) J. Colloid Interf. Sci. 22, 269–93.

CLAYFIELD, E. J. and LUMB, E. C. (1968). Macromolecules 1, 133–38.

COCKBAIN, E. G. (1954). Trans. Faraday Soc. 50, 874–81.

COCKBAIN, E. G. (1956). J. Colloid Sci. 11, 575–84.

COKER, J. N. (1957). Ind. Eng. Chem. 49, 382–85.

CRISP, D. J. (1946). J. Colloid Sci. 1, 161–84.

CRISP, D. J. (1958). 'Surface Phenomena in Chemistry and Biology' by Danielli, J. F. et al. Pergamon Press London, 1968, page 23–54.

DAVIES, J. T. (1954). J. Colloid Sci. Suppl. 1, 9, 9–13.

DUNN, A. S. and TAYLOR, P. A. (1965). Makromolek, Chem. 83, 207–19.

EIRICH, F. R. (1956). 'Rheology, theory and applications'. Vol I. Acad. Press, page 446–456.

FAINERMAN, A. E., LIPATOV, YU. S., and KULIK, V. M. (1969). Kolloidn. Zh. 31, 140–46.

FINCH, C. A. (1968). 'Properties and applications of polyvinylalcohol'. Soc. Chem. Ind. Monograph nr. 30.

FLEER, G. J. and LYKLEMA, J. (1968). Proc. 5th Int. Congr. Surface Activity. Barcelona 1968. Vol 2, 247–256.

FLEER, G. J. (1970). personal communication.

FOWKES, F. M. (1964). J. Phys. Chem. 68, 3515–20.

FRISCH, H. L. and SIMHA, R. (1954). J. Phys. Chem. 58, 507–12.

FRISCH, H. L. (1955). J. Phys. Chem 59. 633–36.

FRISCH, H. L. and SIMHA, R. (1957). J. Chem. Phys. 27. 702–706.

FRISCH, H. L. and AL-MADFAI, S. (1958). J. Am. Chem. Soc. 80, 3561–65.

FRUMKIN, A. (1925). Z. Physik. Chemie 116, 466–84.

FRUTON, J. S. and SIMMONDS, S. (1953) 'General Biochemistry' John Wiley, New York, pag. 512.

FUKAWA, K., ASAKURA, T. and DAIMON, H. (1958). Kobunshi Kagaku 18, 596–604.

GAINES, G. L. (1966). 'Insoluble monolayers at liquid-gas interfaces'. Intersc. Publ. New York.

GLASS, J. E. (1968a). J. Phys. Chem. 72, 4450–58.

GLASS, J. E. (1968b). J. Phys. Chem. **72**, 4459–67.

GOPAL, E. S. R. (1968). 'Emulsion Science' by P. Sherman, Acad. Press. Chapter 1.

GOULDEN, J. D. S. (1958). Trans. Faraday Soc. **54**, 941–45.

GROMOV, E. V., KREMNEV, L. YA, EGOROVA, E. I., BARENBAUM, R. K., ABRAMZON, A. A., DOKUKIMA, L. F., and OSTROVSKII, M. V. (1967). Kolloidn. Zh. **29**, 484–88.

HACKEL, E. (1968). Soc. Chem. Ind. Monograph nr. 30 1968.

HANSEN, R. S. and WALLACE, T. C. (1959). J. Phys. Chem. **63**, 1085–1091.

HAYASHI, S., NAKANO, C. and MOTOYAMA, T. (1964). Kobunshi Kagaku **21**, 300–304.

HELLER, W., NAKAGAKI, N. and WALLACH, M. L. (1959. J. Chem. Phys. **30**, 444–50.

HOEVE, C. A. J., DI MARZIO, E. A. and PEYZER, P. (1965). J. Chem. Phys. **42**, 2558–63.

HOEVE, C. A. J. (1965). J. Chem. Phys. **43**, 3007–3008.

HOEVE, C. A. J. (1966). J. Chem. Phys. **44**, 1505–1509.

HOEVE, C. A. J. (1969). Manuscript to be published.

HORACEK, J. (1962). Chem. Prumysl **12**, 385–7 (C.A. **58**, 10305 f).

HOTTA, H. (1953). Bull. Chem. Soc. Japan **26**, 386–390.

HUBER, H. F. and THIES, C. (1970). J. Polymer Sci. **8** (A–2) 71–80.

INKLAAR, P. A. and FORTUIN, J. (1969). Food Techn. **23**, 103–107.

ISEMURA, T. and HAMAGUCHI, K. (1952). Bull. Chem. Soc. Japan **25**, 40–5.

ISEMURA, T., HOTTA, H. and MIWA, T. (1953). Bull. Chem. Soc. Japan **26**, 380–385.

JAFFE, J., BERLINER, C. and LAMBERT, M. (1967a). J. Chim. Phys. **64**, 499–505.

JAFFE, J. BRICMAN, G. and GELBCKE, A. (1967b). J. Chim. Phys. **64**, 942–949.

JOHNSON, M. C. R. and SAUNDERS, L. (1968). Proc. 5th Internat. Congr. Surface Activity, Barcelona 1965 Vol **2**, 535–541.

JOOS, P. (1968). Proc. 5th Internat. Congr. Surface Activity Barcelona 1968 Vol **2**, 513–519.

KATCHALSKY, A. and MILLER, I. (1951). J. Phys. Chem. **55**, 1182–94.

KAWAI, T. (1959). J. Polymer Sci. **35**, 401–7.

KITCHENER, J. A. and MUSSELWHITE, P. R. (1968). 'Emulsion Science' by P. Sherman, Acad. Press Chapter 2.

KUHLMAN, R. A. (1965). Nature **207** (5003) 1289–90.

KUHLMAN, R. A., VLODAVETS, I. N., ESTERMAN, A. I. and Nikulina, T. F. (1968), Kolloidn. Zh. **30**, 860–62.

KUHLMAN, R. A. (1969). Kolloidn. Zh. **31**, 305–306.

KUNDU, L. and GHOSH, B. N. (1969). J. Indian Chem. Soc. **46**, 39–43.

LANKVELD, J. M. G. and LYKLEMA, J. (1968). Proc. 5th Internat. Congr. Surface Activity. Barcelona 1968 Vol **2**, 633–41.

LLOPIS, J. and REBOLLO, D. V. (1956). J. Colloid. Sci. **11**, 543–554.

LOEB, G. I. (1968a). J. Colloid Interface Sci. **26**, 236–39.

LOEB, G. I. and BAIER, R. E. (1968b). J. Colloid Interface Sci. **27**, 38–45.

LUCASSEN, J. (1968). Trans. Faraday, Soc **64**, 2221–35.

MAC RITCHIE, F. and ALEXANDER, A. E. (1963) J. Colloid Sci. **18**, 453–57.

MAC RITCHIE, F. and OWENS, N. F. (1969). J. Colloid Interface Sci. **29**, 66–71.

MAHROUS, H. A. F. and LEMBERGER, A. P. (1968). J. Pharm. Sci. **57**, 1836–44.

MATSUO, T. and INAGAKI, (1962). Macromol. Chem. **53**, 130–44 and **55**, 150–66.

MATTHEWS, J. B. (1939). Trans. Faraday Soc. **35**, 1113–1122.

MIE, G. (1908). Ann. Physik **25**, 377.

MINGINS, J. and STANDISH, M. M. (1966). Ann. Rep. Progr. Chem. **63**, 91–111.

MONTE-BOVI, A. J. (1969) J. Assoc. Offic. Anal. Chem. **52**, 891–93.

MOORE, W. R. A. D. and O'DOWD, M. (1968). Soc. Chem. Ind. Monograph nr. 30 77–87.

MOTOMURA, K. and MATUURA, R. (1963). J. Colloid Sci. **18**, 52–64.

MUKERJEE, L. N. and SHUKLA, S. D. (1967). Indian J. Appl. Chem. **30**, 17–24.

O'DONNELL, J. F., MESROBIAN, R. B. and WOODWARD, A. E. (1958). J. Polym. Sci. **28**, 171–77.

PADDAY, J. F. (1957). Proc. 2nd Internat. Congr. Surface Activity, London 1957 Vol **1**, 1–6.

PATAT, F., KILLMAN, E. and SCHLIEBENER, C. (1964). Fortschr. Hochpolym. Forsch. **3**, 332–93.

PETER, S. and FASBENDER, H. (1964). Kolloid Z. Z. Polymere **196**, 125–35.
REHFELD, S. J. (1967). J. Phys. Chem. **71**, 738–45.
REYNOLDS, G. E. J. and GULBEKIAN, E. V. (1968). Soc. Chem. Ind. Monograph nr 30, 131–153.
RIES, H. E. AHLBECK, R. A. and GABOR, J. (1959). J. Collid Sci. **14**, 354–56.
RIES, H. E., BEREDJICK, N. and GABOR, J. (1960). Nature **186**, 883–84.
RIES, H. E. and WALKER, D. C. (1961). J. Colloid Sci. **16**, 361–74.
SCHULLER, H. (1965) Tenside, **2**, 83–93.
SCHWARZ, T. W. (1962). Am. Perfumer Cosmet. **77**, 85–88.
SHERMAN, P. (1968). 'Emulsion Science' A.C.S. Monograph, Acad. Press.
SHOTTON, E. and KALYAN, K. (1960). J. Pharm. Pharmacol **12**, 109–18.
SHOTTON, E. and DAVIES, S. S. (1986). J. Pharm. Pharmacol. **20**, 430–48.
SILBERBERG, A. (1962a). J. Phys. Chem. **66**, 1872–83.
SILBERBERG, A. (1962)b). J. Phys. Chem. **66**, 1884–1907.
SILBERBERG, A. (1967). J. Chem. Phys. **46**, 1105–14.
SILBERBERG, A. (1968). J. Chem. Phys. **48**, 2835–51.
SINGER, S. J. (1948). J. Chem. Phys. **16**, 872–76.
STROMBERG, R. R., TUTAS, D. J. and PASSAGLIA, E. (1965). J. Phys. Chem. **69**, 3955–63.
STROMBERG, R. R. (1967). 'Treatise on Adhesion and Adhesives' Vol **1** Chap. 3. Ed. by R. Patrick, Dekker Publ.
TANFORD, C. (1961). 'Physical Chemistry of Macromolecules', Wiley and Sons, Inc. New York.
TEMPEL, M. VAN DEN (1960). Proc. 3rd Intern. Congr. Surface Activity Cologne 1960, **2** 573–79.
TEMPEL, M. VAN DEN (1965). Proc. 2nd Scandinavian Symp. Surface Activity, Stockholm, 1964.
TOYOSHIMA, K. (1968). Soc. Chem. Ind. Monograph nr. 30, 154–87.
TSUNEMITSU, K. and SHOHATA, H. (1968). Soc. Chem. Ind. Monograph nr. 30, 104–130.
TRURNIT, H. J. (1960). J. Colloid Sci. **15**, 1–13.
VOCHTEN, R., JOOS, P. and RUYSEN, R. (1968). Proc. 5th Internat. Congr. Surface Activity. Barcelona 1968 Vol **2**, 543–550.
VOORST, VADER, F. VAN (1960). Proc. 3rd Intern. Congr. Surface Activity Cologne 1960 Vol **1**, 248–54.
WALSTRA, P. (1964). Brit. J. Appl. Phys. **15**, 1545–52.
WALSTRA, P. (1965a). Brit J. Appl. Phys. **16**, 1187–92.
WALSTRA, P. (1965b). Neth. Milk. Dairy J. **19**, 93–109.
WALSTRA, P. (1965c). Neth. Milk. Dairy J. **19**, 1–7.
WALSTRA, P. (1968). J. Colloid Interface Sci. **27**, 493–500.
WALSTRA, P. and OORTWIJN, H. (1969a). J. Colloid Interface Sci. **29**, 424–31.
WALSTRA, P. (1969b). Neth. Milk. Dairy J. **23**, 238–44.
WARD, A. F. H. and TORDAI, L. (1946). J. Chem. Phys. **14**, 453–61.
WILSON, A, EPSTEIN, M. B. and ROSS, J. (1957). J. Colloid Sci. **12**, 345–55.
YAMASHITA, T. and BULL, H. B. (1968). J. Colloid Interface Sci. **27**, 19–24.
ZILVERSMIT, D. B. (1963). J. Colloid Sci **18**, 794–97.
ZWICK, M. M. (1964). Textile Res. J. **34**, 417–430.
ZWICK, M. M. (1965). J. Appl. Polymer Sci. **9**, 2393–2424.
ZWICK, M. M. (1966). J. Polymer Sci. **4** (A–1) 1642–44.

LIST OF SYMBOLS

A	area available per segment
A_0	limiting area per segment
A_i	area of the interface
a_0	interfacial area occupied by one polymer molecule
c	concentration
c_p	polymer concentration
D	diffusion coefficient
$f(x)$	droplet diameter distribution
$\bar{h}$	radius of gyration of the polymer
I	intensity of transmitted light
I_0	intensity of incident light
K	light scattering coefficient
K^*	light scattering coefficient corrected for the forward scattering
k	Boltzmann's constant
l	optical pathlength
$\bar{M}$	average molecular weight
N	number of emulsion droplets per unit volume
n_b	number of polymer molecules in the bulk
n_c	refractive index of the continuous phase
n_d	refractive index of the dispersed phase
n_s	number of polymer molecules in the boundary layer
n_t	number of molecules per unit area at time t
n_0	number of segments in the interface
n_z	number of segments at a distance z from the interface
O	optical density
P	degree of polymerization
p	spread in droplet size
R	gas constant
S	interfacial area of the emulsion
T	absolute temperature
t	time
V	volume of the dispersed volume
v_b	volume fraction of the polymer in the bulk
w	volume per segment
x	diameter of the emulsion droplet
$\bar{x}_{32}$	volume-surface diameter
y	$\bar{\rho}_{32}/\bar{x}_{32}$
Z	reduced turbidity
z	coordination number of the polymer segment in the interface
$z_{0 \cdot 1}$	thickness at which $n_z = 0.1\ n_0$
α	intercept of the γ-log c_p curves
α	angle of acceptance of the turbiditymeter (Chapter 5)

β	slope of the γ-log c_p curves
β_1	slope of the γ_∞-$t^{1/2}$ curves
Γ	adsorption
Γ_c	interfacial concentration increased by compression
Γ_s	interfacial concentration increased by spreading
γ	interfacial tension
γ_0	interfacial tension of a clean interface
γ_t	interfacial tension at time t
$\gamma_{t\to 0}$	interfacial tension extrapolated to time is zero
γ_∞	final value of the interfacial tension
δ	thickness of the boundary layer
ε	elasticity modulus
$[\eta]$	intrinsic viscosity
η_c	viscosity of the continuous phase
η_d	viscosity of the disperse phase
η_s	interfacial dilational viscosity
Θ	proportion of the interface occupied by polymer
λ	wave length
ν	number of adsorbed segments per polymer
Π	interfacial pressure
Π_t	interfacial pressure at time t
Π_∞	final value of the interfacial pressure
Π_0	interfacial pressure for a compact monolayer
ρ	dimensionless droplet size diameter
τ	relaxation time
Φ	volume fraction of the paraffin
ψ	free energy of adsorption per molecule
ω	interaction energy between two polymer segments in units kT