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# Electroadsorption of Colloids on Electrodes

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## Abstract

The electrically induced adsorption of suspended colloidal particles on charged electrodes is studied by the HHF-Hamaker theory. Surface potentials are calculated by the Gouy-Chapman model for a diffuse double layer. Particle-particle and particle-surface interaction energies are compared for several cases of surface-to-particle charge density ratios. It is shown that electroadsorption of colloidal particles is hindered when their surface charge density is larger then that of the electrode.

## INTRODUCTION

The process of adsorption of small colloidal particles onto large surfaces is termed "heterocoagulation" and was studied extensively by Hull and Kitchener (*1*), Vincent, Young, and Tadros (*2*), Tamai et al. (*3–6*), and others. The latter discussed, in a series of articles, the influence of pH and solution concentration on the rate of deposition and the amount of polystyrene latices deposited on such synthetic fibers as polyamide, polyester, and polyacrylonitrile. It was found that pH is of prime importance in determining adsorption characteristics since it controls the surface charge and thus the zeta potential measured on both latex particles and fibers. A maximum in the rate of adsorption was found near the isoelectric point of the latex rather than in the expected region of zeta potentials of opposite sign. These systems were treated via the heterocoagulation theory of Hogg, Healy, and Fuerstenau (HHF) (*7*). It was also suggested that particle-particle (PP) interactions have to be considered in

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addition to particle–surface (PS) interactions, a point also discussed by Vincent et al. (*2*).

Heterocoagulation studies are inspired by the need for efficient filtration beds for very fine particles. This phenomenon is utilized in the so-called "deep bed filters" where filtration of fine suspended particles is effected by adsorption of the particles on a porous matrix throughout the filter depth. In most cases the porous filtration bed is made of a fibrous matrix which allows good solution permeability as well as high adsorption surface area. The possibility of inducing electroadsorption of colloidal particles on high surface area electrodes was discussed by us in previous articles (*8, 9*). Perhaps the most striking advantage of colloid filtration by electroadsorption is the possibility of inducing the filtration of fine colloids in a low-pressure process and without the addition of chemicals. This is important when environmental and cost considerations are taken into account.

It was found (*8*) that bacteria, which can be considered as colloids, are removed from aqueous pH buffered solutions by forcing the solution through a charged graphite felt. The process is based on the attractive electrostatic interactions between the double layer of the electrically charged outer bacteria membrane and the double layer of the oppositely charged electrode. Upon reversing the electrode charge, part of the adsorbed bacteria is returned to solution. In later work (*9*) it was shown that when highly charged carboxylated polystyrene colloidal particles are considered, their adsorption on a graphite felt electrode is hardly affected by the electrode charge when it is varied in the double layer potential range. It was deduced that interparticle repulsive forces are prominent since the maximum electrode double layer charge is much smaller then that of the particles. Adsorption or desorption of the particles was induced by controlling the pH of the suspension electrochemically by applying potentials remote from the double layer range. At these potentials, water electrolysis or radox reactions involving surface groups (when the electrode is made of carbon (*10*)) can occur according to the following scheme (*11*):

$$2\underline{e} + 2H_2O \rightarrow H_2 + 2OH^-$$

$$S| + \underline{e} + H_2O \rightarrow S|H + OH^-$$

in the cathodic range, and

$$H_2O \rightarrow 2H^+ + \tfrac{1}{2}O_2 + 2\underline{e}$$

$$S| + H_2O \rightarrow S|O + 2H^+ + 2\underline{e}$$

in the anodic range. S| indicates a surface group.

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When the electrode has a high surface area, these reactions can change the pH of the bulk suspension and, consequently, the surface charge of the colloidal particle. This, according to Tamai et al. (*3*), may change the adsorption rate and the amount adsorbed on the electrode.

The mutual influence of PP and PS interactions on the overall characteristics of the suspension-electrode system can, in principle, be predicted and analyzed by virtue of the HHF (*7*) treatment for double layer interactions and the Hamaker theory for the van der Waals attraction forces between particles (*12*). However, it should be kept in mind that the HHF model, being based on the linear approximation of the Gouy-Chapman equation, is limited to small surface potentials, i.e., 75–100 mV (*7*). Moreover, surface potentials which appear in the HHF equations for the two interacting surfaces are not measurable quantities. Thus, they either have to be calculated or, as commonly done by many authors, approximated by the use of the measurable zeta potential. An additional drawback is the fact that the Hamaker constant is available for only a limited number of materials; thus, it often has to be approximated too.

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The HHF treatment can therefore provide only a qualitative and limited overview on suspension–adsorbate systems. This is also true for the presently studied system since relatively high charge densities on the colloidal particles (and therefore high surface potentials) may be involved.

In the following discussion, use is made of the HHF-Hamaker theory, within its limitations, to study the interaction energy characteristics of the above-mentioned system. The analysis is restricted to the double layer potential range; thus, surface potentials of the electrode are calculated via the Gouy-Chapman model. *These calculations can also be applied for the verification of the colloids' surface potential provided that its surface charge density is known* (for instance, in the case of the carboxylated polystyrene latex the charge density can be obtained as a function of pH by titration).

## PP AND PS INTERACTION ENERGIES CALCULATIONS

Electrostatic interaction energy between two particles having radii $a_1$ and $a_2$ is calculated by means of (7)

$$V_E = \frac{\varepsilon a_1 a_2}{4kT(a_1 + a_2)} \left[ 2\psi_1\psi_2 \ln\left(\frac{1 + e^{-\kappa H}}{1 - e^{-\kappa H}}\right) + (\psi_1^2 + \psi_2^2) \ln\left(1 - e^{-2\kappa H}\right) \right] \tag{1}$$

where $H$ is the separation distance between the particles, $\psi_1$ and $\psi_2$ are the respective surface potentials, $\kappa^{-1}$ is the Debye length, $\varepsilon$ is the dielectric constant, $k$ is the Boltzman coefficient, and T is the absolute temperature.

By applying the conditions $a_2 = \infty$* and $a_1 = a_2$, the equations for PS and PP interactions, respectively, are obtained.

Provided that the charge density of the electrode is known, its surface potential can be estimated from the Gouy-Chapman model, i.e., from the equation (*13*)

$$Q = 11.74(C)^{1/2} \sinh(19.46Z\psi) \tag{2}$$

where $\psi$ is the potential at the distance of the inner Helmholtz plane from the surface, $Q$ is the charge density, C is the bulk electrolyte solution concentration, and Z is the valency of the ions in the solution.

The surface potential of the colloidal particle can be estimated by measuring the zeta potential and assuming that the potential at the shear plane is close to the surface potential (this is a fairly good approximation at very low ionic strengths). Furthermore, if the charge density on the particle is known (as in the cases where the particle carries a known amount of defined ionic surface groups such as carboxylic, sulfonic, or amine), its surface potential can also be calculated by the use of Eq. (2). In the calculations shown below, charge densities on the colloid and the electrode were taken into account and both surface potentials were calculated according to Eq. (2). The van der Waals attractive interaction energies are calculated according to Hamaker (*12*) by

$$V_A = -\frac{A}{12kT}\left[\frac{a_2}{\frac{H^2}{4a_1}+\frac{a_2H}{2a_1}+\frac{H}{2}} + \frac{a_2}{\frac{H^2}{4a_1}+\frac{a_2H}{2a_1}+\frac{H}{2}+a_2} + 2\ln\frac{H+2(a_1+a_2)}{H+\frac{4a_1a_2}{H}+2(a_1+a_2)}\right] \tag{3}$$

where $A$ is the combined Hamaker constant. Again, by applying the same conditions as above, the expressions for PS and PP interactions are

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*In this case a plain electrode is assumed. However, this condition is also assumed to be valid for the adsorption of small (diameter 0.15 μm) polystyrene latex particles on fibrous carbons carrying a much larger fiber diameter (8–10 μm) (*9*).

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obtained. Total interaction energy as a function of distance is calculated by

$$V_T = V_A + V_E \tag{4}$$

In the following calculations, the Hamaker constant is taken as $4 \times 10^{-13}$ erg, which is within the recommended range (*12*).

## RESULTS AND DISCUSSION

Figure 1 shows the PS interaction energy profiles when the charge on the electrode is varied while the charge density on the colloid is constant. It is evident that attractive and repulsive interactions between the electrode and the colloidal particle can be induced by varying the charge density on the electrode. Nevertheless, as was mentioned above, PP forces have to be considered in conjunction with PS forces. This is shown in Figs. 2 and 3 where two extreme but not rarely existing cases are depicted. In Fig. 2 the calculations are performed for the case where the charge density on the particles is low compared to that on the electrode. It is evident that PP interactions are very weak while PS interactions are

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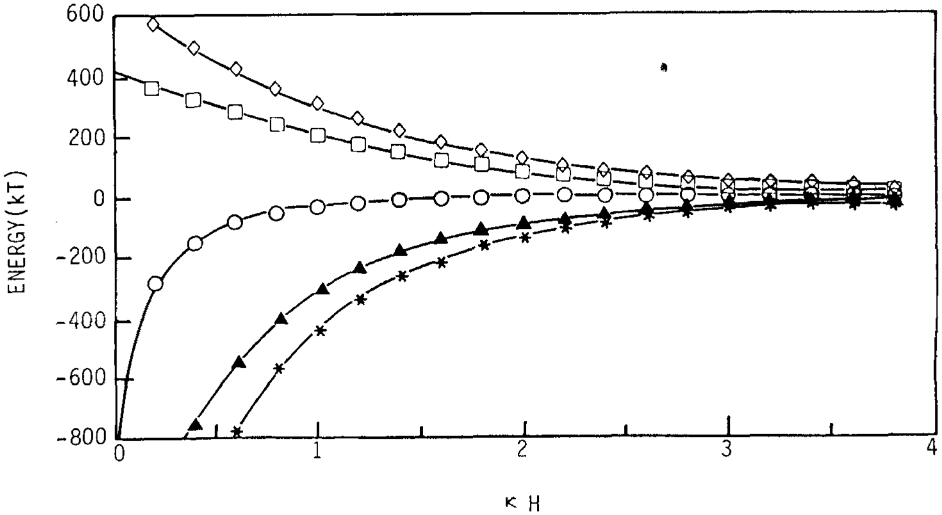

FIG. 1. PF interaction energies at ionic strength $10^{-4}$ *M*. Charge on the particle: −0.5 μC/cm$^2$. Electrode charge: 0.5 (∗), 0.25 (▲), 0 (○), −0.25 (□), −0.5 (◇) μC/cm$^2$.

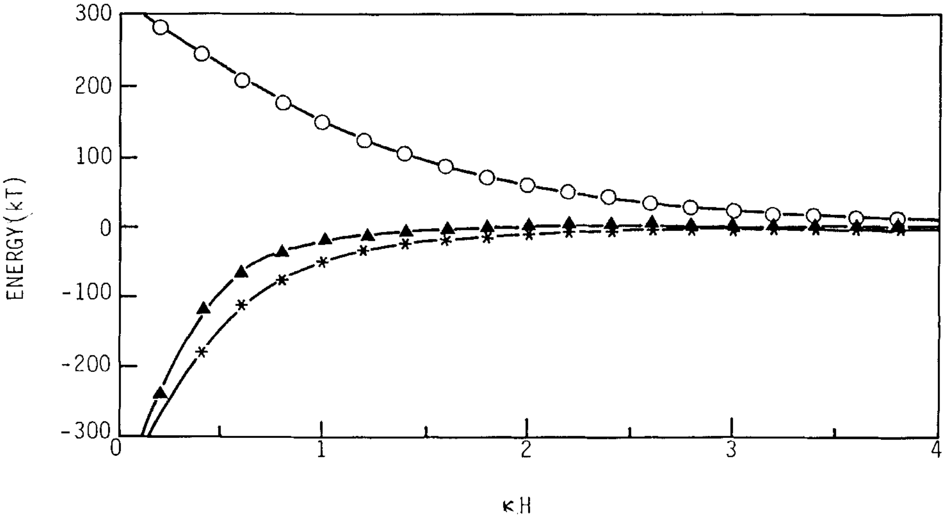

FIG. 2. Interaction energies at $10^{-4}$ *M*. ○, PP (−0.01 μC/cm$^2$); *, PS (particle: −0.01 μC/cm$^2$; electrode: 0.5 μC/cm$^2$); ▲, PS (particle: −0.01 μC/cm$^2$; electrode: −0.5 μC/cm$^2$).

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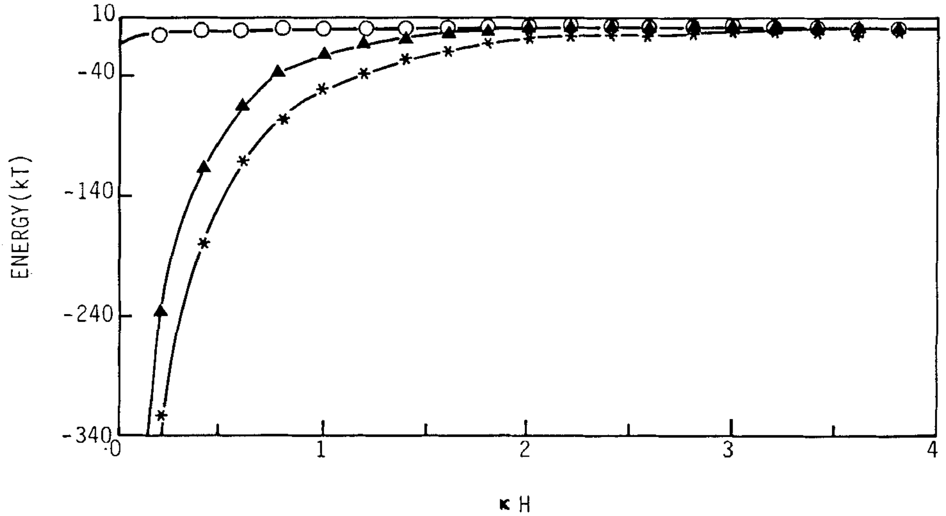

FIG. 3. Interaction energies at $10^{-4}$ *M*. ○, PP (−0.5 μC/cm$^2$); *, PS (particle: −0.5 μC/cm$^2$; electrode: 0.01 μC/cm$^2$); ▲, PS (particle: −0.5 μC/cm$^2$; electrode: −0.01 μC/cm$^2$).

attractive with only a slight dependence on the sign of the electrode charge. It is expected that in this case, either coagulation in the suspension or adsorption of the particles on the electrode will occur. In Fig. 3 the inverse case is shown, i.e., the particles are highly charged with respect to the electrode. This case can be found with particles chemically treated for the implantation of surface groups, thus resulting in surface charge densities as high as 100–250 μC/cm$^2$ (*9*). Since the charge density on carbon, graphite, and commonly used metallic electrodes does not exceed 5–20 μC/cm$^2$ (*14*), high charge density ratios are obtained. Due to the symmetry of Eq. (2) with respect to the particles and the surface, the same behavior as in Fig. 2 is obtained for PS interactions. However, PP interactions are strongly repulsive and may be more effective as the particles approach the electrode since, while doing this, interparticle distances may become smaller. It is thus expected that a very slight or null adsorption will occur in this case. As shown in Fig. 4, the relative weight of PP and PS interactions changes significantly due to the increased screening of double layer interactions as the ionic strength increased to $10^{-3}$ *M*. In Fig. 5, PP and PS interactions are compared for an intermediate case, i.e., where the colloidal particles and the electrode carry the same charge densities. PS electrostatic attractive interactions are

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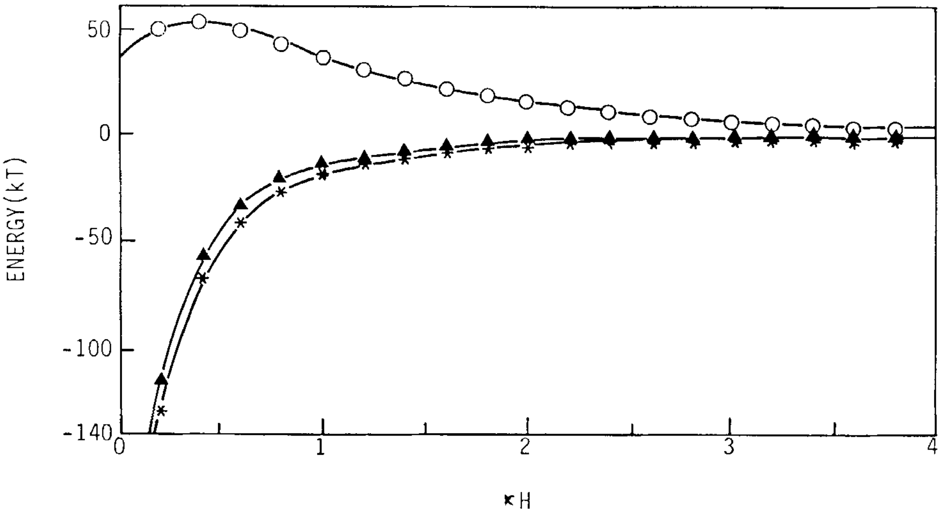

FIG. 4. Interaction energies at $10^{-3}$ *M*. ○, PP; * and ▲, PS. The same charge densities as in Fig. 3.

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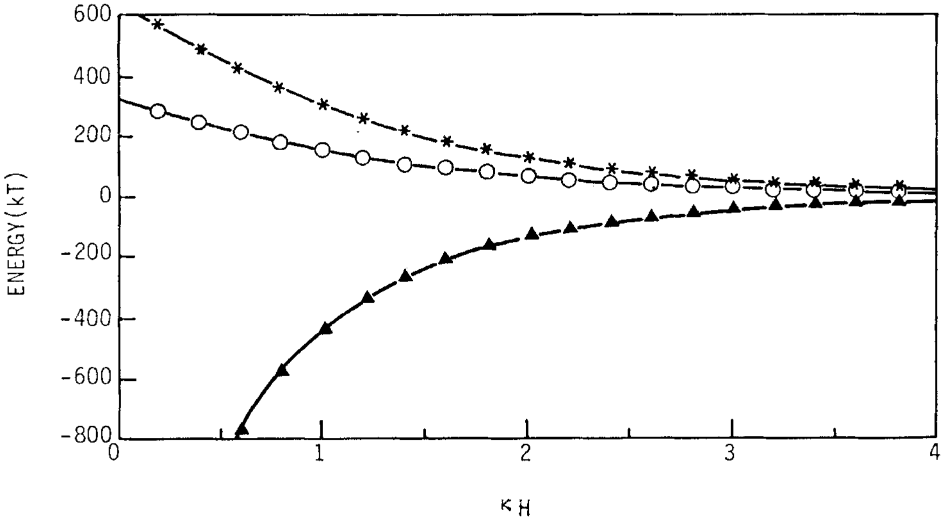

FIG. 5. Interaction energies at $10^{-4}$ *M*. ○, PP ($-0.5\ \mu C/cm^2$); ▲, PS (particle: $-0.5\ \mu C/cm^2$; electrode: $0.5\ \mu C/cm^2$); *, PS (particle: $-0.5\ \mu C/cm^2$; electrode: $-0.5\ \mu C/cm^2$).

much stronger than PP repulsive interactions; thus, strong adsorption on the electrode can be expected in this case.

## CONCLUSIONS

The induction of adsorption or desorption of colloidal particles on an electrically charged electrode is qualitatively governed by the electrostatic and van der Waals forces in the same way as in the case of adsorption of colloids on fixed charge surfaces. In the present case, however, the electric charge can be varied continuously, thus providing a convenient way of controlling adsorption.

## REFERENCES

1. M. Hull and J. A. Kitchener, *Trans. Faraday Soc.*, *65*, 3093 (1969).
2. B. Vincent, C. A. Young, and T. F. Tadros, *Faraday Discuss. Chem. Soc.*, *65*, 296 (1978).
3. H. Tamai, A. Hamada, and T. Suzawa, *J. Colloid Interface Sci.*, *88*, 378 (1982).
4. H. Tamai and T. Suzawa, *Ibid.*, *88*, 372 (1982).
5. H. Tamai and T. Suzawa, *Colloid Polym. Sci.*, *258*, 870 (1980).

*6.* H. Tamai, Y. Nagai, and T. Suzawa, *J. Colloid Interface Sci., 91,* 464 (1983).
*7.* R. Hogg, T. W. Healy, and D. W. Fuerstenau, *Trans. Faraday Soc., 62,* 1638 (1966).
*8.* Y. Oren, H. Tobias, and A. Soffer, *Bioelectrochem. Bioenerg., 11,* 347 (1983).
*9.* D. Hall, Y. Oren, Z. Priel, and A. Soffer, *Sep. Sci. Technol.,* In Press.
*10.* H. P. Boehm, U. Hofman, and A. Clauss, *Proceedings of the 3rd Carbon Conference,* Pergamon, London, 1959, p. 241.
*11.* A. Soffer and M. Folman, *J. Electroanal. Chem., 38,* 25 (1972).
*12.* H. C. Hamaker, *Physica, 4*(10), 1058 (1937).
*13.* P. Delahay, *Double Layer and Electrode Kinetics,* Wiley-Interscience, New York, 1965.
*14.* Y. Oren, H. Tobias, and A. Soffer, *J. Electroanal. Chem., 162,* 87 (1984).

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