NOTES

An Alternative Interpretation of Flocculation of Dispersions by Preferential Adsorption of Solvents from Polymer Solution

INTRODUCTION

It was shown in a previous study[1] that the flocculation of a dispersion is enhanced by preferential adsorption of solvents from polymer solution (negative adsorption of polymer). A theory to account for this mechanism was proposed recently by one of the authors[2] based on the assumption that the adsorption is irreversible and the solvation layers on particles are impenetrable. The result showed that the energy of osmotic attraction between two solvated particles is large enough to overcome the energy of the electrostatic repulsion between the particles.

An alternative theory is proposed in this note to account for the adverse effect of negative adsorption of polymer based on the assumption that the adsorption is reversible and the solvation layers are mutually penetrable by each other on approach of the particles. This assumption is more likely to occur in the system studied by Sato[1] than the previous assumption,[2] leading to osmotic attraction.

THEORY

A negative adsorption of polymer onto particle occurs when the solvents are preferentially adsorbed on the particle. The particles are thereby shielded by solvation layers in which no solute molecule exists. When the two such solvated particles approach one another so that the solvation layers overlap, the volume of solvent available to the polymer is increased, assuming that desorption of solvents takes place. The increase in the volume of solvent is equal to the volume of the overlapping region in Figure 1. The maximum overlap will occur when the two particles touch. The free energy change of the system due to dilution can be expressed as a virial equation

$$-\Delta G = NkT(C/M_2 + B_2C^2 + B_3C^3 + \cdots)\Delta V \tag{1}$$

where N is Avogadro's number, C is the polymer concentration (g/ml), M_2 is the molecular weight of the polymer, and ΔV is the volume change of the overlapping region resulting from a change in the separation distance H_0. If the solution is diluted and the molecular weight of the solute molecule is small, eq. (1) is approximated by

$$-\Delta G = NkTC\Delta V/M_2 \tag{2}$$

If the molecular weight of the polymer is very large, eq. (1) is approximated by

$$-\Delta G = NkTB_2C^2\Delta V \tag{3}$$

The change in the overlap volume with separation distance H_0 can be obtained from the geometry of the system as

$$\Delta V = (2\pi/3)(\delta - H_0/2)^2(3r + 2\delta + H_0/2) \tag{4}$$

where δ is the thickness of solvation layer and r is the radius of the particle. Substituting eq. (4) into (2) or (3), one obtains

$$-\Delta G = \frac{2\pi NkTC}{3M_2}\left(\delta - \frac{H_0}{2}\right)^2\left(3r + 2\delta + \frac{H_0}{2}\right) \tag{5}$$

or

$$-\Delta G = \frac{2\pi NkTB_2C^2}{3}\left(\delta - \frac{H_0}{2}\right)^2\left(3r + 2\delta + \frac{H_0}{2}\right) \tag{6}$$

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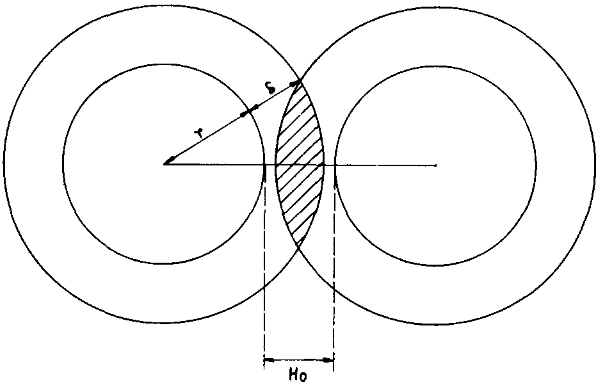

Fig. 1. Model for calculation of repulsion energy between two spherical solvated particles.

Expression (6) is similar to that derived by Fischer[3] for an osmotic repulsive energy between two particles which are shielded by the adsorbed polymer layers.

In order for the solvation layers to overlap, however, the solvent molecules must be desorbed. This desorption costs free energy. The molecules in the multilayer are considered to be physically adsorbed except for the molecules in the first layer. According to the Polanyi treatment, the potential of the molecules in the multilayer decreases exponentially with the distance from the surface.[4] In the physical adsorption, the diffusion owing to the thermal agitation must be taken into account, since the energy owing to the thermal agitation is of the same order of magnitude as that of physical adsorption. The thermal agitation tends to diffuse the solvent molecules throughout the solution and tends to prevent the formation of physical adsorption layer. Therefore, the formation of the solvation layer and desorption is the result of competition between the adsorption and the thermal agitation. Each molecule in the solution possesses the same kinetic energy at a given temperature, which is given by $1kT$.

Therefore, the thermal energy ΔG_{the} is given by

$$\Delta G_{\text{the}} = (\Delta V/V)NkT \tag{7}$$

where V is a molar volume of solvent molecule and N is Avogadro's number. For isopropyl alcohol, $V = 76.1$, then

$$\Delta G_{\text{the}} = 0.013RT\Delta V \tag{8}$$

In order for the solvation layers to be overlapped, the sum of free energy change owing to dilution and thermal agitation must be greater than adsorption energy.

If the isosteric adsorption energy of the solvent molecule is q_1 (cal/mole), the energy required to desorb the molecules from the solvation layer is given by

$$\Delta G_{\text{des}} = (\Delta V/V_1)q_1 = 0.013q_1\Delta V \tag{9}$$

The condition for the desorption is given by

$$\Delta G_{\text{dil}} + \Delta G_{\text{the}} \geq \Delta G_{\text{des}} \tag{10}$$

$$RTC(\Delta V/M_2) + 0.013RT\Delta V \geq 0.013q_1\Delta V \tag{11}$$

For polyamide C, $M_2 = 900$.

By solving eq. (11), we get

$$q_1 \geq 603 \text{ cal/mole}$$

Therefore, if the energy of adsorption of the solvent molecule is less than 603 cal/mole, the solvation layer can be overlapped. It is likely that the adsorption energy of multilayer is less than 600 cal/mole. It appears that the desorption of solvent molecules can take place by the collision of the solvated particles.

TABLE I
Data for Various Polymers

Solute polymer[a]	Molecular weight	Polymer concentration (g/ml)	Thickness of solvation layer[b] (Å)	Stability of dispersion[c]
Polyamide A	3000	0.05	85	fair
Polyamide C	900	0.05	175	very poor
Polyamide E	500	0.05	187	very poor

[a] The characteristics are shown in ref. 1.
[b] Calculation is given in ref. 2.
[c] Experimentally determined in ref. 1.

RESULTS

The above-mentioned theoretical treatment was applied to the previous experimental data[1] to account for the adverse effect of negative adsorption of polymers on the stability of dispersion. The polymers, pigment, and solvent used were fatty polyamides, red iron oxide, and isopropyl alcohol, respectively. The polymer concentration, the molecular weight, and the thickness of solvation layer in various polymers are given in Table I. The radius of the particle is 500 Å. It is interesting to note that the thickness of the solvation layer is dependent upon the nature of the polymer in the solution although no solute molecules exist in the layer. This indicates that the extent of adsorption of solvent from the polymer solution depends not only on the solvent-adsorbent affinity, but also on the balance of three interactions: solvent/adsorbent, adsorbent/polymer, and polymer/solvent. The free energy owing to dilution on a collision of the two solvated particles was calculated using eq. (5), since the molecular weight of polyamides used in this work is fairly small. The electrical repulsive energy between the particles in the isopropyl alcohol solution of polyamide C was calculated by using eq. (12) (refs. 5–7):

$$\Delta F_{\mathrm{el}} = \frac{\epsilon r^2 \xi^2}{H_0 + 2r} \tag{12}$$

where ϵ is the dielectic constant of liquid (18.6 at 20°C) and ξ is the zeta potential of particle. The zeta potential of the particle was found to be +30 mV in the previous work.[1] At normal temperature, $1kT = 4.1 \times 10^{-14}$ erg $= 10^{-21}$ cal. Figure 2 shows the change in the attractive and the repulsive

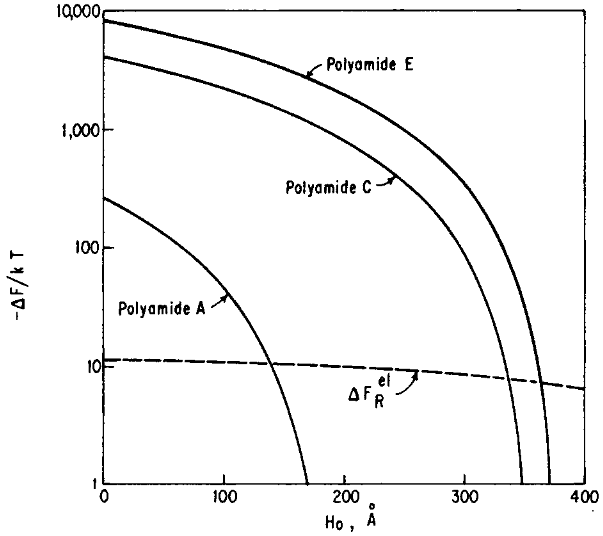

Fig. 2. Potential energy between solvated particles in various polyamide solutions vs. distance of separation.

potential energies with the separation distance. Both the attractive and the repulsive energies are shown in the same quadrant on the graph although the signs are opposite. The figure shows that the energy of attraction caused by dilution of polymer is large enough to overcome the electrostatic repulsive energy. The greater attractive energies in the solutions of polyamides C and E than that of polyamide A accounts for the greater flocculation tendency in the solutions of polyamides C and E.

It is concluded from the foregoing that the flocculation caused by negative adsorption of polymer can be accounted for by the attractive energy caused by dilution of polymer.

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