On the Theory of the Stabilization of Dispersions by Adsorbed

Macromolecules.   II.   Interaction between Two Flat Particles

by F. Th. Hesselink,*[1] A. Vrij, and J. Th. G. Overbeek

van't Hoff Laboratorium der Rijksuniversiteit, Sterrenbos 19, Utrecht, The Netherlands   (*Received December 14, 1970*)

Publication costs borne completely by The Journal of Physical Chemistry

A theory for the stabilization of dispersions by adsorbed macromolecules ("protective action") is given in terms of a volume restriction repulsion, due to the decrease of configurational entropy of adsorbed loops and tails on the approach of a second particle, an osmotic repulsion due to the mixing of the adsorbed polymeric clouds when two particles approach each other (in a very poor solvent this can be an attraction effect), and the van der Waals attraction between the particles. The adsorbed macromolecules are described by a random walk model. No molecules are adsorbed on more than one particle (no "bridging"). The interaction between two flat particles covered by adsorbed macromolecules is described using the Flory–Huggins approximation for four different modes of attachment of the macromolecules: equal loops, equal tails, and the loop size distributions found before for an adsorbed homopolymer and for an adsorbed copolymer. Interaction curves are found which predict reversible flocculation and the occurrence of thixotropic systems as intermediates of flocculated and deflocculated systems. The main parameters determining the interaction are the average loop (tail) size and the size distribution of these loops (tails), the amount of polymer adsorbed, the quality of the solvent, the Hamaker attraction constant, and the particle size. For flat particles the stability is inversely proportional with the square of the linear dimension of the particles, whereas for spherical particles in Derjaguin's approximation the stability is shown to be inversely proportional with the radius of the spheres. In general, stabilization is enhanced by long adsorbed chains and an extreme size distribution, a high amount of polymer adsorbed, a good solvent, a low Hamaker constant, and a small particle size. These predictions appear to be in reasonable agreement with the only scarcely available experimental evidence on this subject.

Introduction

Adsorbed nonionic macromolecules are known to stabilize emulsions and suspensions in aqueous and nonaqueous media. Examples[2] are alkyd resins, cellulose derivatives, uncharged proteins, and block copolymers which are used for the stabilization of pigment dispersions, latices, emulsions, etc. The mechanism by which adsorbed polymers can keep the particles dispersed in solution by counteracting the ever-existing attraction, due to van der Waals forces[3] and occasionally to magnetic forces,[4] is of two kinds.[5]

(I) A macromolecule adsorbed on a colloidal particle loses configurational entropy on the approach of a second particle. This is called the *volume restriction effect.*

(II) When the layers of adsorbed macromolecules on the two particles interpenetrate, the higher polymer segment concentration between the particles will lead to a local "*osmotic pressure*" in most cases counteracting the approach.

The volume restriction effect has a certain resemblance to the concept of rubber elasticity, as if the dispersion is stabilized because of an elastic wrapping[6] around the particles. Mackor and van der Waals[7,8] have shown for rather short, rodlike molecules that when the loss of configurational entropy leads to desorption the interfacial free energy rises in agreement with Gibbs' adsorption isotherm. Using a Monte Carlo simulation technique permitting only self-avoiding walks on a cubic lattice, Clayfield and Lumb[9] have calculated the rise in free energy due to volume restriction for macromolecules adsorbed on an impermeable interface. Their calculations apply to irreversibly adsorbed "tails" (chains terminally adsorbed with one end group) and to copolymers attached to the particles by anchor segments in a solvent having no net interaction with the unadsorbed part of the molecule. Fischer[10] was probably the first to point out that the increase of the free energy due to the overlapping of segment clouds should be taken into account. For irreversibly adsorbed tails Meier[5] considered both effects I and II using random flight statistics to calculate the volume

(1) Address correspondence to this author at the Department of Chemistry, Cornell University, Ithaca, N. Y. 14850.

(2) J. Lyklema, *Advan. Colloid Interface Sci.*, **2**, 65 (1968).

(3) (a) B. Derjaguin and L. D. Landau, *Acta Physicochim. URSS*, **14**, 633 (1941); (b) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, Amsterdam, 1948.

(4) J. P. McTague, *J. Chem. Phys.*, **51**, 133 (1969); J. R. Thomas, *J. Appl. Phys.*, **37**, 2914 (1966).

(5) D. J. Meier, *J. Phys. Chem.*, **71**, 1861 (1967).

(6) K. Jäckel, *Kolloid-Z. Z. Polym.*, **197**, 143 (1964).

(7) E. L. Mackor, *J. Colloid Sci.*, **6**, 492 (1951).

(8) E. L. Mackor and J. H. van der Waals, *ibid.*, **7**, 535 (1952).

(9) E. J. Clayfield and E. C. Lumb, *J. Colloid Interface Sci.*, **22**, 285 (1966); *Macromolecules*, **1**, 133 (1968).

(10) E. W. Fischer, *Kolloid Z.*, **160**, 120 (1958).

restriction effect and the Flory–Huggins approach for the osmotic effect. He showed that the osmotic effect contributes substantially to the stabilization, especially at high surface coverage of polymer. This originates from the fact that the volume restriction effect increases linearly with the amount of polymer adsorbed, whereas the osmotic effect increases quadratically, being due to the interaction between the two polymeric clouds. Due to an incorrect derivation of the density distribution[11] for the segments of the adsorbed chains, Meier's values for the osmotic effect are somewhat too low.

In this paper we have corrected this error and extended the theory to systems in which the polymer molecules are adsorbed with many segments, connected by loops dangling in solution. With the results of our previous paper[12] on the configurational statistics of adsorbed macromolecules on the approach of a second interface, the repulsion due to volume restriction and osmotic effects is calculated for four different modes of attachment of the macromolecules: equal tails, equal loops, a loop size distribution derived by Hoeve, et al.,[13] for a homopolymer where all the segments have a priori an equal chance to become adsorbed, and a loop size distribution[12] for a copolymer attached to the surface with anchor segments randomly distributed along the chain.

The repulsion thus calculated is then compared with the van der Waals attraction between the particles. The independent parameters determining the stability are listed and the effect of these parameters on the stability is discussed.

Model

Our previous results[12] on the configurational behavior of adsorbed macromolecules on the approach of a second interface are based on random flight statistics on a six-choice cubic lattice and the spatial dimensions are expressed in units $(il^2)^{1/2}$ where i is the number of segments each with length l. In this paper we need the real dimensions of polymer chains and therefore we will equalize $(il^2)^{1/2}$ with the experimental root mean square end-to-end distance $\langle r^2 \rangle^{1/2}$ of a chain; thus $il^2 = \langle r^2 \rangle$. The expansion α of the chains due to long-range intramolecular interactions is taken into account by using $\langle r^2 \rangle^{1/2} = \alpha \langle r^2 \rangle_0^{1/2}$ where $\langle r^2 \rangle_0^{1/2}$ is the unperturbed root mean square end-to-end distance to be measured in a θ solvent.

As previously[12] we will treat the case of the interaction between two flat interfaces. Extension to the case of the interaction between two spheres highly complicates the mathematics. Ottewill and Walker[14] have calculated the osmotic effect for two spheres covered by rather short polyethylene oxide chains approximating the density distribution by a step function. This, however, is too crude an approximation for a quantitative analysis.[15] As before[12] our argument is limited to

cases where each macromolecule is adsorbed only on one particle. Extension to cases of macromolecules adsorbed on more than one particle would lead to a quantitative treatment of sensitized flocculation.[16] This, however, is beyond the scope of this paper because of the several simultaneous kinetic processes involved. As usual[17] we assume the polymeric clouds around the particles to be interpenetrable whereas the particles are thought of as impenetrable interfaces.

In general, macromolecules adsorbed on colloidal particles will form loops with a certain size distribution. The loop size distribution for an adsorbed homopolymer is given by[12]

$$n_i = na\pi^{-1/2}(\bar{\imath})^{-1}i^{-3/2}\exp[-ia^2/(\bar{\imath})^2] \qquad (1)$$

where n_i is the number of loops of i segments per unit area, $\bar{\imath}$ the average number of segments per loop, n the total number of segments in the loops per unit area, and $a \cong 0.7$ (numerical constant). This loop size distribution has originally been formulated[13,18] in a slightly different form for an infinitely long isolated macromolecule on an infinite surface, neglecting interactions between loops and solvent. Taking into account end effects (each molecule may have one or two loose tails), Roe[19] and recently Motomura and Matuura[20] have found that these tails may contain a considerable fraction of the adsorbed macromolecule. This seems to be confirmed by experiments on the thickness of the adsorbed layer,[21,22] which suggest that in practically all cases investigated, the adsorbed macromolecules are attached to the interface by only a few segments with long chains protruding in solution. However, when the end effects are small eq 1 seems to be valid. Another complication arises because of the fact that for a homopolymer the quality of the solvent, the average size of the adsorbed chains and the amount adsorbed cannot be considered as independent parameters.[13,19–25]

(11) F. Th. Hesselink, J. Phys. Chem., 73, 3488 (1969).

(12) F. Th. Hesselink, ibid., 75, 65 (1971).

(13) C. A. J. Hoeve, E. A. DiMarzio, and P. Peyser, J. Chem. Phys., 42, 2558 (1965).

(14) R. H. Ottewill and T. Walker, Kolloid-Z. Z. Polym., 227, 108 (1968).

(15) For example, applying this approximation to the interaction between two flat interfaces gives that the "osmotic" force between the particles does not depend on the extent of the overlap.

(16) V. K. La Mer, Discussions Faraday Soc. 42, 248 (1966); W. E. Walles, J. Colloid Interface Sci., 27, 797 (1968).

(17) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(18) R.-J. Roe, Proc. Nat. Acad. Sci. U. S., 53, 50 (1965).

(19) R.-J. Roe, J. Chem. Phys., 43, 1591 (1965); 44, 4264 (1966).

(20) K. Motomura and R. Matuura, ibid., 50, 1281 (1969).

(21) R. R. Stromberg in "Treatise on Adhesion and Adhesives," Vol. I, R. L. Patrick, Ed., Marcel Dekker, New York, N. Y., 1967.

(22) E. Killmann and H. G. Wiegand, Makromol. Chem., 132, 239 (1970).

(23) A. Silberberg, J. Chem. Phys., 48, 2835 (1968).

(24) M. J. Schick and E. N. Harvey, Jr., Advan. Chem. Ser., 87, 63 (1968).

The problem of the size distribution being unsolved, no theory can correlate these parameters correctly. Because of these uncertainties we will use eq 1 only to obtain a qualitative picture of the stabilizing action of adsorbed homopolymers. In our more quantitative discussion we shall not investigate this case. It can be said beforehand that the error involved using eq 1 will become more serious the shorter the adsorbed homopolymer and the higher the surface coverage.

For a copolymer attached to the particle by some anchor segments randomly distributed along the chain, we have found, neglecting end effects, an exponential loop size distribution[12]

$$n_i = n(\bar{i})^{-2} \exp(-i/\bar{i}) \tag{2}$$

The repulsion due to volume restriction and osmotic effects can now be calculated for particles covered by adsorbed homopolymers and adsorbed copolymers using eq 1 and 2 and also for particles covered by equal tails and equal loops.

Volume Restriction Effect

On the approach of a second interface adsorbed loops and tails lose configurational entropy. Previously[12] we have derived for this relative loss of configurations for a single tail, $R_1(i,d)$ and for a single loop $R_2(i,d)$

$$R_1(i,d) = \sum_{v=-\infty}^{\infty} [\exp\{-6v^2d^2/il^2\} -$$

$$\exp\{-3(2v+1)^2d^2/2il^2\}] \tag{3}$$

and

$$R_2(i,d) = \sum_{v=-\infty}^{\infty} (1 - 12v^2d^2/il^2) \exp(-6v^2d^2/il^2) \tag{4}$$

where i is the number of segments per tail (loop) and d the distance between the interfaces. When two interfaces both covered by v ($= n/\bar{i}$) tails (loops) per unit area approach each other, the resulting rise in free energy, ΔF_{VR}, per unit area due to volume restriction is given by

$$\Delta F_{VR} = -2kT\sum_i n_i \ln R(i,d) \tag{5}$$

where k is the Boltzmann constant and T the absolute temperature, whereas for $R(i,d)$ either eq 3 or 4 is to be substituted. For the case of equal tails (loops) $n_i = v$ whereas for a homopolymer and a copolymer n_i is given by eq 1 and 2, respectively. Substitution of eq 4 into eq 5 and replacement of the summation over i by an integration gives

$$\Delta F_{VR} = 2vkTV(\bar{i},d) \tag{6}$$

with

$$V(\bar{i},d) = -\bar{i}n^{-1} \int_0^\infty n_i \ln \sum_{v=-\infty}^{\infty} (1 - 12v^2d^2/il^2) \times$$
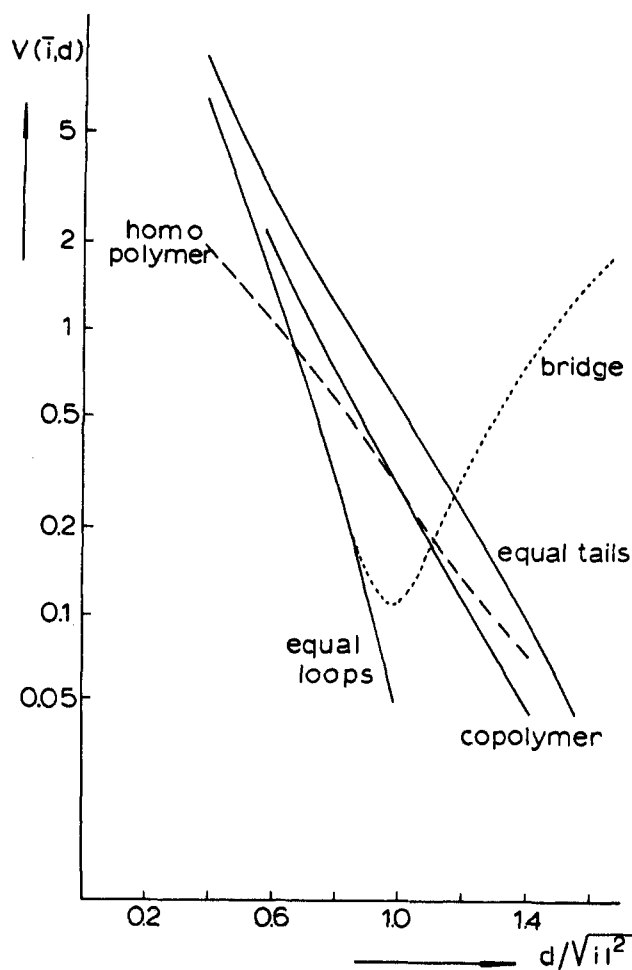
$$\exp(-6v^2d^2/il^2)di \tag{7}$$

Figure 1. The rise in free energy per average chain $V(\bar{i},d)$ (see eq 7) due to the volume restriction imposed by a second interface at distance $d/\sqrt{\bar{i}l^2}$ for several modes of attachment of the macromolecules. Only the homopolymer curve (- - -) depends on $\bar{i}$; it is calculated for $\bar{i} = 10$. The curve for equal tails has been found before by Meier.[5] The curve for a bridge (see ref 12) gives the free energy for a chain connecting two particles.

$V(\bar{i},d)$ gives the rise in free energy per average loop in units kT. It is evaluated as a function of $d/\sqrt{\bar{i}l^2}$ by numerical integration of eq 7 using an Electrologica X8 computer. For equal loops and $d/\sqrt{\bar{i}l^2} \geq 1$ a good approximation[26] for $V(i,d)$ is given by

$$V(i,d) = -2(1 - 12d^2/il^2) \exp(-6d^2/il^2) \tag{7a}$$

In Figure 1 and more precisely in Table I the results are given for particles covered by equal tails, equal loops, and copolymers. Figure 1 also shows $V(\bar{i},d)$

(25) The relevance of this point is easily demonstrated; e.g., raising the quality of the solvent for the adsorbed polymer generally increases the stability of the system (see Discussion) but it decreases the amount adsorbed[23,24] which effect tends to destabilization of the system.

(26) For equal loops the integration in eq 7 over i vanishes whereas for $d/\sqrt{\bar{i}l^2} \geq 1$ the summation over v converges rapidly. Equation 7a is found by taking only the first terms of this sum ($v = 0, \pm 1$), developing the logarithm in a power series, and neglecting the higher terms of this series.

Table I: Values for the Dimensionless Volume Restriction Function, $V(\bar{\imath},d)$ (eq 7), and Osmotic Function, $M(\bar{\imath},d)$ (eq 11), Independent of $d/\sqrt{\bar{\imath}l^2}$

$d/\sqrt{\bar{\imath}l^2}$	$V(\bar{\imath},d)$			$M(\bar{\imath},d)$		
	Equal tails	Equal loops	Copolymer	Equal tails	Equal loops	Copolymer
0.6	2.996	1.476	2.030	3.723	2.974	3.428
0.8	1.284	0.339	0.760	2.397	1.716	2.078
1.0	0.582	0.0561	0.307	1.585	0.837	1.280
1.2	0.262	0.00578	0.1282	1.043	0.314	0.801
1.4	0.1118	0.00035	0.0542	0.667	0.0940	0.480
1.6	0.0439		0.0231	0.406	0.0204	0.281
1.8	0.01582		0.0109	0.232	0.0034	0.150
2.0	0.00497		0.0041	0.127		0.081
2.5	0.00018			0.018		

for adsorbed homopolymers. The curves of $V(\bar{\imath},d)$ against $d/\sqrt{\bar{\imath}l^2}$ for equal tails, equal loops, and copolymers are independent of the particular choice of $\bar{\imath}$, whereas the curve for a homopolymer depends on $\bar{\imath}$. This is directly related to the fact that for the first three cases[12] the root mean square extension of the segments from the interface, $\langle x^2 \rangle^{1/2}$, is proportional to $(\bar{\imath})^{1/2}$ whereas for a homopolymer[12,23] $\langle x^2 \rangle^{1/2}$ is proportional to $\bar{\imath}$. Figure 1 will be discussed further in connection with the results for the osmotic effect.

Osmotic Effect

The increase in free energy, ΔF_M, per unit area caused by the increased mixing of polymer segments at the approach of two interfaces covered with polymeric material gives rise to a local osmotic repulsion between the particles. In spite of its shortcomings,[27,28] mostly due to ignored changes in volume on mixing, we will use the classical Flory–Huggins approximation[17] to evaluate this repulsion.[29]

Meier[5] has derived for ΔF_M in this approximation

$$\Delta F_M = kTV_s^2 V_1^{-1}(1/2 - \chi) \times$$
$$\left[\int_0^d (\rho_a + \rho_b)_d^2 \, dx - \int_0^\infty (\rho_a + \rho_b)_\infty^2 \, dx \right] \quad (8)$$

Here V_s and V_1 are the volumes of a polymeric segment and a solvent molecule, χ is the Flory–Huggins interaction parameter, ρ_a and ρ_b are the number densities of the segments of the macromolecules adsorbed on interface A and B per unit volume, while suffix d and ∞, respectively, indicate the distance between A and B; the integration of $(\rho_a + \rho_b)^2$ is to be performed over the interval between A and B. The quality of the solvent is characterized both by $(1/2 - \chi)$ and by the expansion parameter α. Therefore we will express $(1/2 - \chi)$ in terms of α using Flory's[17] relation[30]

$$\alpha^5 - \alpha^3 = \frac{27\bar{\imath}^2 V_s^2(1/2 - \chi)}{(2\pi)^{3/2} V_1(\bar{\imath}l^2)_0^{3/2}} \quad (9)$$

With eq 9 we find from eq 8 taking into account that

$$\int \rho_a^2 \, dx = \int \rho_b^2 \, dx; \quad \int (\rho_a\rho_b)_\infty \, dx = 0$$
$$\Delta F_M = 2(2\pi/9)^{3/2}(\alpha^2 - 1)kT\nu^2\langle r^2 \rangle M(\bar{\imath},d) \quad (10)$$

where $\langle r^2 \rangle = \alpha^2 \bar{\imath}l^2$ and

$$M(\bar{\imath},d) = \langle r^2 \rangle^{1/2} \left[\int_0^d (\hat{\rho}_a)_d^2 \, dx + \int_0^d (\hat{\rho}_a\hat{\rho}_b)_d \, dx - \int_0^\infty (\hat{\rho}_a)_\infty^2 \, dx \right] \quad (11)$$

The caret at the top of ρ indicates that this $\hat{\rho}$ is normalized so that $\int\hat{\rho}dx = 1$. Equation 10 has been given before by Meier[5] using slightly different symbols.

Now we will derive $\hat{\rho}_a$ for several modes of attachment of the macromolecules. For the normalized density distribution of the segments of a single tail, $\hat{\rho}_1(x,i,d)$, and of a single loop, $\hat{\rho}_2(x,i,d)$, both of i segments in the direction x normal to the interface in a slab of thickness d we have derived previously[12]

$$\hat{\rho}_1(x,i,d) = 3(il^2)^{-1}R_1^{-1}(i,d) \times$$

$$\sum_{v=-\infty}^{+\infty} \left[v \int_0^d \{\exp[-q(vd - d + x - b/2)^2] - 2\exp[-q(vd - b/2)^2] + \exp[-q(vd + d - x - b/2)^2]\} \, db + \int_x^d \{\exp[-q(vd + b/2)^2] - \exp[-q(vd + x - b/2)^2]\} \, db \right] \quad (12)$$

(27) D. Patterson, *Macromolecules*, **2**, 672 (1969).

(28) P. J. Flory, J. L. Ellenson, and B. E. Eichinger, *ibid.*, **1**, 279 (1968); B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968).

(29) The Flory–Huggins interaction parameter χ is then to be regarded as an empirical parameter to be determined from, *e.g.*, osmotic and light-scattering experiments and not to be associated with a heat of solution of the polymer. The concentration dependence of χ will be neglected.

(30) Strictly speaking we should not use Flory's relation between α and χ because it is derived from the swelling equilibrium of a free coil in solution and not of an adsorbed chain. The swelling equilibrium of adsorbed chains however, has not been described yet and Flory's relation is expected to be a reasonable approximation.

where $q = 6/(il^2)$ and $R_1(i,d)$ is given by eq 3. Further[12]

$$\hat{\rho}_2(x,i,d) = 12(il^2)^{-1}R_2^{-1}(i,d) \times$$

$$\sum_{v=-\infty}^{\infty} \{(v + 1)(vd + x) \exp[-q(vd + x)^2] -$$

$$v^2d \exp(-qv^2d^2)\} \quad (13)$$

where $R_2(i,d)$ is given by eq 4. For particles covered by equal tails the number density ρ_a is given by

$$\rho_a = n\hat{\rho}_1(x,i,d) \quad (14)$$

ρ_b is then found by substitution of $(d - x)$ instead of x. For particles covered by loops[31] we have

$$\rho_a = \sum_i in_i\hat{\rho}_2(x,i,d) \quad (15)$$

In the case of equal loops eq 15 reduces to

$$\rho_a = n\hat{\rho}_2(x,i,d) \quad (16)$$

For a homopolymer and for a copolymer we substitute eq 1 and 2 in eq 15. Replacing the summation over i by an integration and substituting eq 13 we obtain

$$\rho_a = ns \int_0^\infty i^{-t} \exp(-iu) \times$$

$$\left\{ \sum_{v=-\infty}^{\infty} [(v + 1)(vd + x) \exp\{-q(vd + x)^2\} - \right.$$

$$\left. dv^2 \exp(-qv^2d^2)] \right/ \sum_{v=-\infty}^{\infty} (1 - 2qv^2d^2) \times$$

$$\exp(-qv^2d^2) \right\} \, di \quad (17)$$

with $q = 6/il^2$, while for a copolymer $s = 12(il)^{-2}$, $t = 0$, and $u = (i)^{-1}$ and for a homopolymer $s = 12a\pi^{-1/2}(il^2)^{-1}$, $t = {}^3/_2$, and $u = a^2(i)^{-2}$. For neither of these two cases does the integration over i have an analytic solution. For a copolymer numerical evaluation of the integrand shows that the integration over i is satisfactorily performed with $0.1\bar{i} < i < 10\bar{i}$. This is due to the factor $\exp(-iu)$ with $u = (\bar{i})^{-1}$. For a homopolymer, however, u is proportional with $(\bar{i})^{-2}$ and this causes the integral to be very slowly convergent until $i \cong (\bar{i})^2$. Now, numerical integration is very unattractive but fortunately an analytic approximation is close at hand.

The fact is that we reasonably can neglect for the moment the sum in the denominator for eq 17, for we are mainly interested in cases when $d/\sqrt{\bar{i}l^2} > 1$ and then this sum has values between 0.95 and 1. Putting the denominator equal to 1 we can solve the integration over i and the summation in the numerator over v and we get

$$\hat{\rho}_a = bP\{\exp(-xb/2) -$$

$$\exp(-bd + bx/2)\}^2\{1 - \exp(-bd)\}^{-2} \quad (18)$$

where $b = 2a\sqrt{6}/\bar{i}l$ and P is introduced to account

for the normalization necessary due to the neglect of the sum in the denominator. P is easily found from $\int_0^d \hat{\rho}_a dx = 1$ to be

$$P = \{1 - \exp(-bd)\}^2 /$$

$$\{1 - 2bd \exp(-bd) - \exp(-2bd)\} \quad (19)$$

For $d \to \infty$, $P \to 1$ and eq 18 gives the exponential decrease of ρ with x as found before (eq 5 in ref 12).

Now we have expressions for $\hat{\rho}_a$ for the case of equal tails (eq 14), equal loops (eq 16), and for the loop size distribution for an adsorbed copolymer (eq 17) and homopolymer (eq 18). Substitution of the results in eq 11 and subsequent numerical integration gives the osmotic repulsion between particles covered by these specific combinations of polymer chains. Only for a homopolymer an analytic function is found after substitution of eq 18 in eq 11 and subsequent integration

$$M(\bar{i},d) = 2a(6/\bar{i})^{1/2}p[1 - 2bdp - p^2]^{-2} \times$$

$$[3bd - 7 + p(1 + 10bd - 2b^2d^2) +$$

$$p^2(7 - bd) - p^3] \quad (20)$$

where $p = \exp(-bd)$ and $b = 2a\sqrt{6}/\bar{i}l$.

For the case of equal loops and for $d/\sqrt{\bar{i}l^2} \geq 1$ a good approximation (deviations $<2\%$) for $M(i,d)$ is given by[32]

$$M(i,d) = (3\pi)^{1/2}\{6d^2/(il^2) - 1\} \exp(-3d^2/il^2) \quad (21)$$

In Figure 2 and with more precision in Table I the results are given for the dimensionless osmotic repulsion function $M(\bar{i},d)$ as a function of $d/\sqrt{\bar{i}l^2}$ for particles covered by equal tails, equal loops, and copolymers. Figure 2 shows also $M(\bar{i},d)$ for adsorbed homopolymers. As in Figure 1 the curves for the first three cases are independent of $\bar{i}$ whereas the curves for homopolymers depend on the particular choice of $\bar{i}$. Qualitatively, however, it can be used as representative for the osmotic effect with adsorbed homopolymers.

Both Figure 1 and 2 show that under comparable conditions, *i.e.*, an equal amount of polymer adsorbed and an equal average size ($\bar{i}$) per adsorbed chain, a cover of equal loops is less effective in preventing flocculation of the particles than a cover of loops adsorbed in an exponential size distribution as in the case of a copolymer. A cover of equal tails, however, gives even more repulsion and it is an obvious extrapolation to expect that an exponential tail size distribution would again be more effective. This order of effectivity is an completely in line with the density distribution curves shown be-

(31) For particles covered by loops and tails a combination of eq 14 and 15 is to be used. We shall not investigate this case.

(32) Putting $M(i,d) = \langle r^2 \rangle_1^{1/2} \int_0^d (\hat{\rho}_a)_\infty(\hat{\rho}_b)_\infty \, dx$ with $(\hat{\rho}_a)_\infty = 12x(il^2)^{-1}$ $\exp(-6x^2/il^2)$ as derived previously[11] (and as can be seen from eq 13) and leaving out some minor terms, eq 21 is found.
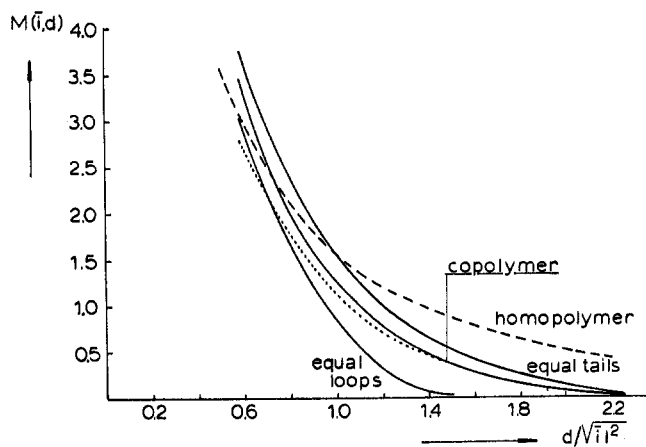
Figure 2. The dimensionless osmotic repulsion function
$M(\bar{\imath},d)$ (see eq 11) for several modes of attachment of the
macromolecules. Only the homopolymer curve depends on
$\bar{\imath}$; it is calculated for $\bar{\imath} = 10$. The dotted curve gives Meier's
results[5] for equal tails.

fore,[11,12] since the curve for tails extends farthest from
the adsorbing interface whereas the curve for equal
loops is the most compressed one and the curve for a
copolymer takes a middle position. This is also di-
rectly demonstrated by the root mean square extension,
$\langle x^2 \rangle^{1/2}$, of the segments from the interface, for in the case
of equal loops we have[12] $\langle x^2 \rangle_e = \bar{\imath}l^2/6$, for a copolymer
$\langle x^2 \rangle_c = \bar{\imath}l^2/3$, and for equal tails[11] $\langle x^2 \rangle_t = 7\bar{\imath}l^2/18$. Also
the curve for the homopolymer fits into this picture, for
the density distribution for an adsorbed homopolymer
falls off much less sharply than for the other cases (see
Figure 1 in ref 12), and now we find also that the repul-
sion works over a larger range. This suggests that
homopolymers might be very effective as stabilizers
for colloidal dispersions. This conclusion, however, is
liable to the same serious doubt as its "mother" equa-
tion 1. Another drawback of the use of homopolymers
is that ν, $\bar{\imath}$, and α cannot be controlled independently.

For the case of equal tails Meier[5] has also calculated
$M(\bar{\imath},d)$ (or actually $M(\bar{\imath},d)/9$ is tabulated in his Table
IV), but he used a density distribution which we showed
before[11] to be too compressed to the adsorbing interface.
Table II shows his values for $M(\bar{\imath},d)$ to be about 20–30%
too low.

Table II: Osmotic Repulsion Function, $M(\bar{\imath},d)$, for
Equal Tails According to Meier,[5] M (Meier), and
to the Present Paper, M(HVO)

$d/\sqrt{\bar{\imath}l^2}$	M (Meier)	M (HVO)	$\dfrac{M\ (\text{Meier})}{M\ (\text{HVO})}$
0.4	4.995	6.313	0.79
0.6	2.780	3.723	0.75
0.8	1.809	2.397	0.75
1.0	1.161	1.585	0.73
1.2	0.738	1.043	0.71
1.4	0.459	0.667	0.69

Interaction

According to the classical picture of colloid stability[2,3]
particles in a medium attract each other due to van der
Waals–London forces. The free energy of attraction
per unit area between two flat particles is given by

$$\Delta F_A = -A/12\pi d^2 \qquad (22)$$

where A is the Hamaker constant. This equation
neglects effects of electromagnetic retardation, of ad-
sorbed polymer layers,[33] and of the finiteness of the
particle thickness. In this paper we are mainly in-
volved in deriving a correct theory for the repulsion
between two particles due to adsorbed macromolecules,
and therefore we will use eq 22 anyhow for the attrac-
tion between the particles.

The change in free energy, ΔF, per unit area when
two particles approach each other is now found by
adding the repulsion terms ΔF_{VR} and ΔF_M and the
attraction term ΔF_A or

$$\Delta F = \Delta F_{VR} + \Delta F_M + \Delta F_A \qquad (23)$$

Substitution of eq 6, 10, and 22 in eq 23 gives

$$\Delta F = 2\nu k TV(\bar{\imath},d) + 2(2\pi/9)^{1/2}\nu^2 kT \times$$
$$(\alpha^2 - 1)\langle r^2 \rangle M(\bar{\imath},d) - A/12\pi d^2 \qquad (24)$$

Thus the main parameters determining the change in
free energy on the approach of the two particles are:
a, the average number of segments per loop (tail), $\bar{\imath}$,
or rather the mean square loop size $\bar{\imath}l^2 = \langle r^2 \rangle_0 \alpha^2$ in
which $\langle r^2 \rangle_0$ is proportional to the molecular weight, M,
of the loops; b, the number of adsorbed loops (tails)
per unit area of surface, ν, here expressed in grams of
adsorbed polymer, ω, with $\omega = \nu M/N_a$ (N_a is Avo-
gadro's constant); c, the quality of the solvent, χ, here
expressed in the expansion α whereas α and χ are con-
nected by eq 9; d, the mode of attachment of the
macromolecules; e, the Hamaker attraction constant.

We will evaluate eq 24 for a number of cases with
polystyrene as the adsorbed polymer. We choose M
between 10^3 and 10^5. For long-chain polystyrene
Berry[34] has found from light-scattering experiments
$\langle s^2 \rangle_0/M \cong 7.5 \times 10^{-18}$ cm² where $\langle s^2 \rangle_0^{1/2}$ is the radius of
gyration in a θ solvent of a free chain with molecular
weight M. With[17,35,36] $\langle r^2 \rangle_0 = 6\langle s^2 \rangle_0$ we then have ad-
sorbed chains with a root mean square end-to-end dis-
tance in solution between 21.2 and 212 Å. We take
the amount adsorbed ω between 10^{-10} and 5×10^{-7}

(33) M. J. Vold, *J. Colloid Sci.*, **16**, 1 (1961); B. W. Ninham and
V. A. Parsegian, *J. Chem. Phys.*, **52**, 4575 (1970).

(34) G. C. Berry, *ibid.*, **44**, 4550 (1966).

(35) Of course, the use of the factor 6 in the relation between $\langle r^2 \rangle_0$
and $\langle s^2 \rangle_0$ and the extrapolation of Berry's result to such low values
of M is not without question because of the deviations[36] of short
chains from random walk behavior. However, our whole argument
is based on random walk behavior, and therefore it is not incon-
sistent to use this approximation.

(36) H. Sotobayashi and J. Springer, *Advan. Polym. Sci.*, **6**, 473
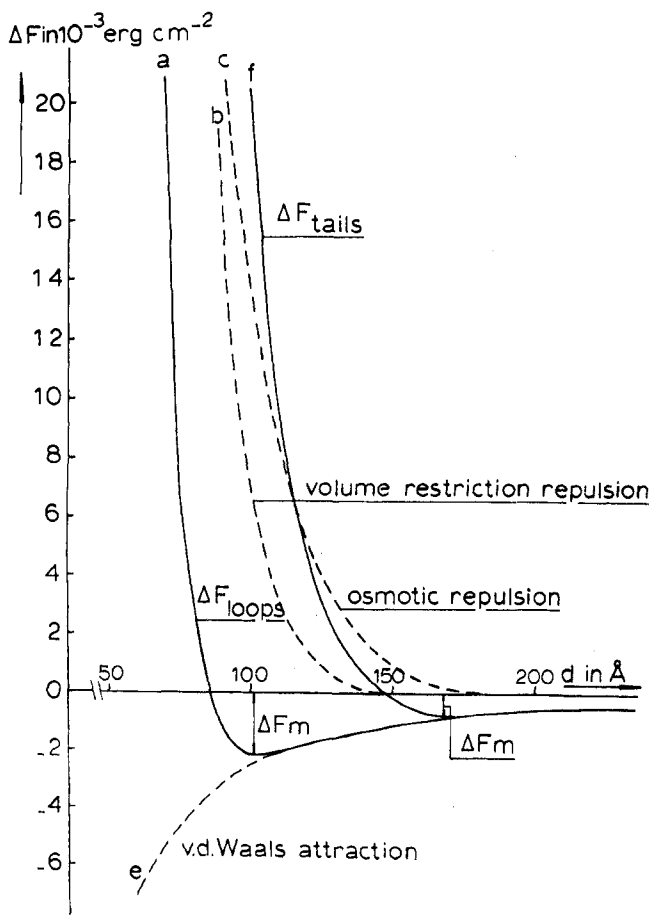(1969).

Figure 3. The free energy of interaction vs. the distance between particles covered by equal tails (curve f) and equal loops (curve a). For particles covered by equal tails b gives the volume restriction effect and c the osmotic repulsion; f is the result of the adding up of b, c, and the van der Waals attraction (e). ΔF_m is the depth of the minimum. The curves are calculated for $A = 10^{-13}$ erg, $\alpha = 1.2$, $\omega = 2 \times 10^{-8}$ g cm^{-2}, $M = 6000$ (then $\langle r^2 \rangle_0^{1/2} = 52$ Å and the area per chain = 5000 Å^2).

g cm^{-2} and the quality of the solvent[37] between $\alpha = 0.9$ (very poor solvent) and $\alpha = 1.6$ (good solvent). The Hamaker constant is varied between 3×10^{-14} and 3×10^{-12} erg. In the next section we show some of the results mainly for adsorbed tails. The behavior of adsorbed loops and copolymers is then found by comparison having in mind Figures 1 and 2.

Results and Discussion

Figure 3 illustrates the procedure to find the interaction curve for two particles covered by adsorbed macromolecules from the attraction and the two repulsion terms in eq 24. Curve f is found by adding the curves b, c, and e; it is the free-energy curve for two flat particles covered by equal tails. Curve a is the interaction curve found in an analogous way for particles covered by equal loops. These curves are typical for the stabilization of dispersions by adsorbed macromolecules. At large values of d the van der Waals

attraction is predominant, but at shorter distance a very steep repulsion prevents further approach. Unlike the case of electrocratic colloids,[3] we find only one minimum even at very low surface coverage ($\omega = 10^{-10}$ g cm^{-2}); the van der Waals attraction may then be predominant over the whole range of d up to very short distances. The osmotic repulsion curve c starts at higher values of d than the curve for the volume restriction. This makes sense because osmotic repulsion starts at the incipient overlap of the polymeric clouds, whereas volume restriction starts when the cloud is hindered by the approaching particle.

The depth ΔF_m of the minimum in the free-energy curve determines the stability of the colloidal state.[38,39] This minimal free energy per cm^2, ΔF_m, multiplied by the area of interaction h^2 (for flat particles with an edge h), is to be compared with the thermal energy of the particles. When $h^2 \Delta F_m < kT$, the particles will not adhere but they will remain single kinetic units, i.e., a stable dispersion. When $h^2 \Delta F_m > kT$, they will have a tendency to adhere and thus to form structures in solution. When this tendency is small, e.g., $kT < h^2 \Delta F_m < 5kT$, simple stirring of the solution may redisperse the particles. Such systems are called thixotropic, and already Freundlich[38] gave an explanation of thixotropy on the basis of free-energy curves of the same general shape as those shown in Figure 3. This thixotropic effect is often found (and essential) in pigment dispersions stabilized by resinlike material.[40] When $h^2 \Delta F_m > 5kT$, the particles will remain together and the system is flocculated. This means that flat, square particles with an edge h of 0.1 μm are stabilized when $\Delta F_m < 5kT/h^2 = 2 \times 10^{-3}$ erg cm^{-2}. Thus for the case illustrated in Figure 3 particles covered by tails are stabilized whereas particles covered by loops under otherwise equal conditions are flocculated. For particles with $h = 0.2$ μm stabilization is found at $\Delta F_m \leq 5 \times 10^{-4}$ erg cm^{-2}. Thus in Figure 3 both loops and tails give insufficient stabilization for such particles. Figure 4 shows that a twofold increase in the linear dimension of the particles requires a fourfold increase in the average tail size to ensure stabilization. This influence of particle size on the stability of dispersions stabilized by polymeric layers was already pointed out by Koelmans.[41]

For spherical particles with radius b large compared to the thickness of the adsorbed layer, the free energy

(37) With Berry's result the relationship between α and χ (eq 9) can be approximated for polystyrene to $\alpha^3(\alpha^2 - 1) = 0.11(^1/_2 - \chi)M^{1/2}$ so that for a good solvent ($\chi = 0.4$) we find $\alpha > 1.2$ for $M > 4000$ (e.g., $\alpha = 1.4$ for $M = 50,000$) whereas for a poor solvent ($\chi = 0.49$) we find $\alpha \leq 1.1$ for $M \leq 10^5$ (e.g., $\alpha = 1.05$ for $M = 10^4$).

(38) H. Freundlich, "Thixotropy," Hermann & Cie., Paris, 1935.

(39) H. C. Hamaker, Recl. Trav. Chim. Pays-Bas, 56, 727 (1937).

(40) F. K. Daniel, VII Fatipec Congress, 1964, p 280.

(41) H. Koelmans, Dissertation, Utrecht, 1955; H. Koelmans and J. Th. G. Overbeek, Discuss. Faraday Soc., 18, 52 (1954).
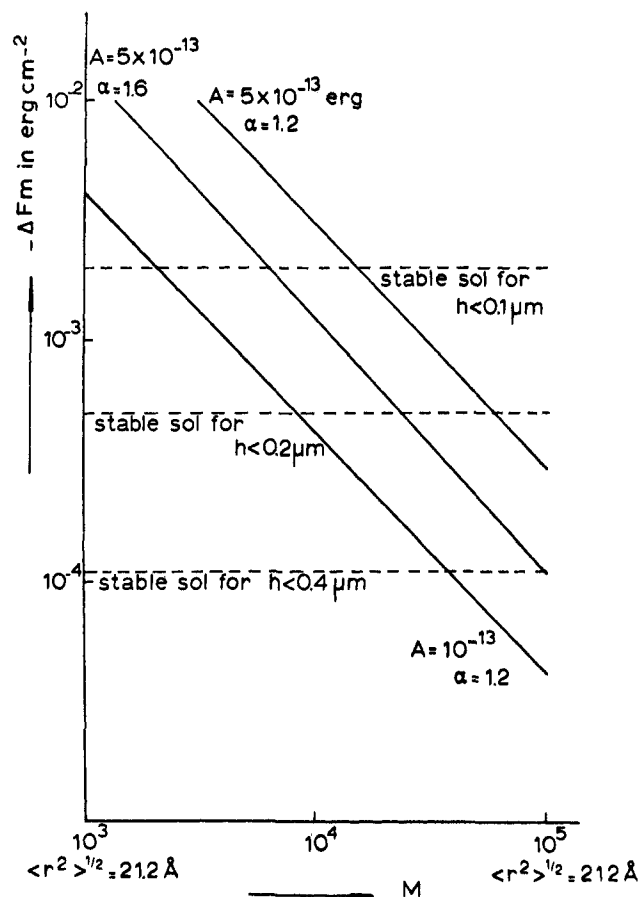
Figure 4. The depth $-\Delta F_m$ in the interaction curve as a function of the molecular weight of the adsorbed tails for $\omega = 2 \times 10^{-8}$ g cm^{-2}. The stability of the colloidal system is determined by the value of $h^2 \Delta F_m$ compared to kT. For $M = 1000$, $\langle r^2 \rangle_0^{1/2} = 21.2$ Å and for $M = 10^5$, $\langle r^2 \rangle_0^{1/2} = 212$ Å.
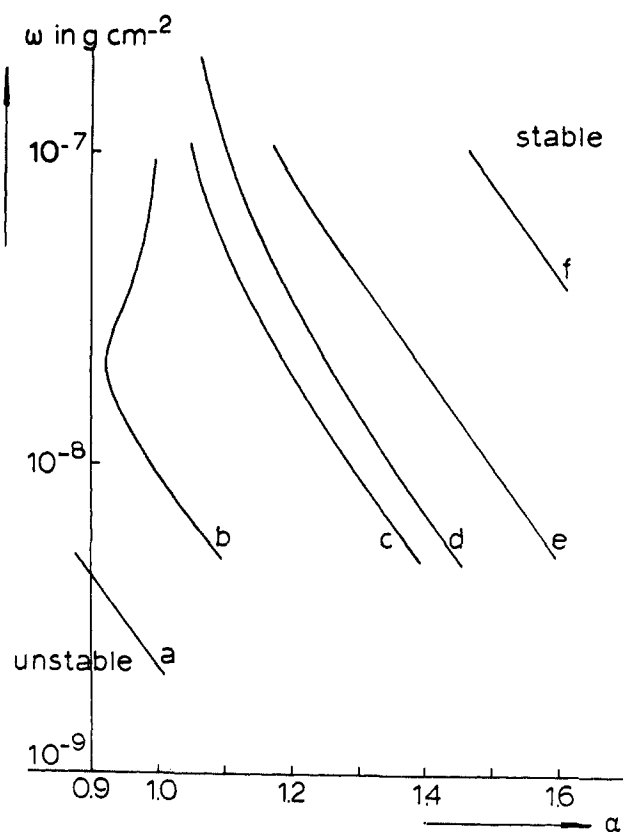

Figure 5. Dependence of the stability on the quality of the solvent and on the amount of polymer adsorbed for some values of the Hamaker constant, of the average molecular weight per tail, and of particle size. To the right of the stability curve the system is stable, to the left it is flocculated. (a), $A = 10^{-13}$ erg, $M = 10^4$, $h = 0.1$ μm; (b), $A = 5 \times 10^{-13}$, $M = 6 \times 10^4$, $h = 0.1$; (c), $A = 10^{-13}$, $M = 10^4$, $h = 0.2$; (d), $A = 10^{-13}$, $M = 2000$, $h = 0.1$; $A = 5 \times 10^{-13}$, $M = 6 \times 10^4$, $h = 0.2$; (e), $A = 5 \times 10^{-13}$, $M = 10^4$, $h = 0.1$; (f), $A = 5 \times 10^{-13}$, $M = 10^4$, $h = 0.2$.

of interaction can be calculated using Derjaguin's[42] procedure to be porportional with b (see Appendix). Thus for spherical particles the influence of particle size will be less dramatic than for flat particles, since for spheres the stability is inversely proportional with b, whereas for flat particles it is inversely proportional with h^2. Napper's experiments[43a] on the stability of dispersions in heptane containing particles of polyvinyl acetate (PVAc) and polymethylmethacrylate (PMMA) stabilized by oleophilic chains with some PVAc or PMMA anchor segments and of PVAc[43b] dispersions in aqueous solution stabilized by polyethylene oxide (PEO) chains indeed show a decrease in stability with increasing particle size, just as Toole, et al.,[44] found for a phthalocyanine blue pigment dispersion stabilized by alkyd resins[45] in an oil medium.

The two upper curves in Figure 4 show the influence of the solvent on ΔF_m. In Figure 5 the dependence of the stability on the quality of the solvent (α) and on the amount of polymer adsorbed (ω g cm^{-2}) is shown. These curves represent cases where $h^2 \Delta F_m \cong 5kT$. To the right of these curves the systems are stable

$(h^2 \Delta F_m < 5kT)$, to the left unstable $(h^2 \Delta F_m > 5kT)$. Figure 5 shows that with decreasing α the stability decreases. Napper[43] found indeed that instability was induced by decreasing the solvent power of the dispersion medium for the stabilizing moieties. Incipient flocculation occurred in media which were either θ solvent ($\alpha = 1$) or which were only of somewhat better solvent power than θ solvents. Heller and Pugh[46] have found that gold sols in aqueous solution stabilized by adsorbed PEO are flocculated by addition of KCl at a concentration of about 0.5 mol/l. Several[47,48] authors

(42) B. Derjaguin, Kolloid Z., 69, 155 (1934).

(43) (a) D. H. Napper, Trans. Faraday Soc., 64, 1701 (1968); (b) D. H. Napper, J. Colloid Interface Sci., 32, 106 (1970).

(44) J. Toole, J. S. F. Gill, and R. G. Tainturier, VII Fatipec Congress, 1964, p 289.

(45) W. Black, F. Th. Hesselink, and A. Topham, Kolloid-Z. Z. Polym., 213, 150 (1966).

(46) W. Heller and T. L. Pugh, J. Polym. Sci., 47, 203 (1960).

(47) Yu. M. Glazman, Discuss. Faraday Soc., 42, 255 (1966).

(48) K. G. Mathai and R. H. Ottewill, Trans. Faraday Soc., 62, 750 (1966).

have described the same phenomenon for other hydro-phobic sols (AgI, As_2S_3, latex) stabilized by a nonionic surfactant with a long PEO chain. This is completely in line with Napper's result because water becomes a poor solvent for PEO when the salt concentration comes in this range (salting-out effects). This same phenomenon is also demonstrated by van der Waarde's[49] finding that the equilibrium thickness of an aqueous film stabilized by a nonionic (PEO) surfactant decreases with increasing NaCl or urea concentration, especially at concentrations above 1 mol/l. Here the decrease of α is directly seen in a decrease of the film thickness.
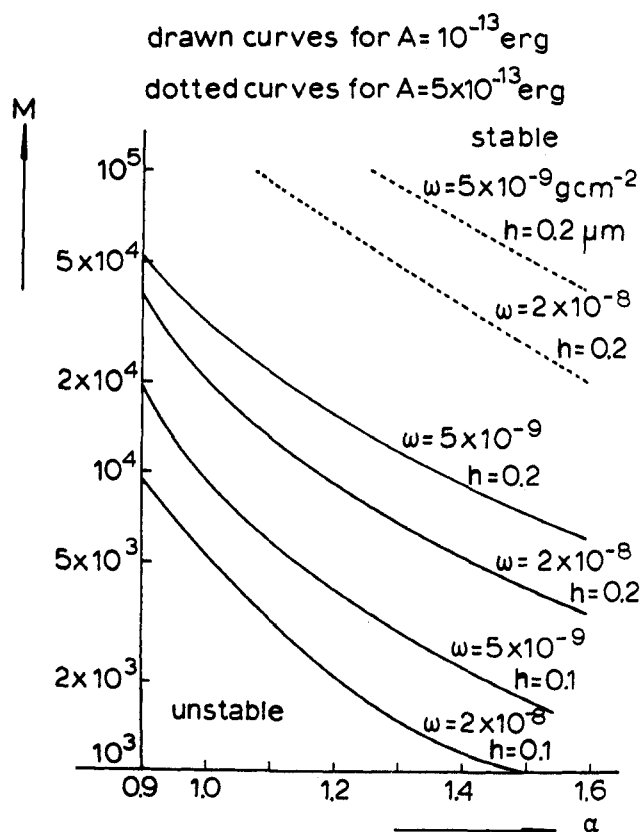

Figure 6. Dependence of the stability on the quality of the solvent (α) and on the average molecular weight per adsorbed tail.

Napper found that the flocculation brought about by decreasing the solvent power of the medium was a reversible process. The system redisperses when the quality of the solvent is restored. The reversibility of flocculation is a general consequence of interaction curves, as shown in Figure 3, which have only one minimum.

Figures 5 and 6 show that also in a good solvent instability can occur when the other stability-determining parameters (ω, M, A, h) are chosen too unfavorably. Curve b in Figure 5 shows an interesting extremum. For an intermediate value of the amount

adsorbed the solvency required for stabilization has a minimum at $\alpha < 1$. The osmotic effect causes an attraction at $\alpha < 1$ ($\Delta F_M < 0$, see eq 10), but at these intermediate values of ω the repulsion due to volume restriction prevails over both van der Waals attraction and osmotic attraction. This is also the reason that in Figure 6 stability is found at $\alpha = 0.9$ at high enough average tail size. At higher ω the stability line b in Figure 5 curves back to $\alpha = 1$, for with increasing ω the osmotic attraction at $\alpha = 0.9$ increases faster than the repulsion due to volume restriction because, as Meier[5] pointed out, ΔF_M is proportional with ω^2 whereas ΔF_{VR} is proportional with ω.

Figure 6 shows stability lines as a function of average tail size M and solvency of the medium α. The strong influence of M on the stability is understood from the notion that highly extended layers cause repulsion when the particles are far away from each other and the van der Waals attraction is still small. Heller and Pugh find indeed that PEO of $M = 9000$ is more effective than PEO of $M = 6000$ as a stabilizer for gold sols in aqueous solution. Napper,[43b] however, found that the stability of PVAc dispersions stabilized by PEO was relatively insensitive to the molecular weight of the stabilizing moieties. This difference might in part be due to their different method of measuring the stability (Heller and Pugh increase the salt concentration up to flocculation and Napper the temperature), but also, e.g., to changes in the average tail size due to extra adsorption. For Molau's[50] polymeric "oil in oil" emulsions—polybutadiene (PB)-polystyrene (PS) in benzene as common solvent stabilized by a two-block PB-PS copolymer with blocks of approximately equal size—the stability is found[50b] to increase, as we expected, very much with increasing size of the blocks.

In conclusion, we have a theory which gives a satisfactory description of protective action and which is in qualitative agreement with several known aspects of protection. Notable shortcomings of the theory are the a priori assumption of the macromolecules being adsorbed on only one particle and the unclear relation between χ and α. Protection by adsorbed homopolymers is not a completely solved problem because of the unreliability of eq 1. Experiments to test the stability of protected sols on systematic variations of the various stability-determining parameters (ω, M, α, A, h) are desirable. Adsorption studies on variations of ω, M, and α (or χ) could give useful additional information.

(49) K. M. van der Waarde, private communication, 1968.
(50) (a) G. E. Molau, J. Polym. Sci., A3, 1267, 4235 (1965);   (b) G. E. Molau, Kolloid-Z. Z. Polym., 238, 493 (1970).

Appendix

Derjaguin[42] considered the repulsive energy between two spheres in a first approximation to be formed by the contributions of infinitesimal small rings parallel to each other at a distance d. The repulsive free energy between two parallel rings covered by adsorbed macromolecules is approximately given by $\Delta F_{VR} + \Delta F_M$. The free energy of repulsion between two spheres of radius b at a minimal distance d_0 (the distance between the centers of the spheres being $2b + d_0$) is then found by integration.[51] The value of the integral does not

$$V_R = 2\pi b \int_{d_0}^{\infty} (\Delta F_{VR} + \Delta F_M) \, dd$$

depend on b, so that V_R is proportional with b. The van der Waals attraction energy between two spheres is also proportional with b, so that the total free energy of interaction is proportional with b. The stability of the colloidal system is determined by the minimum in the free-energy curve, and of course also this minimal value of the interaction energy is proportional with b.

(51) Reference 3b, Chapter IX, eq 54.

The Adsorption of Fibrinogen. An Electron Microscope Study[1]

by R. R. Gorman, G. E. Stoner,* and A. Catlin

Department of Materials Science, University of Virginia, Charlottesville, Virginia 22901 (Received September 25, 1970)

The process of adsorption of fibrinogen onto mica and evaporated carbon has been characterized as completely diffusion controlled by the direct counting of individual molecules through the use of the electron microscope. As applied to adsorption on mica the method produced Hall and Slayter triad molecules, and the deposits were reproducibly and uniformly distributed over the specimens. Under the experimental conditions, the adsorption was strongly dependent on the composition of the substrate, and in the case of mica, it was insensitive to the composition of the suspending buffer.

Introduction

The adsorption of proteins and macromolecules from aqueous suspensions has been investigated by means of several experimental techniques, including streaming potentials,[2a] isotope and fluorescence labeling,[2b] depletion of suspension,[3] ellipsometry,[4] and visual observation in the electron microscope.[5] Fibrinogen adsorption is of special importance because of its unique configuration in the adsorbed stage, its strong tendency to adsorb, and its possible involvement in the initial stages in the interaction of human blood *in vivo* with devices such as artificial heart valves and arteries.[2b,6,7]

The objective of this investigation was to characterize the adsorption of fibrinogen onto muscovite mica and evaporated carbon at short adsorption times from a dilute, unstirred suspension of the protein molecules, and to investigate the effect of the properties of the suspending buffer on the adsorption. An additional objective was to establish a methodology which could be applied to other proteins and solids. The method was the visualization of the adsorbed protein molecules in the electron microscope and the obtaining of kinetic

data by direct counting of the individual adsorbed molecules.

Materials and Equipment

The bovine fibrinogen was the diagnostic product of the General Diagnostics Division of Warner-Chilcott, packaged in vials as 6 mg of clottable protein, 17 mg of sodium chloride.

The human fibrinogen was prepared in this labora-

(1) This work supported by the National Institutes of Health under Grant DE 02111-07.

(2) (a) R. D. Falb, G. A. Grode, M. M. Epstein, B. G. Brand, and R. I. Leininger, June 29, 1965. P. B. 168, 861, U. S. Dept. of Commerce; (b) R. D. Falb, G. A. Grode, M. T. Takshashi, and R. I. Leininger, March 30, 1967. P. B. 175, 668, U. S. Dept. of Commerce.

(3) A. D. McLaren, *J. Phys. Chem.*, **58**, 129 (1954).

(4) L. Vroman, "Blood Clotting Enzymology," W. H. Seegers, Ed., Academic Press, New York, N. Y., 1967, p 279.

(5) D. Lang and P. Coates, *J. Mol. Biol.*, **36**, 137 (1968).

(6) L. Vroman, *J. Biomed. Mater. Res.*, **3**, 669 (1969).

(7) D. J. Lyman, J. L. Brash, and K. G. Klein, Proceedings of the Artificial Heart Conference, R. J. Hegyeli, Ed., Washington, D. C., 1969, pp 113-122.