

Table III—Repellent Evaluations on Cloth

Compound	Rate of Application on Cloth, mg./cm. ²	Number of Bites Obtained at Indicated Hour				
		0	24	96	144	192
1	1.0	0	0	0	0	0
2	1.0	30	—	—	—	—
3	1.0	35	—	—	—	—
4	1.0	25	—	—	—	—
Dimethyl phthalate	1.0	0	0	10	—	—
	0.5	0	20	—	—	—
N,N-Diethyl-m-toluamide	0.25	2	10	—	—	—
	0.25	0	10	—	—	—
	0.125	0	25	—	—	—

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* Present address: Laboratory of Pharmaceutical Chemistry, University of Camerino, Camerino, Italy.

† Present address: Laboratory of Pharmaceutical Chemistry, University of Athens, Athens, Greece.

‡ Present address: Division of Dermatology, School of Medicine, University of California, San Francisco Medical Center, San Francisco, Calif.

▲ To whom inquiries should be directed.

Comparison of Theoretical Equations for Potential Energy of Electrostatic Repulsion of Colloidal Particles at Constant Surface Charge

N. F. H. HO[▲], H. TOGUCHI, and W. I. HIGUCHI

Abstract □ Recently, derived and relatively simple expressions for the energy of electrostatic repulsion between flat plates and spheres at constant surface charge were compared with the more rigorous expressions of Jones and Levine and of Müller. They are quantitative of the electrostatic barrier to the collision of colloidal particles in electrolyte solutions within the limitation of small surface potentials, $\psi_0 < 25$ mv. They are also useful in the general approximation of colloidal stability of most practical systems, despite the limitations on the validity of the expression at higher surface potentials.

Keyphrases □ Colloidal particles, potential energy of electrostatic repulsion, at constant surface charge—comparison and discussion of simple and complex equations □ Surface potential—comparison of equations for the potential energy of electrostatic repulsion of colloidal particles □ Electrostatic barrier—discussion of several equations for determining potential energy of electrostatic repulsion of colloidal particles at constant surface charge

In those dispersed systems in which the primary barrier to flocculation is electrical, the classical theory of the repulsive interaction of overlapping 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 of 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 compared their equations

Table I—Comparison of the Potential Energy of Electrostatic Repulsion Calculated from Various Equations for the Constant Surface Charge Model at Various Interplate Distances

$Z\eta_0$	$\frac{\kappa}{16nkT} V_R$ at $2xd = 1$			$\frac{\kappa}{16nkT} V_R$ at $2xd = 2$		
	Müller (5)	Jones and Levine (4)	Equation 1	Müller (5)	Jones and Levine (4)	Equation 1
0.5	0.0330	0.0302	0.0364	0.0095	0.0094	0.0098
1.0	0.1108	0.1087	0.1455	0.0347	0.0347	0.0391
2.0	0.3219	0.3213	0.5820	0.1106	0.1099	0.1565
4.0	0.8087	0.8567	2.3280	0.2765	0.2651	0.6261

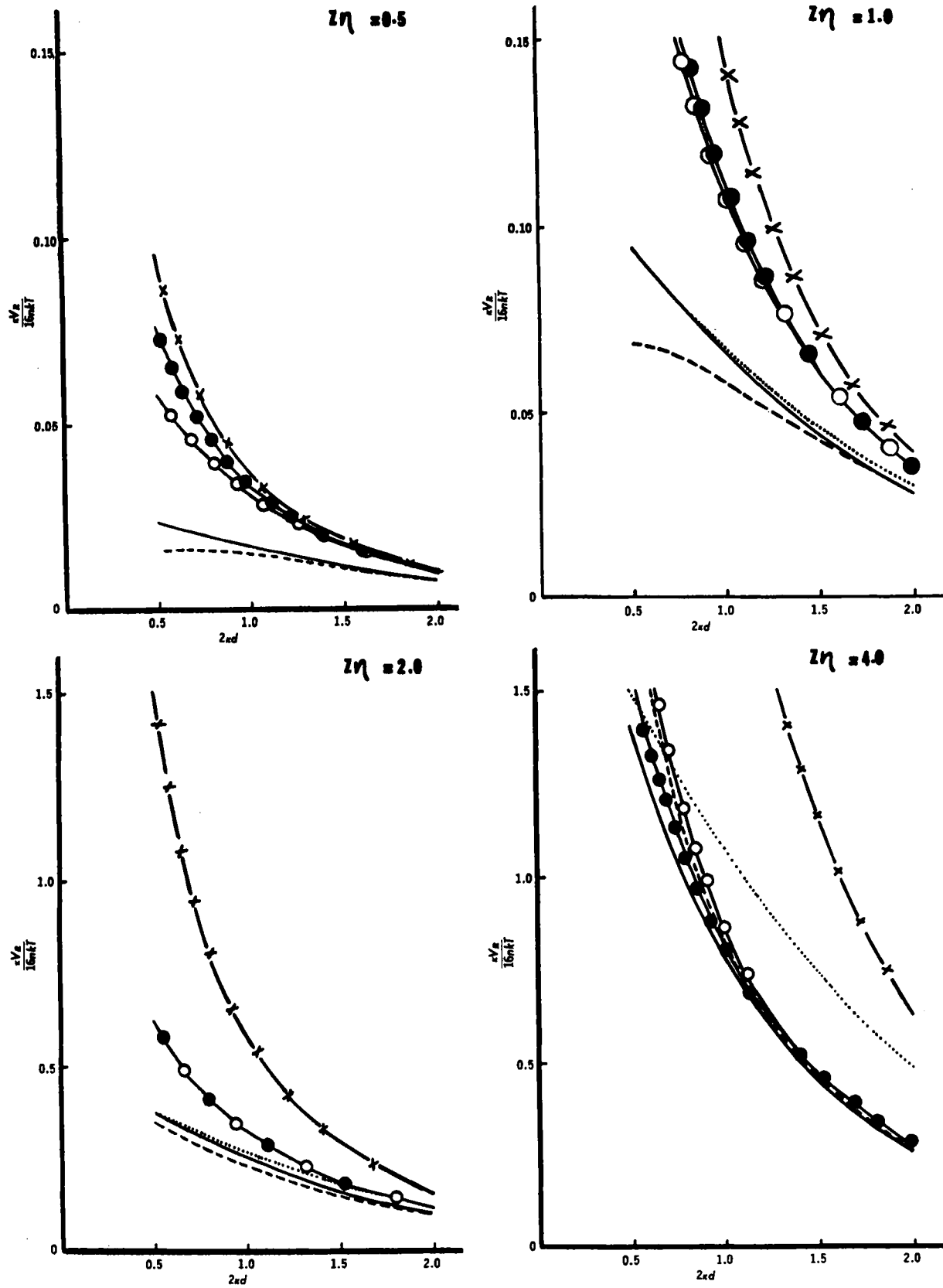


Figure 1—Potential energy—interplate distance profiles for the constant surface charge and constant surface potential models at various surface conditions of $Z\eta_0$. Key:

Müller (5)	ψ_0 const.	σ_0 const.
Jones-Levine (4)	---	●—●
Derjaguin, Landau, Verwey, Overbeek Eq. 1	...	○—○
		×—×

under the conditions of constant plate potential and charge. Likewise, Müller (5) analyzed exact equations expressed in elliptical integral form. In this paper, some rather simple, approximate equations, previously reported (6), for the potential energy of electrostatic repulsion of colloidal particles at constant surface charge are compared with those equations of Jones and Levine and of Müller. Also included is a brief discussion of the equations for the constant potential case.

COMPARISON OF THEORETICAL EQUATIONS

Recently (6), simple expressions for the case of constant surface charge were derived based on the linear approximations of the Poisson-Boltzmann equation, the free energy of the single electrical double layer, and the region of overlapping double layers. For flat plates, the potential energy is:

$$V_R = \frac{2nkTZ^2\eta_0^3}{\kappa} \left[\frac{1 - \tanh \kappa d}{\tanh \kappa d} \right] \quad (\text{Eq. 1})$$

$\psi_0 \text{ const.} \quad (\kappa d \gg 1; Z\eta_0 \ll 1)$

and for equal spheres:

$$V_R = \frac{\epsilon a \psi_0^2}{2} \ln \left(\frac{1}{1 - e^{-\kappa H}} \right) \quad (\text{Eq. 2})$$

$\sigma_0 \text{ const.} \quad (\kappa a \gg 1; \psi_0 \ll 25 \text{ mv.})$

where $\eta_0 = e\psi_0/kT$, e is the electronic charge, Z is the valence, ψ_0 is the surface potential, k is the Boltzmann constant, T is the absolute temperature, n is the total number of ions per milliliter, κ is the Debye-Hückel reciprocal length parameter, ϵ is the dielectric constant of the medium, a is the radius, σ_0 is the surface charge, d is the middistance between the plates, and H is the closest distance between the spheres. Equations 1 and 2 are analogous to the classical expressions for the constant surface potential case; i.e., for flat plates:

$$V_R = \frac{2nkTZ^2\eta_0^3}{\kappa} (1 - \tanh \kappa d) \quad (\text{Eq. 3})$$

$\psi_0 \text{ const.} \quad (\kappa d \gg 1; Z\eta_0 \ll 1)$

and for spheres:

$$V_R = \frac{\epsilon a \psi_0^2}{2} \ln (1 + e^{-\kappa H}) \quad (\text{Eq. 4})$$

$\psi_0 \text{ const.} \quad (\kappa a \gg 1; \psi_0 \ll 25 \text{ mv.})$

Upon comparing these expressions for flat plates or spheres, one observes that the coefficients of the interparticle distance function are identical. In both the constant surface potential and constant surface charge models, the ψ_0 is the surface potential of a single particle. However, in the later model the increase in the surface potential as two particles approach each other is implicitly accounted for by the distance functions. Furthermore, it is the distance function that characterizes the essential differences of the two models. It is well known that Eqs. 3 and 4 are poorer approximations of the energetics of electrostatic repulsion when $\psi_0 \gtrsim 25$ mv. at room temperature. However, the simplicity of these equations lends itself to rapid qualitative interpretation and semiquantitative estimation of the barrier to the collision of colloidal particles, and herein lies the reason for their wide usage. In this respect, Eqs. 1 and 2 for the constant surface charge model are also useful approximations for most practical systems.

The approach of Jones and Levine (4) is more rigorous. Their expressions are shown here. For flat plates at constant surface potential:

$$V_R = \frac{64nkT}{\kappa} \cdot \tanh^2 (Z\eta_0/4) \cdot \exp(-2\kappa d) \cdot [1 - C_{\psi_0} \tanh^2 (Z\eta_0/4) \cdot \exp(-2\kappa d)] \quad (\text{Eq. 5})$$

$\psi_0 \text{ const.} \quad (\kappa d > 0.5; Z\eta_0 \leq 4)$

and for spheres:

$$V_R = \frac{64\pi nkTa}{\kappa^2} \cdot \tanh^2 (Z\eta_0/4) \cdot \exp(-\kappa H) \cdot [1 - \frac{1}{2} \cdot (1 + C_{\psi_0}) \cdot \tanh^2 (Z\eta_0/4) \cdot \exp(-\kappa H)] \quad (\text{Eq. 6})$$

$\psi_0 \text{ const.} \quad (\kappa a \gg 1; Z\eta_0 \leq 4)$

For the flat plates and spheres of the constant surface charge case, the function C_{ψ_0} in Eqs. 5 and 6 is replaced by C_{σ_0} where:

$$C_{\psi_0} = 4\kappa d - 3 + \frac{4\cosh (Z\eta_0/2)}{\sinh^2 (Z\eta_0/2)} \quad (\text{Eq. 7})$$

$$C_{\sigma_0} = C_{\psi_0} - \frac{8}{\cosh (Z\eta_0/2) \cdot \sinh^2 (Z\eta_0/2)} \quad (\text{Eq. 8})$$

Figure 1 shows the potential energy-interplate distance profiles at constant surface charge and potential according to Eqs. 1, 3, 5, 7, and 8 at various η_0 values. Müllers' (5) Eqs. 2.8 and 1.8 for the constant ψ_0 case and Eqs. 3.10 and 3.11 for the constant σ_0 case were also used. When comparing the curves according to Eqs. 1 and 3, it is observed that the electrostatic repulsion between particles is always greater for the constant σ_0 condition than that at constant ψ_0 . In contrast, the profiles of Jones and Levine (4) and Müller (5) indicate that there are differences in the repulsive energy between the two conditions at small plate potentials; however, when $Z\eta_0 \geq 4$, the two models are essentially indistinguishable in the region of importance to colloidal stability, i.e., $1 \lesssim 2\kappa d \leq 2$. Furthermore, the results of the equations by Jones and Levine are in good agreement with those of Müller at $2\kappa d > 1$. It is readily observed that Eq. 1 is an increasingly poor approximation of the more rigorous expressions at constant σ_0 for $Z\eta_0 > 1$. A comparison of the repulsive energy calculated from the various equations for the constant σ_0 model at various interplate distances is shown in Table I. Although calculations were not made for spherical particles, the discussion of the results would be analogous to those made for flat plates.

CONCLUSION

Relatively simple expressions for the energy of electrostatic repulsion between flat plates (Eq. 1) and spheres (Eq. 2) at constant surface charge have been compared with the more rigorous expressions of Jones and Levine (4) (Eqs. 3 and 4) and of Müller (5). They have utility in the rigorous quantitation of the electrical barrier to the collision of colloidal particles in electrolyte solutions to surface potential conditions of $Z\eta_0 < 1$. As a point of reference, for a 1-1 electrolyte and at room temperature, $\psi_0 = 25$ mv. when $Z\eta_0 = 1$ and $\psi_0 = 50$ mv. when $Z\eta_0 = 2$, etc. In the general approximation of colloidal stability, Eqs. 1 and 2 may even be extended to surface conditions of $Z\eta_0 = 2$.

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▲ To whom inquiries should be directed.