

on thin-layer plates as described in the *Experimental* section. The DIH reagent was used because of its high reactivity toward carbonyl compounds (15, 16). Thermal degradation products of this ascorbic acid-silicic acid system are shown in Fig. 4. Examination of the chromatogram does indicate the absence of furfural, the possible presence of levulinic acid, and, in addition, other unidentified degradation products, and strongly suggests that ascorbic acid in this adsorbed state undergoes a different type of degradation from that in aqueous solution. Although furfural was not detected in this system, it is still possible that any furfural formed could have volatilized from the solid surface or undergone polymerization. It is highly unlikely, however, that levulinic acid results from furfural degradation, since Lamden and Harris (11) pointed out that the formation of furfural in solution degradation does not result from dehydroascorbic acid which, as mentioned before, is probably the first step in the oxidation of ascorbic acid in the adsorbed state. It is, therefore, highly likely that the degradation pathway in the adsorbed state may be quite different from that in solution.

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Electrostatic Interaction of Oil Droplets with Adsorbed Surface-Active Ions in Dilute Electrolyte Solutions

N. F. H. HO, A. SUZUKI*, and W. I. HIGUCHI

Abstract □ Using the Haydon-Taylor model in which the surfactant head groups are situated at some distance from the oil surface, the interaction energy of electrostatic repulsion (V_R) between oil droplets in dilute electrolyte solutions is derived for the two cases: constant-surface potential and constant-surface charge. For comparison, the repulsive energy is also derived for the constant-surface charge case without the effect of this adsorbed layer model. The Haydon-Taylor model accounts for the penetrability of the electrolyte and dielectric constant in the adsorbed surfactant layer of varying thickness, the degree of surface coverage, particle-size effect, ionic strength, and the dielectric constant in the bulk solution. In the constant-potential case, the resulting V_R equation is identical to the classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) one. Computations show that as flat plates and spheres approach each other, V_R (constant-surface charge with impenetrable adsorbed layer) > V_R (constant-surface charge with penetrable adsorbed layer) > V_R (constant-surface potential). Because of the possible 50- to 100-fold difference in magnitude between them, proper choice of the model is important when considering application of the theory to the rigorous kinetic treatment of the coalescence of o/w emulsions and flocculation of suspensions.

Keyphrases □ Oil droplets, electrostatic interaction—adsorbed surface-active ions □ Electrolyte solutions—oil droplets, adsorbed surface-active ion interaction □ Repulsive interaction—flat plates, spheres □ Emulsions—particle collision probability

In those dispersed systems in which the primary barrier to flocculation (or coalescence) is electrical, the classical theory of the repulsive interaction of overlap-

ping electrical double layers between two particles combined with the attractive interaction due to dispersion forces is used. Moreover, the usual model employed for the repulsive energy requires that the surface potential remains constant during the collision of particles, although the model on constant-surface charge, in which case the surface potential increases during the encounter, is applicable in most dispersed systems (1).

Frens *et al.* (2, 3) showed that the collision of silver iodide colloidal particles in aqueous electrolyte solutions was more appropriately explained by the constant-surface charge condition. They employed the exact solution of the Poisson-Boltzmann equation in the form of elliptical integrals. Recently, while examining the question of the surface potential or charge remaining constant during the mutual approach of particles, Jones and Levine (4) derived approximate expressions in series form, and Muller (5) derived exact equations expressed as elliptical integrals.

Haydon and Taylor (6-8) proposed a model for the adsorption of ionic surface-active agents at the oil/water interface, allowing for the penetration of mobile ions into the adsorbed layer of surfactant molecules situated at some equilibrium distance from the interface. They calculated the potential in the aqueous surface phase and related it to surface-pressure area measurements. The Poisson-Boltzmann equation was

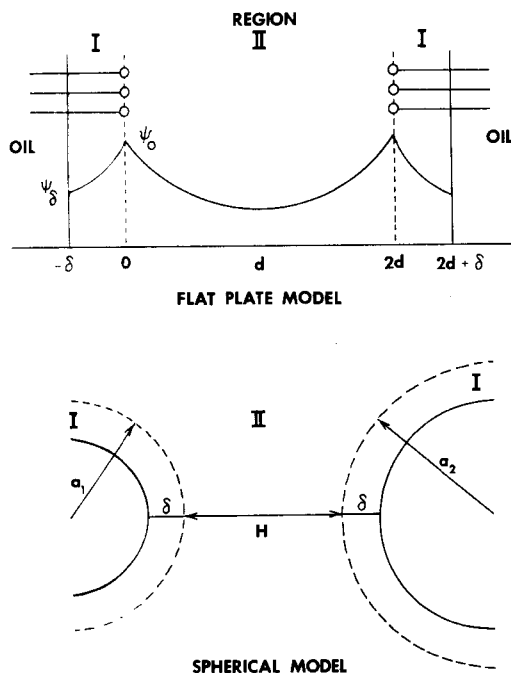


Figure 1—Distribution of potential between weakly interacting electrical double layers of oil droplets in a dilute electrolyte solution with an ionic surfactant layer extending from the o/w interface. Region I is the surfactant layer penetrable to small ions and Region II is the bulk solution.

assumed and applied to both sides of the plane of the head groups. Levine *et al.* (9) criticized Haydon and Taylor's mathematical estimation of the extended equilibrium distance of the ionized monolayer and pointed out that the assumption of a Boltzmann distribution of penetrating counterions behind the plane of the ionized monolayer becomes physically somewhat unrealistic in the limit that the available space for ion penetration becomes small as compared to the size of the penetrating ion. Recently, Gingell (10, 11) used the model to calculate the changes in the potential in the surface and aqueous phases between two approaching particles as a possible physical mechanism for intercellular interactions. The purposes of this paper are to utilize the model for interacting particles to derive simple expressions for the repulsive energy of interaction at constant-surface charge and to compare them with the usual energy expressions for constant-surface potential. As will be seen, this becomes necessary for the rigorous study of the kinetics of flocculation (or coalescence) of emulsions whereby one accounts for the probability of random collision of the entire particle-size distribution through Smoluchowski's fundamental equation and Fuchs' stability factor (12, 13). The results of this paper can also apply to suspensions.

THEORY

The Haydon-Taylor model for o/w emulsions containing ionic surfactants in dilute electrolyte solutions is assumed. The adsorbed surfactant molecules at the o/w interface are arranged in such a manner that the ionized head groups extend to some distance from the interface (Fig. 1). To treat the interaction energy of electrostatic repulsion between two oil droplets by way of the energy of interaction between two flat plates, the following system is used.

1. Region I, in which $(-\delta \leq x \leq 0)$ and $(2d \leq x \leq 2d + \delta)$, is the

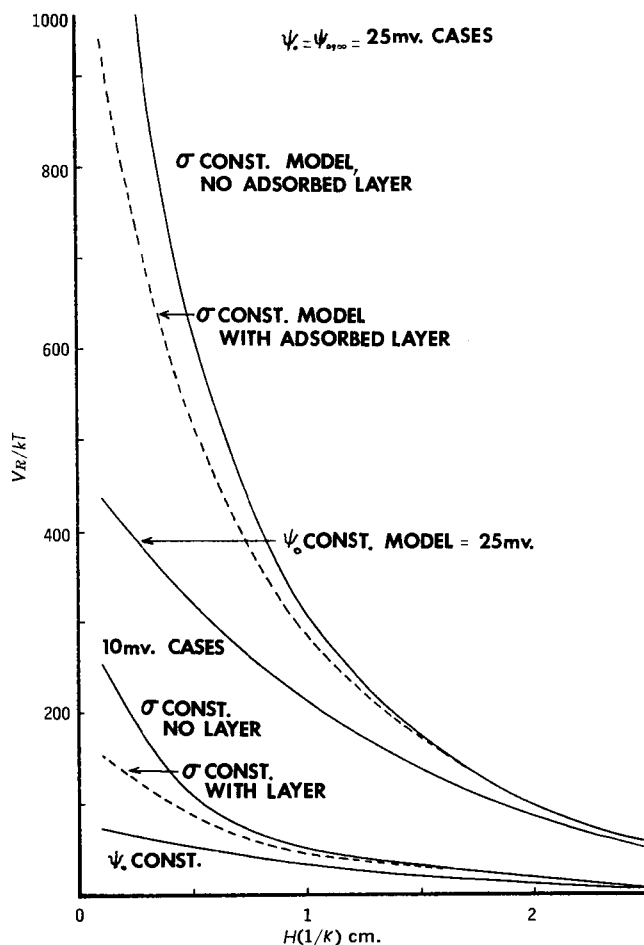


Figure 2—Comparison of repulsive energy profiles for constant-surface charge, constant-surface charge with a penetrable surfactant layer, and constant charge with an impenetrable surfactant layer models for two equal spheres; $\psi_0 = \psi_{0,\infty} = 10$ and 25 mv., $\kappa = 10^7$ cm.⁻¹, $\epsilon = 80$, $\epsilon_1 = 4$, $a = 1.0 \mu$, $\delta = 1/\kappa$ cm., and $\alpha^2 = 0.75$.

region of the adsorbed surfactant layer and with the dielectric constant ϵ_1 . The surface-active ions are mobile, and the ionic head assumes an equilibrium distance δ from the o/w interface. Since solvent and electrolyte are allowed to penetrate this layer, there is an α^2 , the volume fraction of this region accessible to small ions, and the characteristic κ_1 , the reciprocal Debye-Hückel length. The o/w interface is uncharged, and there is no penetration of ions into the oil phase, thus requiring that $(d\psi/dx)_{-\delta} = 0$ (9).

2. Region II, in which $(0 \leq x \leq 2d)$, is the region of the bulk aqueous phase of dielectric constant ϵ and reciprocal length parameter κ . The size of the surface-active head group is neglected.

Repulsive Interaction between Similar Flat Plates—Assuming the modified Gouy-Chapman model of the electrical double layer for a flat plate and the linearized Debye-Hückel approximation for small potentials (<25 mv.), the resulting Poisson equations are:

$$\text{Region I: } \frac{d^2\psi}{dx^2} = \alpha^2 \kappa_1^2 \psi \quad (\text{Eq. 1})$$

$$\text{Region II: } \frac{d^2\psi}{dx^2} = \kappa^2 \psi \quad (\text{Eq. 2})$$

where ψ is the potential and the other terms are previously defined. When the boundary conditions for the left plate are applied, *i.e.*,

$$\text{Region I: } \psi = \psi_0 \text{ at } x = 0$$

$$\frac{d\psi}{dx} = 0 \text{ at } x = -\delta$$

$$\text{Region II: } \psi = \psi_0 \text{ at } x = 0$$

$$\frac{d\psi}{dx} = 0 \text{ and } \psi = \psi_d \text{ at } x = d$$

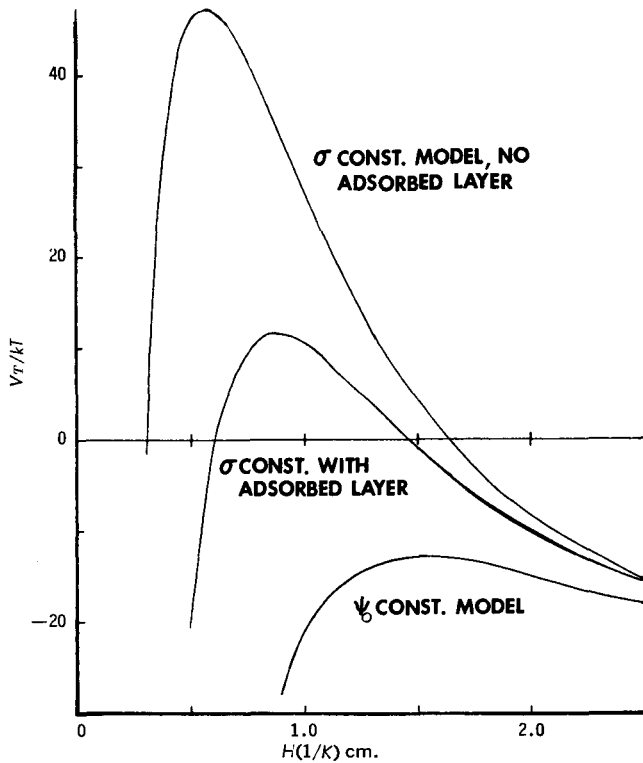


Figure 3—Comparison of total potential energy profiles between three interacting double-layer models; $\psi_0 = \psi_{0,\infty} = 25$ mv., $\kappa = 10^7$ cm.⁻¹, $\epsilon = 80$, $\epsilon_I = 10$, $a = 0.5$ μ , $\delta = 1/\kappa$ cm., and $\alpha^2 = 0.75$.

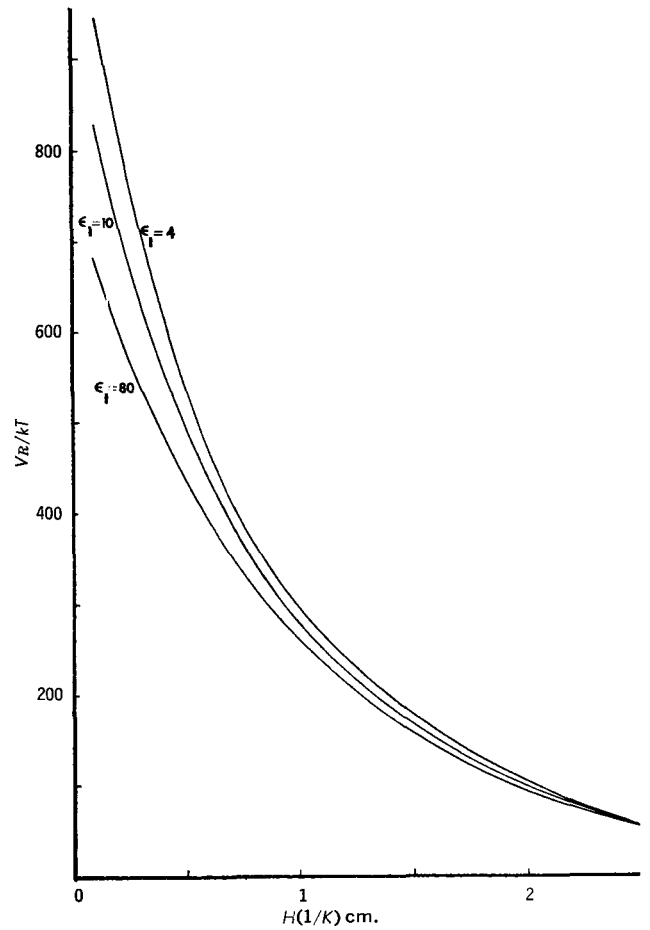


Figure 4—Effect of the dielectric constant in the penetrable ionic surfactant layer on the repulsive energy of interaction between two equal spheres under the condition of constant charge; $\psi_{0,\infty} = 25$ mv., $\kappa = 10^7$ cm.⁻¹, $\epsilon_I = 80$, $a = 1.0$ μ , $\delta = 1/\kappa$ cm., and $\alpha^2 = 0.75$.

the solutions to Eqs. 1 and 2, respectively, are

$$\psi_{I,L} = \frac{\psi_0 \cosh \alpha \kappa_I (\delta + x)}{\cosh \alpha \kappa_I \delta} \quad (\text{Eq. 3})$$

$(-\delta \leq x \leq 0)$

$$\psi_{II,L} = \frac{\psi_0 \cosh \kappa (d - x)}{\cosh \kappa d} \quad (\text{Eq. 4})$$

$(0 \leq x \leq d)$

For the corresponding right plate,

$$\psi_{I,R} = \frac{\psi_0 \cosh \alpha \kappa_I (2d + \delta - x)}{\cosh \alpha \kappa_I \delta} \quad (\text{Eq. 5})$$

$(2d \leq x \leq 2d + \delta)$

$$\psi_{II,R} = \frac{\psi_0 \cosh \kappa (x - d)}{\cosh \kappa d} \quad (\text{Eq. 6})$$

$(d \leq x \leq 2d)$

The surface charge density for the left plate is defined by

$$\sigma_L = \frac{\epsilon_I}{4\pi} \int_{-\delta}^0 \left(\frac{d^2 \psi}{dx^2} \right)_I dx + \frac{\epsilon}{4\pi} \int_0^d \left(\frac{d^2 \psi}{dx^2} \right)_{II} dx \quad (\text{Eq. 7})$$

$$\sigma_L = \frac{\psi_0 \epsilon \kappa}{4\pi} \left[\frac{\alpha}{b} \tanh \alpha b \kappa \delta + \tanh \kappa d \right] \quad (\text{Eq. 8})$$

where $b^2 = \epsilon/\epsilon_I \geq 1$ and, consequently, $\kappa_I = b\kappa$. It can be shown from the symmetry of the system that

$$\sigma_L = \sigma_R \quad (\text{Eq. 9})$$

Depending upon the case when the surface potential or charge is constant, Eq. 8 expresses each parameter as a function of plate distances.

When the plates are brought together from infinity, the general expression for the potential energy of repulsion is

$$V_{R(P/P)} = F_{2d} - F_\infty \quad (\text{Eq. 10})$$

If the surface potential, ψ_0 , is constant and small and the potential between the interacting plates is equal to the sum of the potentials of the individual double layers, the free energy of the two similar plates (14) can be approximated by

$$F_{2d} = -\frac{1}{2}(\sigma_L \psi_{0L} + \sigma_R \psi_{0R}) \quad (\text{Eq. 11})$$

$$= -\sigma \psi_0$$

and

$$F_\infty = \lim_{2d \rightarrow \infty} F_{2d} \quad (\text{Eq. 12})$$

After substituting for σ from Eq. 8 into Eqs. 11 and 12, the potential energy is

$$V_{R(P/P)} = \frac{\epsilon \kappa \psi_0^2}{4\pi} (1 - \tanh \kappa d) \quad (\text{Eq. 13})$$

$$\psi_0 = \text{const.}$$

On the other hand, if the surface charge density, σ , is considered to be constant and small,

$$F_{2d} = \frac{1}{2}(\sigma_L \psi_{0L} + \sigma_R \psi_{0R}) \quad (\text{Eq. 14})$$

$$= \sigma \psi_0$$

Substituting for ψ_0 from Eq. 8 into Eqs. 14 and 12,

$$V_{R(P/P)} = \frac{4\pi \sigma^2}{\epsilon \kappa} \left[\frac{1 - \tanh \kappa d}{(A + 1)(A + \tanh \kappa d)} \right] \quad (\text{Eq. 15})$$

$$\sigma = \text{const.}$$

Table I—Influence of the Constant Potential and Charge Repulsive Energy Models on the Collision Probability of Equal Spherical Particles^a

ψ_0 , mv.	$\ln W_\sigma/W\psi_0$	$W_\sigma/W\psi_0$
5	3.91	5.00×10^1
10	15.65	6.26×10^6
15	35.21	1.95×10^{14}
20	62.60	1.52×10^{25}
25	97.81	$\gg 10^{25}$

^a $a = 1.0 \mu$, $\epsilon = 80$, $\kappa H_m \sim 1$.

where $A = \alpha/b \tanh \alpha b \kappa \delta$ ($0 \leq A < 1$). However, it is recognized from Eq. 8 that because the plates are infinitely apart, the constant-surface charge is

$$\sigma = \frac{\epsilon \kappa}{4\pi} \psi_{0,\infty} (A + 1) \quad (\text{Eq. 16})$$

where $\psi_{0,\infty}$ is the surface potential of a single double layer and is comparable in magnitude to the ζ -potential. Thus, Eq. 15 may be expressed again by

$$V_{R(P/P)} = \frac{\epsilon \kappa \psi_{0,\infty}^2 (A + 1)}{4\pi} \left(\frac{1 - \tanh \kappa d}{A + \tanh \kappa d} \right) \quad (\text{Eq. 17})$$

$$\sigma = \text{const.}$$

If Region I of the adsorbed layer is impenetrable to small ions, *i.e.*, $A = 0$, then Eq. 17 reduces to the interaction energy of repulsion for a classical flat-plate model at constant-surface charge:

$$V_{R(P/P)} = \frac{\epsilon \kappa \psi_{0,\infty}^2}{4\pi} \left(\frac{1 - \tanh \kappa d}{\tanh \kappa d} \right) \quad (\text{Eq. 18})$$

$$\sigma = \text{const.}$$

Repulsive Interaction between Spheres—It has already been shown that the approximate interaction energy of repulsion between two spheres can be derived *via* the flat, double-layer approach (15). In general,

$$V_{R(S/S)} = \frac{2\pi a_1 a_2}{a_1 + a_2} \int_H^\infty V_{R(P/P)} dH \quad (\text{Eq. 19})$$

$(a_1, a_2 \gg H)$
 $(\kappa a_1, \kappa a_2 \gg 1)$

where a_1 and a_2 are the radii of the corresponding spheres, and H is identical to $2d$ for the plate distances. Analogous to the various cases of $V_{R(P/P)}$ in the previous section, it follows that:

(a) If ψ_0 is constant,

$$V_{R(S/S)} = \frac{\epsilon a_1 a_2}{a_1 + a_2} \psi_0^2 \ln(1 + e^{-\kappa H}) \quad (\text{Eq. 20})$$

(b) If σ is constant and the adsorbed ionic surfactant layer model is assumed,

$$V_{R(S/S)} = \frac{\epsilon a_1 a_2 (A + 1)}{(a_1 + a_2)(A - 1)} \psi_{0,\infty}^2 \ln \left[1 + \frac{(A - 1)}{(A + 1)} e^{-\kappa H} \right] \quad (\text{Eq. 21})$$

(c) If σ is constant and the adsorbed layer is impenetrable to small ions,

$$V_{R(S/S)} = \frac{\epsilon a_1 a_2}{(a_1 + a_2)} \psi_{0,\infty}^2 \ln \left(\frac{1}{1 - e^{-\kappa H}} \right) \quad (\text{Eq. 22})$$

It is noteworthy that, in the constant-surface potential case, the resulting $V_{R(S/S)}$ of Eq. 20 is identical to the classical DLVO one (16). It is implicit in Eqs. 17, 18, 21, and 22 that the potential at the surface (ψ_0) increases as the two particles approach each other. In the limit of $a_1 \gg a_2$, the interaction energy of repulsion for a sphere and a plane can be approximated. Here, the energy is dependent upon the particle with the smallest radius of curvature.

Table II—Correction to the ζ -Potential for the Usual Constant-Surface Potential Model of Repulsion Energy Used when the Constant-Surface Charge Case Is the Physically Applicable Model^a

ζ , mv.	ψ_0 , mv.	
	$\kappa H_m = 0.5$	$\kappa H_m = 1$
10	14.0	12.1
15	21.1	18.2
20	28.1	24.2
25	35.1	30.3
30	42.1	36.3
50	70.2	60.5

^a Calculations based on Eq. 26 assuming $\zeta \simeq \psi_{0,\infty}$.

It is possible to estimate the volume fraction α^2 in Region I accessible to small ions in terms of the surface charge density:

$$\alpha^2 = 1 - \frac{3r^2 \delta \sigma}{a} \quad (\text{Eq. 23})$$

where r is the radius of the surfactant chain taken as a cylinder.

RESULTS AND DISCUSSION

Significance of the Repulsive Energy Models on Emulsion Stability—Computation employing Eqs. 20–22 were carried out for a range of conditions. Figure 2 shows that as two particles approach each other, V_R (constant σ without the effect of the adsorbed layer

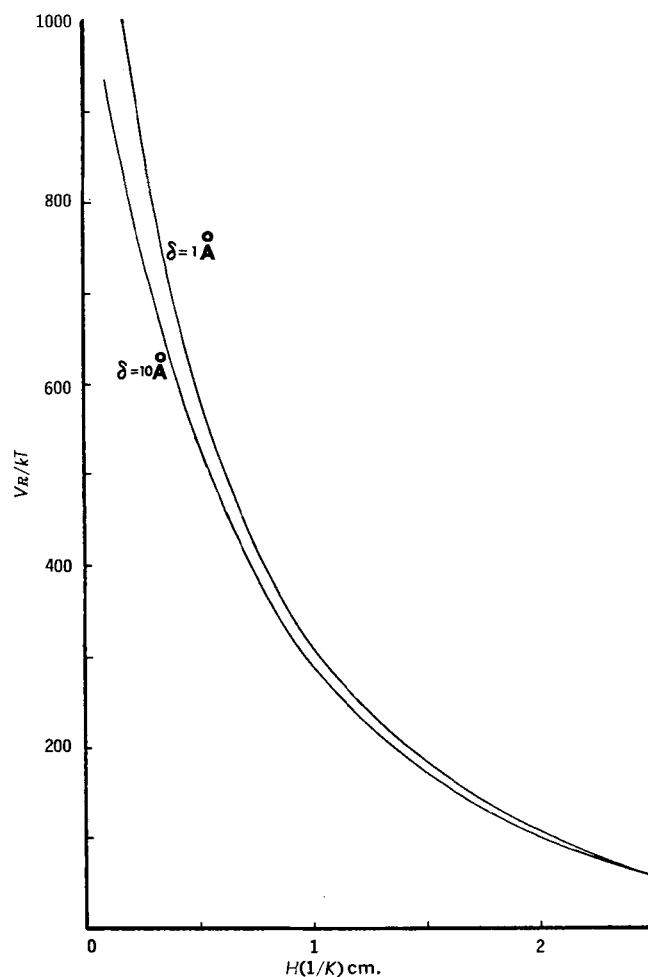


Figure 5—Effect of the thickness of the adsorbed surfactant layer on the repulsive energy between two equal spheres under the condition of constant charge; $\psi_{0,\infty} = 25$ mv., $\kappa = 10^7$ cm.⁻¹, $\epsilon = 80$, $\epsilon_f = 4$, $a = 1.0 \mu$, and $\alpha^2 = 0.75$.

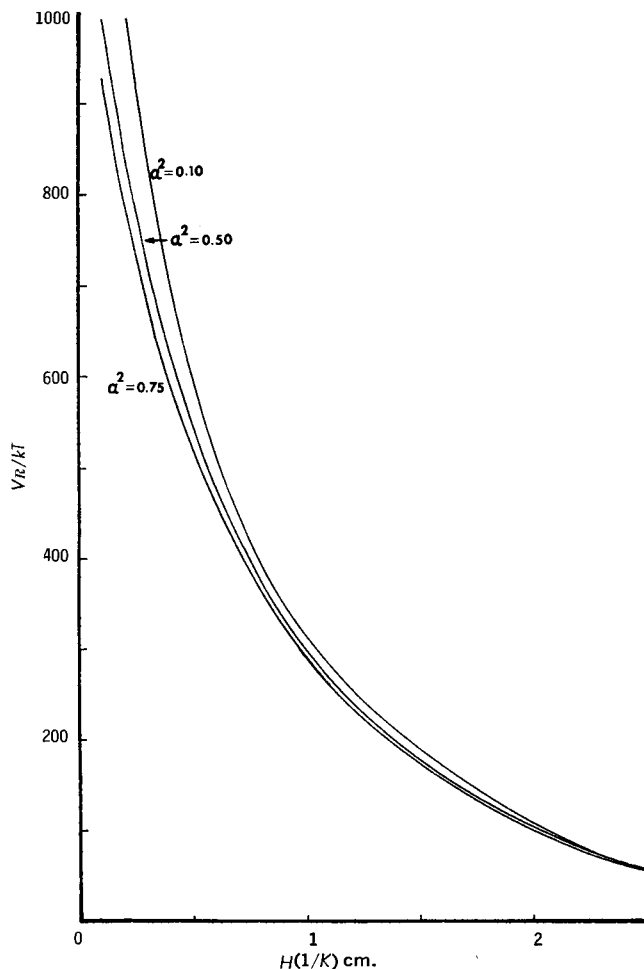


Figure 6—Effect of the volume in the adsorbed layer available for ion penetration on the repulsive energy curve; $\psi_{0,\infty} = 25$ mv., $\kappa = 10^7$ cm.⁻¹, $\epsilon = 80$, $\epsilon_1 = 4$, $a = 1.0$ μ , and $\delta = 1/\kappa$ cm.

model) $> V_R$ (constant σ with effect of the model) $> V_R$ (constant ψ_0). Because a 50- to 100-fold difference in magnitude may exist between the three cases at close interparticle distances under certain environmental conditions, *i.e.*, in the order of $0.5/\kappa$ to $1/\kappa$ cm., the proper choice becomes important when one desires to apply it to the rigorous treatment of the coalescence of o/w emulsions and also the flocculation of suspensions. At far distances, the V_R 's of the three models approach the same asymptotic values.

To illustrate the importance of the proper choice of the repulsive energy model to predict emulsion stability, consider the two extreme models: V_R (ψ_0 constant) and V_R (σ constant for an ion-impenetrable adsorbed surfactant layer). In general, the probability of collision between two equal spheres is given by the reciprocal of

$$W \sim \frac{1}{2\kappa a} e^{V_{T_{\max.}}/kT} \quad (\text{Eq. 24})$$

$$(W \geq 1)$$

where W is the Fuchs probability factor, and $V_{T_{\max.}}$ is the maximum in a potential energy curve consisting of the sum of the repulsive and attractive energy of interaction ($V_T = V_R + V_A$). Using Eqs. 20, 22, and 24, it can be shown that

$$\ln \frac{W_{\sigma \text{ const.}}}{W_{\psi_0 \text{ const.}}} = \left(\frac{V_{R_{\max.}} - V_{R_{\max.}}}{\sigma_{\text{const.}} \psi_{0 \text{ const.}}} \right) / kT \quad (\text{Eq. 25})$$

The results of Eq. 25 for 1.0 - μ radius particles in a dilute electrolyte solution, in which the minimum interparticle distance H_m is approximately $1/\kappa$ cm., are found in Table I. Usually, the V_R (ψ_0 constant) model is used to describe the electrostatic barrier, in which case there must be rapid equilibrium of desorption and ad-

sorption of surface charges during collision. However, in most physical systems it is more reasonable that the surface charge remains constant during the encounter, in which case the double-layer overlap leads to an increase in ψ_0 (1). Therefore, depending upon the model chosen, it becomes evident from Table I that one can overestimate or underestimate the probability of collision (or emulsion and suspension stability) by many orders of magnitude. In Fig. 3 the total potential energy curve illustrates another example. There are experimental evidences that may be explained in part by the constant-surface charge model. In the study of the flocculation of latex particles, Higuchi *et al.* (17) required higher concentrations of electrolyte to reproduce the same initial rate, despite repeated efforts to purify the particles. Also, Johnson *et al.* (18) obtained stable arachidic acid sols at zero ζ -potential. However, later they showed some evidence that the structuring of water about the particles might provide an additional repulsive factor (19).

This discussion leads to the questionable use of ζ -potential measurements to predict the stability of dilute aqueous dispersions in which the primary barrier is electrical. Again consider the two extreme cases and equate Eqs. 20 and 22. It follows that

$$\frac{\psi_0^2}{\psi_{0,\infty}^2} = - \frac{\ln(1 - e^{-\kappa H_m})}{\ln(1 + e^{-\kappa H_m})} \quad (\text{Eq. 26})$$

and some results are shown in Table II. If Eq. 20 is used to estimate the repulsive interaction energy and collision probability and if the constant-surface charge model is more correct, then one should use a surface potential higher in magnitude than the observed ζ -potential ($\zeta \simeq \psi_{0,\infty}$). From a practical viewpoint, the low absolute value of the ζ -potential may underestimate the degree of repulsive interaction and stability of a system unless the potential is sufficiently high so that it does not make a difference.

Repulsive Energy According to the Penetrable Adsorbed-Layer Model—To study the behavior of the properties of the adsorbed

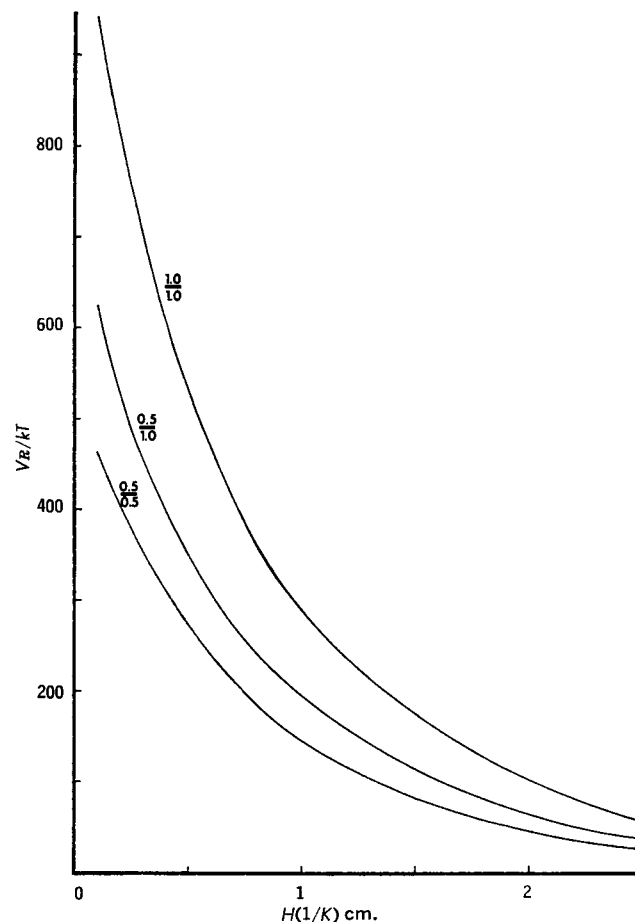


Figure 7—Effect of the particle size of two spheres on the repulsive energy curve; $\psi_{0,\infty} = 25$ mv., $\kappa = 10^7$ cm.⁻¹, $\epsilon = 80$, $\epsilon_1 = 4$, $\delta = 1/\kappa$ cm., and $\alpha^2 = 0.75$.

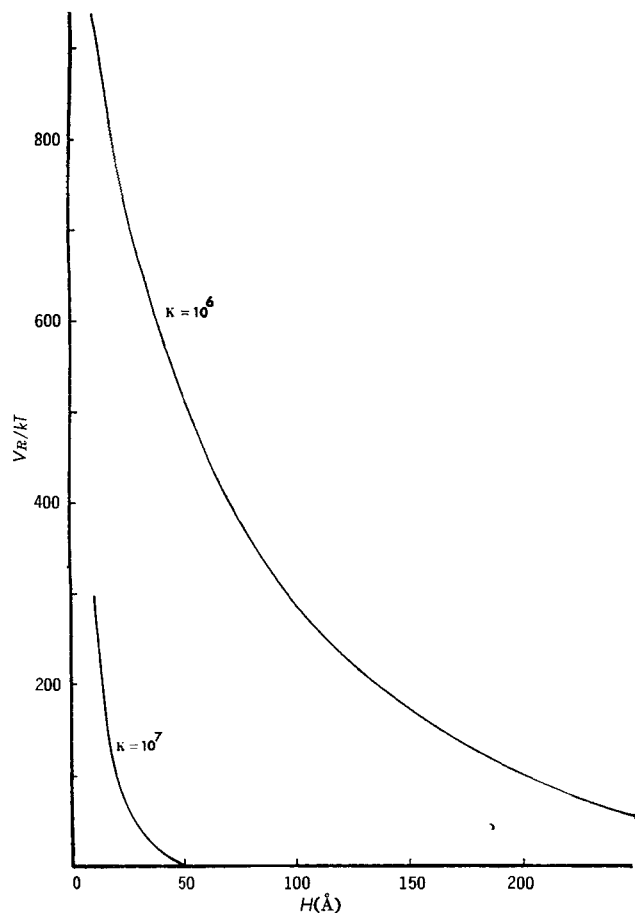


Figure 8—Effect of the electrolyte concentration on the repulsive energy curve; $\psi_{0,\infty} = 25$ mv., $\epsilon = 80$, $\epsilon_l = 4$, $a = 1.0 \mu$, $\delta = 1/\kappa$ cm., and $\alpha^2 = 0.75$.

layer of ionic surfactant on the interaction energy of repulsion, Eq. 21 was used. Figures 4–6 show that a decrease in dielectric constant, the thickness of the adsorbed layer, or the volume fraction of the adsorbed layer accessible to small ion penetration leads to a V_R larger in magnitude than that for the opposite situation and, in effect, makes the layer less penetrable to small ions. The thickness of the layer is about 3–10 Å. The low dielectric constant of the solvent in the layer affects the solubility and ionic distribution. Usually, the dielectric constant of the bulk aqueous solution is taken to be 80, while that in the layer is considerably lower, perhaps 4–10.

It is observed that the V_R (constant-surface charge) of the adsorbed-layer model approaches V_R (constant-surface potential) at close particle separations as the values of ϵ_l , δ , and α^2 are increased. The greater penetrability of ions leads to a more effective screening of the surface charges and a decrease in the interaction energy.

In Fig. 7, it is seen how the particle size has a marked effect on the magnitude of the repulsive energy and a consequential increase in the preference for coalescence (or flocculation) of small particles over larger ones. The usual influence of the electrolyte concentration on the V_R versus H profiles is shown in Fig. 8.

CONCLUSION

In an o/w emulsion, in which the change in the particle-size distribution with time appears to occur primarily through droplet-droplet coalescence after overcoming an electrostatic barrier to the encounter, the repulsive energy of the constant-surface potential model may prevail in the initial kinetic history of the emulsion. The surface coverage of ionic surfactants is low in a freshly prepared emulsion, say about 5–10% of maximum coverage. Here it is believed that rapid equilibrium of desorption and adsorption of surfactant molecules occurs during the close approach of the droplets. However, at later periods when the total surface area of the system is smaller and the surface coverage higher, the repulsive energy according to the Haydon-Taylor model under the condition of constant-surface charge may then prevail. Intermediate situations between these two periods are also conceivable. Kinetic studies of this nature are being conducted on o/w emulsions with ionic surfactants utilizing Smoluchowski's fundamental flocculation equation treatment reported in an earlier paper (13).

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