

POLYMERS AT INTERFACES: STATICS, DYNAMICS AND EFFECTS ON COLLOIDAL STABILITY

M.A. COHEN STUART,
*Department of Physical and Colloid Chemistry,
Dreijenplein 6,
6703 HB Wageningen,
The Netherlands.*

ABSTRACT. This contribution is a short resumé of the lectures given in the ASI course. It was felt by the author that the interested reader would be better served with such a resumé and a list of central references giving access to the field, than with a lengthy tutorial text.

It has been known for a long time that polymers may adsorb on the particles of a colloidal dispersion and, if they do so, affect the stability of the dispersion. We will discuss here **physisorption** (i.e. attachment by weak forces, no chemical bonds) of polymers. Accounts of chemisorption and its effects can be found in a monograph by Napper [1].

The forces generated by the adsorbed polymers can be either **attractive**, namely when the chains form bridges between two neighbouring particles, or **repulsive** when the polymer forms a protective sheath around the particles which precludes any bridge formation [2].

1 Statics

In order to develop an understanding of these forces, adsorption as such was first studied empirically. Already as early as 1951 [3] a qualitative picture was proposed for the structure of an adsorbed chain molecule in terms of **trains** (segments in contact with the substrate), **loops** (subchains starting from the surface and returning there) and **tails** (freely dangling chain ends). Attempts were also made to put the theory of polymer adsorption on a quantitative footing [4,5] but the problem of many interacting chains accumulated at a surface at first seemed formidable and hardly tractable. However, during the seventies much progress was made [6,7] and a very versatile lattice model was developed by Scheutjens and Fleer [8]. This model is already explained in some detail in the contribution by Lyklema (see this volume). Here we emphasize only that a central assumption in the theory (apart from it being a lattice model) is that the segment density is only a function of the distance normal to the interface; in directions parallel to the interface the density is homogeneous. This 'mean field' assumption has been criticized by polymer physicists, notably by de Gennes who developed an alternative scaling theory [9] but for most experimental systems the assumption is very good [10]. In a recent review, [11] the predictions of the Scheutjens Fleer theory have been compared with a vast amount of experimental data, selected from careful studies on well-defined systems. The main conclusions for homopolymers (adsorbing from dilute solution) are :

- (1) for not too small segmental binding energy the adsorption isotherm has a very steep initial rise and a well-defined plateau; ('high affinity' isotherm).
- (2) the plateau adsorption increases with chain length; in good solvents the increase levels off at high chain length, in θ -solvents the plateau adsorbed amount becomes proportional to $\log M$.
- (3) the plateau adsorption increases with increasing segmental binding strength but levels off when this energy exceeds $3 kT$. A sharp transition from adsorption to desorption occurs when the binding strength is outweighed by the elastic (conformational) free energy [11,12].
- (4) The segment density falls monotonously with distance from the surface showing a dense contribution at short distance due to loops and a more dilute contribution but of larger extension due to tails; for long chains, the mass adsorbed in tails may be 10-15% of the total adsorbed mass. Very long tails are possible.
- (5) The thickness of the adsorbed layer is largely a function of the adsorbed mass; unsaturated layers are thin although near saturation the thickness increases very steeply, especially in good solvents. When the thickness is measured by a hydrodynamic method (tangential solvent flow), the effect is largely due to tails.

Essentially all these predictions were rather well corroborated by experiment. In addition, mixtures of polymers with different chain lengths (polydisperse polymers) were studied both theoretically [13] and experimentally [11,14] and the important consequences of preference and exchange were laid bare.

The Scheutjens-Fleer theory is a numerical theory. The quest for analytical expressions was also pursued, but at first the approximations made were too crude. The original recursion formula can be rewritten into a second order differential equation, which was further simplified by assuming (i) low densities, (ii) very ('infinitely') long chains and (iii) a negligible contribution of tails [15]. Especially the latter approximation is a poor one : two eigenfunctions are important, one of which gives rise to tails [16]. A more recent calculation takes this into account [17].

Scheutjens and Fleer went on to apply their formalism to polymer between two surfaces, thus describing the situation of two particles interacting through their polymer layers. They considered two cases : (i) all molecules (solvent and polymer) can leave the gap between the two walls when these are moved together; there is, so to say, an infinite reservoir of molecules and the chemical potentials of all components remain fixed during the approach. (ii) only solvent can leave the gap; the amount of polymer between the plates remains constant.

For case (i) there is attraction at all distances; this does certainly not correspond to experimental results where both attraction and stability can be found. Therefore this was considered an irrelevant case.

Case (ii) is interesting. Here one finds monotonously repulsive situations when the adsorbed amount is high, but when the surface is not saturated with polymer an attractive minimum develops, which first deepens with decreasing adsorption and then disappears again when the surfaces become bare. This is the case of **bridging attraction** which is obviously most effective when the adsorbed amount is somewhat below saturation ('starved layer') [15,18].

This finding is in good agreement with experimental data which show optimum flocculation at some intermediate polymer dose [2]. It seems that the situation is simple and well understood : dispersed particles are repulsive or attractive depending on polymer dose; since an equilibrium (thermodynamic) theory is capable to describe it we need not consider temporal effects. However, reality appeared to be more complex.

2 Dynamics

Under the apparent agreement between theory and experiment (as far as the effect of the polymer dose on flocculation is concerned) lies a little paradox. Most flocculation experiments are conducted with dispersions which are initially stable due to electrostatic repulsion. The particles in such dispersions have little tendency to approach each other closely. However, the attraction due to polymer bridging develops only at very short distances since unsaturated polymer layers tend to be thin. We can only solve this paradox if we assume that the polymer molecules must be in an extended state in order to initiate bridging. But since the extended state cannot persist for starved polymer layers, temporal effects must come into play.

Such effects were showing up soon in an interesting study by Pelssers [19]. For permanently attractive particles (such as particles subjected to Van der Waals forces and little or no electrical repulsion to counteract this) one expects aggregation to occur as described by the Von Smoluchowsky theory (or a refinement thereof). According to this theory, the number of singlets, N_1 , decreases in time(t) with an inverse square law :

$$N_1(t) = N_0 (1 + k_f N_0 t)^{-2}$$

where N_0 is the initial particle concentration, and k_f the flocculation rate constant.

Pelssers carried out studies with polystyrene latex particles which were flocculated with polyethylene oxide (PEO). He measured N_1 as a function of both time and particle concentration, at the optimum PEO dose. Much to his surprise, the singlet number did **not** decrease monotonously in time but came to a complete standstill after some initial rapid drop. Also the initial rapid drop was not a smooth function of N_0 . Rather, there was almost no flocculation below a certain threshold value, after which N_1 dropped steeply to almost zero. In addition, it was found that a certain minimum shear rate was necessary to bring about flocculation [19].

The scenario which finally proved useful in understanding the results is the following. The polymer adsorption process has three steps : (1) mass transfer in the bulk solution (2) attachment (3) conformational relaxation. Step (1) can be conveniently described by classical expressions for collision rates in (sheared) dispersions, and step (2) is, for uncharged flexible polymers too rapid to be rate determining. Therefore, the number of attached molecules per colloidal particle follows a first order rate law. In order to form bridges, these attached molecules must extend far enough to reach the surface of a second particle. However, the electrostatic repulsion between the particles maintains a minimum distance of approach which is still fairly large. Therefore it is conceivable that freshly attached, extended molecules can form a bridge, but relaxed, flattened ones cannot. Hence, it is the number of extended ('active') molecules per particle which counts, and this number will **increase** due to attachment, but **decrease** due to unfolding. Assuming the unfolding rate to be first order (too), one finds that the number of active molecules goes through a maximum depending on concentrations and rate constants.

The idea is now that a certain minimum number of active polymer molecules per particle is needed before bridging starts. If unfolding is too rapid in comparison with attachment, no flocs are formed. If the attachment rate is enhanced, e.g. by shearing or by increasing the particle and polymer concentrations, bridging may be induced. The schedule in fig. 1 illustrates this scenario. A quantitative model was developed which was found to describe the data very well [20].

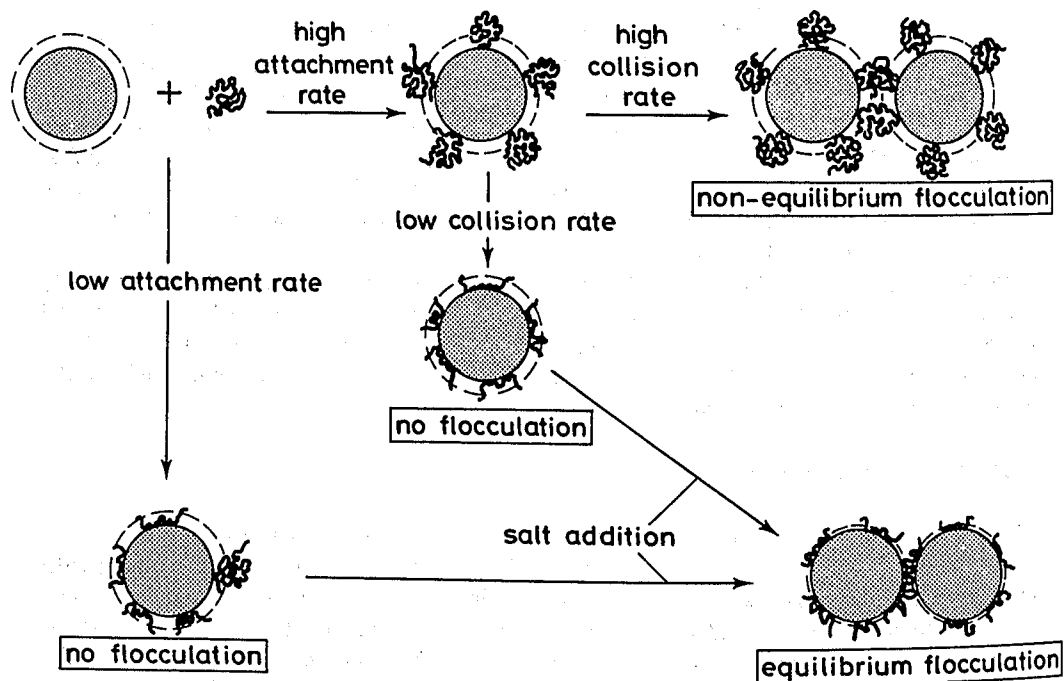


Figure 1. Pathways in bridging flocculation

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