

# Flocculation of Dispersions by Preferential Adsorption of Solvents from Polymer Solution

TATSUO SATO, *Metal Coatings Division, Diamond Shamrock Corporation, Chardon, Ohio 44024*

## Synopsis

An attempt was made to account for the adverse effect of the preferential adsorption of solvents onto particles from polymer solution (negative adsorption of polymer) on the stability of a dispersion in terms of osmotic attraction. The change in the energy of osmotic attraction on collision of solvated particles in a solution of macromolecules was calculated as a function of an osmotic pressure of the media, the thickness of the solvation layers, and the size of solute molecules, based on the assumption that the adsorption is irreversible and the adsorbed layers are impenetrable. The result showed that the energy of osmotic attraction is of the same order of magnitude as that of the electrostatic repulsion, indicating that the flocculation caused by the negative adsorption of polymers is mainly due to the osmotic attraction.

## INTRODUCTION

In a previous study<sup>1</sup> it was shown that the flocculation of a dispersion is enhanced by preferential adsorption of solvents from polymer solution (negative adsorption of polymers). A theoretical approach to the mechanism of the stabilization effect, as a function of the adsorption of polymers, has been reported by several investigators.<sup>2-7</sup> No work, however, has appeared on the effect of negative adsorption of polymers on the dispersion.

This work was initiated for the purpose of accounting for the adverse effect of negative adsorption on the stability of a dispersion in terms of osmotic attraction. The change in the potential energy was calculated on the assumption that the solvation layers should be impenetrable and not be distorted by the collision of particles. The magnitude of the calculated potential energy was compared with that of electrostatic repulsive energy to observe the effect of osmotic attraction.

## THEORY

A preferential adsorption of solvent molecules on the particles from polymer solution results in an increase in polymer concentration in the bulk of the solution. The particles are shielded by solvation layers in which none of solute molecules exists. If the solvated particles approach so close together that the distance between two solvation layers becomes smaller than the diameter of solute molecules, there appears a space between the particles into which solute molecule can enter (see Fig. 1). Then this region becomes a phase of pure solvent. Therefore, interaction takes place between the particles because of the difference in polymer concentrations between the inside and outside of the particles. A force equivalent to the osmotic pressure of the solution acts inwards on each particle.

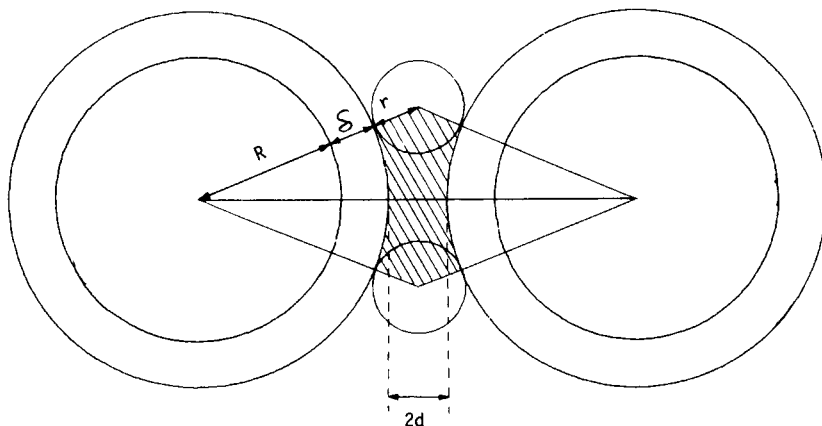


Fig. 1. Model for calculation of osmotic attraction between two solvated particles in a solution of spherical macromolecules.

When the medium is very dilute and the solute is monodisperse, the force  $P$  between two bodies in the medium can be given by<sup>8,9</sup>

$$P = kTN \frac{\partial \ln Q}{\partial H} = \frac{\partial E}{\partial H} \quad (1)$$

where  $E$  denotes the change in free energy with the approach of the particles,  $N$  is the total number of solute molecules,  $Q$  is the partition function of the system, and  $H$  is the distance between the two particles.

Applying the formula to the case of a collision of two spherical particles of radius  $R$ , each of which has a solvation layer of thickness  $\delta$ , as shown in Figure 1, the force is expressed as a function of the distance of approach. The area of the plane of intersection is given by

$$\pi[(R + \delta + r)^2 - (R + \delta + d)^2] = \pi(r - d)(2R + 2\delta + r + d) \quad (2)$$

Therefore the force between two particles is given by

$$P = -p_o \pi(2R + 2\delta + r + d)(r - d) \quad \times 0 \leq d \leq r \quad (3)$$

where  $p_o$  is the osmotic pressure of the medium,  $d$  is the distance between the surface of the solvation layer and the center of separation distance, and  $r$  is the radius of the solute molecules. When the interparticle distance  $2d$  equals the diameter of the solute molecule  $2r$ ,  $P$  vanishes, since there is no region of pure solvent phase in this condition. The change in attractive energy between the solvated particles as they approach is obtained by integrating  $p$  over the separating distance:

$$E(d) = 2 \int_d^r P dH = \frac{-2}{3} \pi p_o (r - d)^2 \{2r + d + 3(R + \delta)\} \quad (4)$$

Since  $3(R + \delta) \gg 2r + d$ , eq. (3) can be approximated by

$$E(d) = 2\pi p_o (r - d)^2 (R + \delta) \quad (5)$$

The change in the force and the energy of attraction with the distance of approach are illustrated in Figure 2.

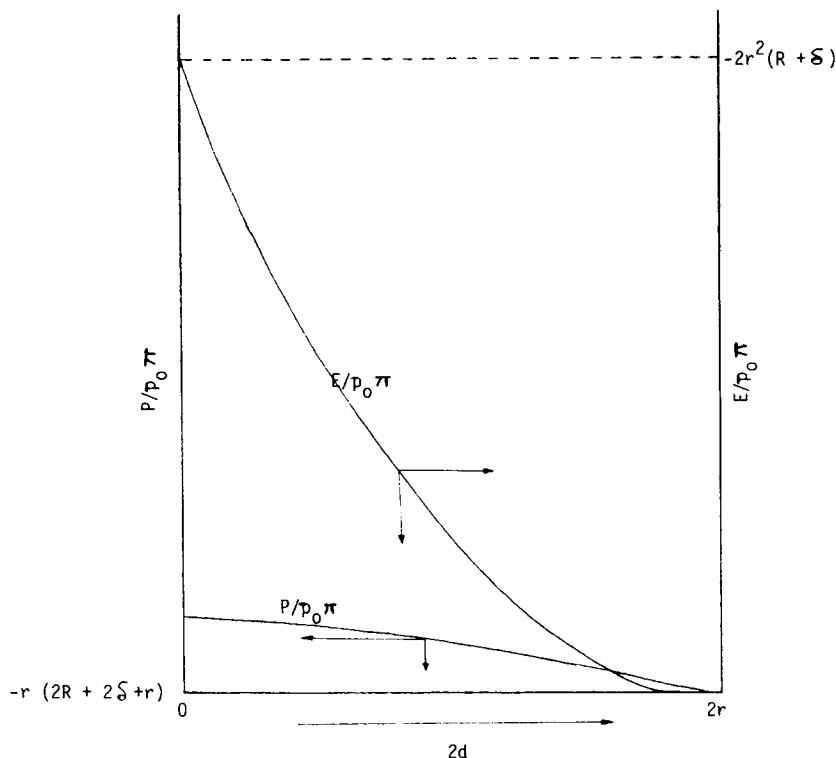


Fig. 2. Change in force and energy of osmotic attraction between two solvated particles upon their approach.

### COMPUTATIONS

If the concentration of polymer in the bulk of the solution has increased from  $C$  (g/ml) to  $C'$  by the negative adsorption of polymers, the volume of solvent adsorbed onto the surface of particles from a unit volume of the solution is given by  $1 - (C/C')$ .

Assuming that the dispersion is comprised of monodispersed spherical particles and that these particles are evenly covered with solvent molecules, the thickness of the layer is obtained by solving the following equation for  $\delta$ :

$$\frac{4}{3} \pi [(R + \delta)^3 - R^3] = \frac{4R^3 D}{3} \frac{1 - (C/C')}{W} \tag{6}$$

where  $W$  is the weight of total particles per unit volume of the solution and  $D$  is the density of the particle. It should be noted that the amounts of negative adsorption of polymers reported up to date,<sup>1,10,11</sup> although very limited, are almost of the same order of magnitude as those for positive adsorption. This indicates that the thickness of the solvation layers, due to the negative adsorption, is in general much greater than those of the layers of adsorbed polymers.

The osmotic pressure  $p_o$  of polymer solution is given by

$$p_o/C = RT(1/M_2 + BC)$$

where  $B$  is a second virial coefficient and  $M_2$  is the molecular weight of the polymer. If the solution is dilute and the molecular weight of the solute molecule is small, the osmotic pressure of the solution obeys van't Hoff's equation

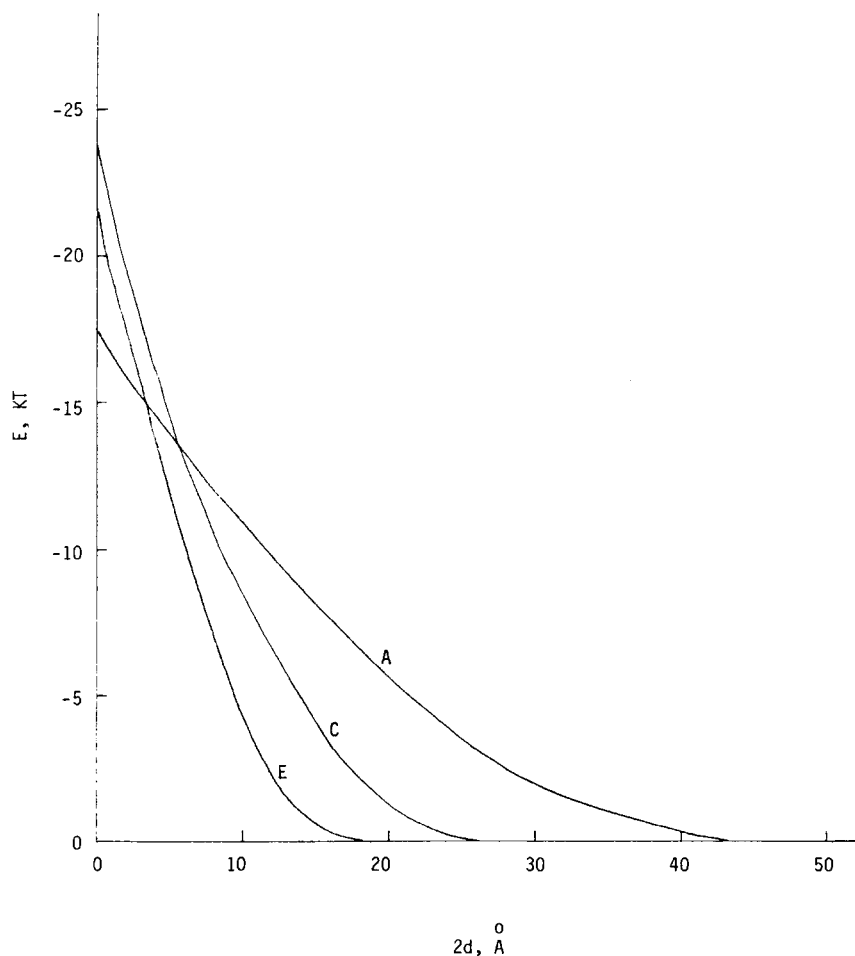


Fig. 3. Potential energy of osmotic attraction between solvated particles vs distance between surfaces of solvation layers.

$$p_o/C = RT/M_2 \quad (7)$$

Therefore, the osmotic attraction energy is given by

$$\frac{E}{kt} = \frac{2\pi CN(r-d)^2(R+\delta)}{M_2} \quad (8)$$

TABLE I  
Summary of Results of Calculation

Solute polymer <sup>a</sup>	Amount of negative absorption, mg/g	$\delta$ , $\text{\AA}$	$\langle r^2 \rangle^{1/2}$ , $\text{\AA}$	$p_o \times 10^{-19}$
Polyamide A	-6	85	22	1.0
Polyamide C	-15	175	13	3.3
Polyamide E	-16	187	9	6.0

<sup>a</sup> The characteristics are shown in ref. 1.

The mean size of an isolated polymer molecule in solution may be estimated from the intrinsic viscosity.<sup>12,13</sup> Flory's theory predicts that the intrinsic viscosity is related to the mean square radius of gyration,  $\langle r^2 \rangle$ , by

$$[\eta] = \Phi 6^{3/2} \langle r^2 \rangle^{3/2} / M_2 \quad (9)$$

where  $\Phi$  should be a universal constant independent of the nature of macromolecule and the solvent medium. Using the result of the calculation of Auen and Gardnen<sup>14</sup> or Zimm,<sup>15</sup>  $\Phi$  should have the value of  $2.1 \times 10^{-21}$ .

## RESULTS

The above-mentioned theoretical treatment was applied to the previous experimental data to account for the adverse effect of negative adsorption of polymers on the stability of dispersions. The polymers, pigment, and solvent used were fatty polyamides, red iron oxide, and isopropyl alcohol, respectively. The amount of negative adsorption of polyamides, the thickness of solvation layers, the osmotic pressure of the media, and the size of macromolecules in solution were calculated and are given in Table I.

The potential energy of osmotic attraction under the conditions of the previous work ( $R = 500 \text{ \AA}$ ,  $C = 0.05 \text{ g/ml}$ ) is shown in Figure 3 as a function of the distance of approach of the particles. By referring to the previous results, it will be found that the energy of osmotic attraction is large enough to reduce the energy barrier of electrostatic repulsion to the order of the thermal energy. It must be concluded from the foregoing that the flocculation caused by the negative adsorption of polymers is mainly due to the osmotic attraction.

The author wishes to thank Dr. C. L. Sieglaff of Diamond Shamrock Corporation for his helpful discussions.

## References

1. T. Sato, *J. Appl. Polym. Sci.*, **15**, 1053 (1971).
2. E. L. Mackor, *J. Colloid Sci.*, **6**, 494 (1951).
3. A. L. Romo, *J. Phys. Chem.*, **67**, 386 (1963).
4. E. J. Clayfield and E. C. Lumb, *J. Colloid Interfac. Sci.*, **22**, 269 (1966).
5. R. H. Ottewill, *Non-ionic Surfactants*, Merce! Dekker, New York, 1967, Chap. 19.
6. D. H. Napper, *J. Colloid Interfac. Sci.*, **33**, 384 (1970).
7. A. Dorszkowski and R. Lambourne, *J. Polym. Sci.*, **C34**, 253 (1971).
8. F. Oosawa and S. Asakura, *J. Phys. Chem.*, **22**, 1255 (1954).
9. A. Asakura and F. Oosawa, *J. Polym. Sci.*, **3**, 183 (1958).
10. Y. Oyabu, *Hyomen* (Japan), **4**, 100 (1966).
11. G. D. Parfitt and E. Willis, *J. Phys. Chem.*, **68**, 1780 (1964).
12. G. J. Haward and P. McConnell, *J. Phys. Chem.* **71**, 2981 (1967).
13. H. Morawetz, *Macromolecules in Solution*, Interscience, New York, 1965.
14. P. L. Auer and C. S. Gardner, *J. Chem. Phys.*, **23**, 1546 (1955).
15. B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).

Received October 17, 1975

Revised April 28, 1978