Role of the Hydration Force in the Stability of Colloids at High Ionic Strengths

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It is shown that the repulsion between colloidal particles or emulsion droplets depends both on the surface charge density and on the surface dipole density, the latter being a result of the presence of ion pairs on the surface. For illustration purposes, one considers the case in which a surfactant, such as sodium dodecyl sulfate, is adsorbed on the surface of droplets or particles. As the concentration of electrolyte (NaCl) increases, the charge on the surface decreases, and the number of ion pairs increases, because of the association–dissociation equilibrium. At relatively low salt concentrations, the repulsion due to the double layer is dominant and decreases as the electrolyte concentration increases. At relatively high electrolyte concentrations, the hydration repulsive force due to the ion pairs present on the surface becomes dominant. Consequently, as the salt concentration increases, the total repulsion decreases and passes through a minimum, after which it increases. If the hydration repulsion is large, the emulsion or colloidal system will remain stable at any electrolyte concentration. If the hydration repulsion is small, the system will be stable only for sufficiently low electrolyte concentrations. At intermediate strength of the hydration repulsion, the stability depends on the size of the particles or droplets and the Hamaker constant. The rate of coagulation of particles of small radii and small Hamaker constants reaches a maximum and then decreases with increasing ionic strength. For particles of large radii, the increase of the maximum of the interaction energy with increasing electrolyte concentration can be so large ($\sim$30 kT) that it can forbid the coagulation at the primary minimum; however, the particles can aggregate at the secondary minimum, which is deep.

I. Introduction

The cornerstone of colloid science is the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, which explains the stability of colloids in terms of a repulsive (double-layer) force and an attractive (van der Waals) one. The double-layer repulsion, due to the charge on the surface of the particles, can be indefinitely diminished by increasing the electrolyte concentration. The combination of the two interactions typically generates a potential barrier, between a low (and hence stable) primary minimum and a weak secondary minimum. The latter, with a typical depth of the order of kT, generates a weak bonding between particles (flocculation), which can be reversed by stirring or shaking the system. Coagulation of colloids occurs when two neighboring particles acquire enough energy from the random Brownian motion to overcome the potential barrier. At low electrolyte concentrations, the potential barrier is high, and this ensures a long lifetime for the colloidal dispersion; however, by adding electrolyte, the double-layer repulsion is screened and the colloidal particles eventually coagulate.

While the DLVO theory has the advantage of simplicity and often offers "almost quantitative results",[1] it is well-known to be incomplete. A striking example is offered by some colloids (e.g., silica) which do not coagulate even at high electrolyte concentrations, when the double layer is expected to collapse.[1] Recently, it was also shown that the rate constant for aggregation of paraffin wax particles covered by a long-chain carboxylic acid (C_{22}) passes through a maximum when plotted against NaCl concentration.[2] This means that the repulsive force passes through a minimum.

The above behaviors can be explained by additional forces, which also exist between noncharged surfaces and are particularly strong at low separation distances. These forces are generically called non-DLVO forces. An important interaction, for colloids dispersed in water, was related to the organization of water in the vicinity of a surface.[3] This structural force, often called hydration force, was exhaustively investigated experimentally for neutral[4] or weakly charged[5] phospholipid bilayers and was reasonably well described by an exponential decay, with a decay length between 1.5 and 3 Å and a preexponential factor that varied in a rather large range. While the origin of this interaction is attributed to the changes in the local organization of water, there are still debates over the theoretical models which describe the interaction at the molecular level. The interaction was associated with the orientational correlation of water molecules,[6] with the mutual polarization of water layers,[7] disruption of hydrogen bonding,[8] protrusion interactions,[9] or truncation of ion atmosphere by walls.[10] A detailed examination of the above models is made in another paper dedicated to hydration forces.[11]

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(1) Hunter, R. J. *Foundations of Colloid Science*; Oxford Science Publications: New York, 1987.

(2) Alfridsson, M.; Ninham, B.; Wall, S. *Langmuir* **2000,** *16*, 10087.

(3) Derjaguin, B. V.; Churaev, N. V.; Muller, V. M. *Surface Forces*; Plenum: New York, 1987.

(4) Rand, R. P.; Parsegian, V. A. *Biochim. Biophys. Acta* **1989,** *988*, 351.

(5) Cowley, A. C.; Fuller, N. L.; Rand, R. P.; Parsegian, V. A. *Biochemistry* **1978,** *17*, 3163.

(6) Marcelja, S.; Radic, N. *Chem. Phys. Lett.* **1976,** *42*, 129.

(7) Schiby, D.; Ruckenstein, E. *Chem. Phys. Lett.* **1983,** *95*, 435.

(8) Attard, P.; Batchelor, M. T. *Chem. Phys. Lett.* **1988,** *149*, 206.

(9) Israelachvili, J. N.; Wennerstrom, H. *Langmuir* **1990,** *6*, 873.

(10) Marcelja, S. *Nature* **1997,** *385*, 689.

(11) Manciu, M.; Ruckenstein, E. *Langmuir*, in press.

The hydration force is important for distances between plates less than a few nanometers. Since the DLVO potential barrier between spherical particles or droplets is located at separation distances of the order of the Debye length, it is clear that at least at high electrolyte concentrations the hydration force becomes relevant. The qualitative effect of hydration was earlier recognized, regarding the stability of silica colloids at high electrolyte concentrations[1] or the stability of amphoteric latex particles at high concentrations of some electrolytes.[12]

The main goal of this paper is to show that a variant of an earlier model of Schiby and Ruckenstein[7] can account for the stabilization of some colloids or emulsions at high electrolyte concentrations. In the present model, the hydration force has a strong dependence on the density of ion pairs on the surface of the particles or droplets, which is enhanced by the addition of electrolyte. This is due to the reassociation on the surface, which decreases the charge but generates additional ion pairs. The dipole moments of the ion pairs polarize the nearby water molecules and thus induce a hydration force. For large surface dipole densities, the hydration repulsion is strong enough to prevent (together with the double-layer repulsion) the coagulation at any electrolyte concentration. For low surface dipole density, the system coagulates for ionic strength higher than a critical value, as predicted by the DLVO theory. At intermediate surface dipole densities, the increase in the hydration repulsion with increasing electrolyte concentration can explain the restabilization of some colloidal and emulsion systems at high ionic strength.

In what follows, one considers for illustration purposes the case in which the charge is generated on the surface of colloidal particles or droplets by the adsorption of a surfactant, namely sodium dodecyl sulfate (SDS). We selected this case because information about the adsorption of SDS on an interface is available in the literature, and as it will become clearer later the number of parameters involved is smaller than in the case of silica. A more complex calculation about the silica and the amphoteric latex particles will be presented in a forthcoming paper. It involves several kinds of surface dipoles and equilibrium constants.

II. Theoretical Framework

In this section, the equations needed to calculate the interaction potential between two spherical particles will be presented. It will be assumed that the double-layer, hydration, and van der Waals interactions are independent of each other.

II.A. Surfactant Adsorption. The surface density of surfactant has a relevant role for both the double-layer (via the surface charge density) and the hydration interaction (via the dipole moment density of the ion pairs formed). It will be computed using the Frumkin adsorption isotherm:

$$b_1 C_{R^-} = \frac{\dfrac{\Gamma}{\Gamma_\infty}\exp\left(-2b_2\dfrac{\Gamma}{\Gamma_\infty}\right)}{1 - \dfrac{\Gamma}{\Gamma_\infty}} \tag{1}$$

where Γ is the surfactant surface density, Γ_∞ is the surface density at saturation, b_1 and b_2 are empirical parameters, and C_{R^-} is the concentration of the surfactant anions in

the liquid in the vicinity of the interface. The surfactant in the bulk is assumed to be completely dissociated, and hence the concentration of surfactant in the vicinity of the interface is related to the bulk surfactant concentration through the expression

$$C_{R^-} = C_s \exp\left(\frac{e\psi_s}{kT}\right) \tag{2}$$

where C_s is the bulk surfactant concentration; ψ_s is the surface potential, which is negative; e is the protonic charge; k is the Boltzmann constant; and T is the absolute temperature.

II.B. The Surface Charge. Denoting by α the dissociation constant, the surface charge density σ is given by

$$\sigma = -e\alpha\Gamma \tag{3}$$

For simplicity, it will be assumed that the electrolyte is 1:1 and has the same type of cations as the surfactant (e.g., NaCl and SDS). The charge is generated through the dissociation

$$R-X|_{\text{SURFACE}} \leftrightarrow R^-|_{\text{SURFACE}} + X^+|_{\text{LIQUID AT SURFACE}}$$

where $R^-|_{\text{SURFACE}}$ denotes the surface surfactant anion group and X^+ denotes the cation in the liquid at the surface. At equilibrium, one can write

$$K_D = \frac{C_{R^-,S}C_{X^+}}{C_{R-X}} = \frac{\alpha\Gamma C_{X^+}}{(1-\alpha)\Gamma} = \frac{\alpha}{1-\alpha}C_{X^+} \tag{4}$$

where $C_{R^-,S}$ is the surface density of the surfactant anions, C_{R-X} is the surface density of the nondissociated surfactants, C_{X^+} is the concentration of the cations in the liquid in the vicinity of the surface, and K_D is the equilibrium constant. Assuming that the electrolyte is completely dissociated, one obtains

$$C_{X^+} = (C_s + C_e)\exp\left(-\frac{e\psi_s}{kT}\right) \tag{5}$$

where C_e is the bulk electrolyte concentration.

II.C. Double-Layer Interaction. The calculation of the double-layer interaction accounts for the association–dissociation at the interface. Assuming two parallel plates at a distance x apart, the potential ψ_m at the middle distance between plates can be very well approximated by the following equation, due to Ohshima and Kondo:[13]

$$\tanh\left(\frac{e\psi_m}{4kT}\right) = \gamma_0\frac{1}{\cosh\left(\frac{\kappa x}{2}\right)} - \gamma_0^3\frac{\left(\frac{\kappa x}{2}\right)\sinh\left(\frac{\kappa x}{2}\right)}{\cosh^4\left(\frac{\kappa x}{2}\right)} +$$

$$\gamma_0^5\left\{\frac{\cosh^2\left(\frac{\kappa x}{2}\right) - 2\left(\frac{\kappa x}{2}\right)^2 - 1}{4\cosh^5\left(\frac{\kappa x}{2}\right)} - \right.$$

$$\left.\frac{3\left(\frac{\kappa x}{2}\right)\sinh\left(\frac{\kappa x}{2}\right)}{4\cosh^6\left(\frac{\kappa x}{2}\right)}\left(1 - 4\left(\frac{\kappa x}{2}\right)\tanh\left(\frac{\kappa x}{2}\right)\right)\right\} \tag{6}$$

where $\gamma_0 = \tanh(e\psi_s/4kT)$, ψ_s is the surface potential, $\kappa = \sqrt{2e^2C_e/\epsilon\epsilon_0 kT}$ is the reciprocal Debye length for a 1:1

(12) Healy, T. W.; Homola, A.; James, R. O.; Hunter, R. J. *Faraday Discuss. Chem. Soc.* **1978**, *65*, 156.

(13) Ohshima, H.; Kondo, T. *J. Colloid Interface Sci.* **1988**, *122*, 591.

electrolyte, ϵ_0 is the vacuum permittivity, and ϵ the dielectric constant of water. The surface charge density is related to the surface and midplane potentials via[1]

$$\sigma = -\frac{\kappa\epsilon\epsilon_0 kT}{e}\sqrt{2\left(\cosh\left(\frac{e\psi_s}{kT}\right) - \cosh\left(\frac{e\psi_m}{kT}\right)\right)} \quad (7)$$

Equations 1–7 can be solved simultaneously to obtain the surface charge density and the surface and midplane potentials. The double-layer force per unit area is given by the Langmuir equation,[1]

$$p_{DL} = 2C_e kT\left(\cosh\left(\frac{e\psi_m}{kT}\right) - 1\right) \quad (8)$$

and the double-layer interaction energy per unit area, between two parallel plates at a distance H apart, is obtained by integrating the double layer force:

$$U_{DL,p}(H) = \int_H^\infty p_{DL}(x)\,dx \quad (9)$$

For two identical spheres of radius a separated by the distance of closest approach z, the interaction energy is given, in the Derjaguin approximation, by[1]

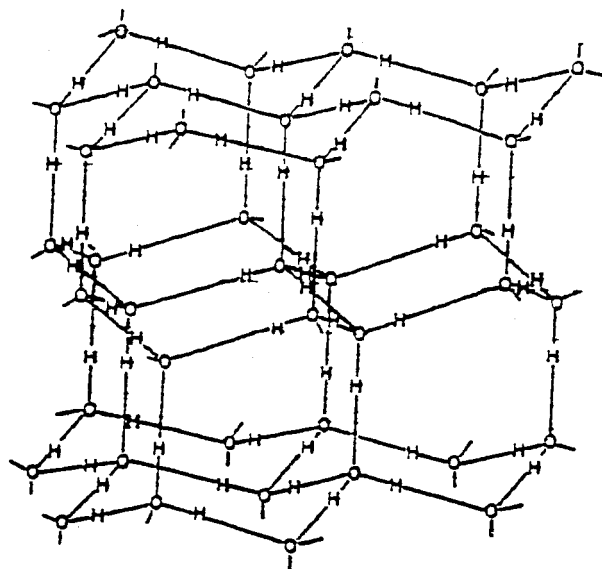$$U_{DL,s}(z) = \pi a \int_z^\infty U_{DL,p}(H)\,dH \quad (10)$$

II.D. The van der Waals Attraction. For the van der Waals attraction between identical spheres of radius a, separated by the distance of closest approach z, we will use the formula derived by Hamaker:[14]

$$U_{vdW} = -\frac{A_H}{6}\left\{\frac{2a^2}{(z+2a)^2 - (2a)^2} + \frac{2a^2}{(z+2a)^2} + \ln\left(\frac{(z+2a)^2 - (2a)^2}{(z+2a)^2}\right)\right\} \quad (11)$$

where A_H is the Hamaker constant.

The Lifshitz theory of dispersion forces, which does not imply pairwise additivity and takes into account retardation effects, shows that the Hamaker constant A_H is actually a function of the separation distance. However, for the stability calculations that follow, only the values of the attraction potential at distances less than a few nanometers are relevant, and in this range one can consider that A_H is constant.

II.E. Hydration Interaction. A molecule in liquid water has a first-neighbor coordination number between 4 and 5, which is closer to the coordination number in ice, 4, than to that in a normal liquid, 12.[15] This suggests that the tetrahedral coordination in ice, due to the hydrogen bonding, is almost preserved in the liquid state. To account for this characteristic, Nemethy and Scheraga proposed a model in which the liquid water is composed of icelike clusters of various sizes.[16] It is then reasonable to assume that in the vicinity of a surface the icelike clusters are reorganized in a layered structure, similar to that of ice I, with successive layers containing out-of-plane hexagonal rings of water molecules, parallel to the external surface, as depicted in Figure 1. Each layer is composed of two planar sublayers; a water molecule from a sublayer has three hydrogen bonds with three molecules of the other

(14) Hamaker, H. C. *Physica IV* **1937**, *10*, 1058.
(15) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: New York, 1969.
(16) Nemethy, G.; Scheraga, H. A. *J. Chem. Phys.* **1962**, *36*, 3382.

Figure 1. The structure of ice I (reproduced from ref 16). Each site is connected by hydrogen bonding with three sites from the same layer and one site from either one or the other of the neighboring layers. Copyright 1962 by the American Institute of Physics.

sublayer of the same layer and one with a molecule belonging to a sublayer of one of the adjacent layers. While the alignment gradually decreases with the distance from the surface, it is reasonable to consider that for not too large distances this decrease can be neglected.

The treatment of the hydration interaction follows the model employed earlier by Schiby and Ruckenstein,[7] based on the mutual interactions of dipoles. In this model, it is considered that the dipoles of the surface polarize the water molecules of the first layer of water and the polarization propagates from layer to layer. When two surfaces approach each other, the polarized layers will increasingly overlap. As a result, the local dipole moment of the water molecules will be decreased. This increases the free energy of the system and thus generates a repulsive force.

II.E.1. Mutual Polarization of the Water Molecules. Assuming that all the water molecules from the layer i have the same average polarization m_i, normal to the layer, the field E_i^{local}, acting on a site of layer i, due to all the other polarized molecules can be formally written as

$$E_i^{local} = (C_0 m_i + C_1(m_{i-1} + m_{i+1}) + ... + C_k(m_{i-k} + m_{i+k}) + ...) \quad (12)$$

where the coefficient C_k accounts for the contribution of the dipoles of layer $i \pm k$ to the local field at a site of layer i (C_0 corresponds to the field at a site of layer i generated by all the other dipoles of the same layer i). An evaluation of the coefficients C will be provided in section II.E.4.

If there is no external electric field and the molecules of the first water layer have an average dipole moment m_1 oriented perpendicular to the layer, caused by the surface dipoles, the average dipole moment of the molecules of the layer i situated at the distance $x = i\Delta$, $m_i = m(x)|_{x=i\Delta}$ is given by

$$m_i = m(x)|_{x=i\Delta} = \gamma E_i^t = \gamma E_i^{local} = \gamma(C_0 m(x) + C_1(m(x - \Delta) + m(x + \Delta)) + ...) \quad (13)$$

where Δ is the distance between the centers of two

successive layers and γ is the molecular polarizability, as defined and calculated in the Appendix.

An approximate solution can be obtained by expanding $m(x \pm \Delta)$ in series:

$$m(x \pm \Delta) = m(x) \pm \frac{dm(x)}{dx}\Delta + \frac{1}{2}\frac{d^2m(x)}{dx^2}\Delta^2 \pm ...$$

Because of symmetry the odd derivatives cancel, and when the terms of order 4 and higher are neglected, eq 13 becomes

$$m(x)(1 - \gamma(C_0 + 2C_1 + 2C_2 + ...)) =$$
$$\gamma\Delta^2(C_1 + 4C_2 + ...)\frac{d^2m(x)}{dx^2}$$

which is of the form

$$\frac{d^2m(x)}{dx^2} - \frac{1}{\lambda^2}m(x) = 0 \qquad (14)$$

with a decay length λ given by

$$\lambda = \sqrt{\frac{(C_1 + 4C_2 + 9C_3 + ...)\gamma\Delta^2}{1 - (C_0 + 2C_1 + 2C_2 + ...)\gamma}} \qquad (15)$$

II.E.2. Polarization of the First Water Layer. In a homogeneous medium with uniform dielectric properties, an infinite, planar, uniform and continuous distribution of dipoles produces a vanishing electric field. This is due to the long range of the electrostatic interactions, which leads to the cancellation of the strong fields, generated by the nearest dipoles, by the weakest fields produced by the infinite number of remote dipoles. A discrete distribution of planar dipoles generates an oscillating field above the surface, whose average vanishes.

However, the dielectric constant of the interactions of the water molecule from the first layer with the nearest dipole of the surface, denoted ϵ_1, is expected to be much smaller than the bulk dielectric constant of water, ϵ. Denoting as E^d the field generated (in a vacuum) by a surface dipole, the field generated by all the dipoles of the surface is

$$E = \frac{1}{\epsilon_1}E^d_{nearest} + \frac{1}{\epsilon}\sum_{all\ others}E^d = \frac{\epsilon - \epsilon_1}{\epsilon\epsilon_1}E^d_{nearest} +$$
$$\frac{1}{\epsilon}\sum_{all\ dipoles}E^d = \frac{\epsilon - \epsilon_1}{\epsilon\epsilon_1}E^d_{nearest} \equiv \frac{1}{\epsilon'}E^d_{nearest} \quad (16)$$

where it was assumed that the interaction with the nearest dipole is screened by a medium with the dielectric constant ϵ_1, while all the other interactions are screened by a medium with the dielectric constant ϵ. Equation 16 accounts for the fact that the average field of all the dipoles distributed on the interface, $(1/\epsilon)\sum_{all\ dipoles}E^d$, in a medium with constant ϵ vanishes. This implies that the net average field acting on the first layer can be calculated by considering only the field generated by the nearest dipole, in a medium of effective dielectric constant ϵ'.

After some distance from the surface, the fields of all dipoles of the interface are screened by the intervening water molecules. Hence, the spatial average of the field induced by the surface dipoles vanishes, since the depolarization field of the remote dipoles is no longer negligible compared to the polarization field of the nearest dipoles.
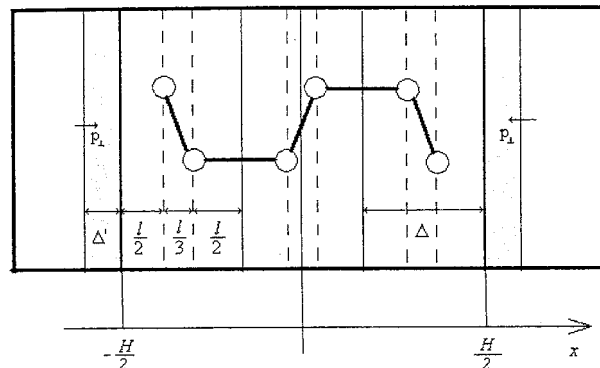
Figure 2. Sketch of three water layers between parallel plates. The dotted lines represent the two planar sublayers of the layers. Only two hydrogen bonds (thick lines) are shown for each water molecule (circles): one with a molecule from the other sublayer of the same layer and one with a molecule from an adjacent layer. The distance between two water molecules is denoted by l; Δ is the distance between two water layers, and Δ' is the distance between the center of the surface dipoles and the interface.

It will be assumed that the field induced by the surface dipoles becomes negligible after the first water layer.

The interfaces are located at the external boundaries of the first organized water layers, while the surface dipoles are situated at a distance Δ' below the interface (see Figure 2). There are also water molecules absorbed among the headgroups of the surface, which do not have the icelike structure but are organized differently, due to the strong interactions with the surfactant headgroups. The high local electric field generated by a dipole of the surface, as well as the small number of water molecules which are screening the water molecules of the first layer, make the local dielectric constant, ϵ_1, near the dipole small.

Let us approximate the area A per surface dipole, which is polarized by the corresponding dipole, by a disk of radius R, located at a distance Δ' from the dipole $\vec{p}$, which has the components $p_{\parallel}$ and $p_{\perp}$ parallel and normal, respectively, to the surface.

The field produced by $p_{\parallel}$ vanishes because of symmetry, and so does the electric field parallel to the surface. The electric field, normal to the surface, generated by the dipole, at a point whose position vector makes an angle θ with the normal, is given by

$$E^d_{\perp} = \frac{1}{4\pi\epsilon'\epsilon_0 r^3}\{p_{\perp}(3\cos^2(\theta) - 1)\} \qquad (17)$$

where $r = \Delta'/\cos(\theta)$. For the average field produced by a surface dipole, one obtains

$$\bar{E} = \frac{1}{\pi R^2}\int_0^R \frac{2\pi\rho\ d\rho}{4\pi\epsilon'\epsilon_0(\Delta'^2 + \rho^2)^{3/2}}\left\{p_{\perp}\left(3\frac{\Delta'^2}{(\Delta'^2 + \rho^2)} - 1\right)\right\} =$$
$$\frac{p_{\perp}}{\epsilon'}\frac{1}{2\pi\epsilon_0(R^2 + \Delta'^2)^{3/2}} \qquad (18)$$

II.E.3. The Hydration Interaction. The solution of eq 14 for two planar, parallel surfaces separated by the distance H (hence for the boundary condition $m(-H/2) = m_1, m(H/2) = -m_1$) is

$$m(x) = -m_1\frac{\sinh\left(\frac{x}{\lambda}\right)}{\sinh\left(\frac{H}{2\lambda}\right)} \qquad (19)$$

where m_1 is the dipole moment of the water molecules at the interface, which is proportional to the total field $E^t = \bar{E} + E_1^{local}$:

$$m_1 = \gamma(\bar{E} + E_1^{local}) = \gamma(\bar{E} + m_1 C_0 + m_2 C_1 + ...) \quad (20)$$

Since from eq 19, $m_2 = m[-(H/2) + \Delta] = m_1 \sinh[(H - 2\Delta)/2\lambda]/\sinh(H/2\lambda)$, eq 20 becomes

$$m_1(H) = \frac{\gamma \bar{E}}{\left(1 - \gamma\left(C_0 + C_1 \dfrac{\sinh\left(\dfrac{H - 2\Delta}{2\lambda}\right)}{\sinh\left(\dfrac{H}{2\lambda}\right)} + ...\right)\right)} \quad (21)$$

The electrostatic energy of a water molecule with the polarizability γ, which acquires the polarization m in the field E_e, is

$$U = -\int_0^{E_e} m(E)\,dE = -\int_0^{E_e} \gamma E\,dE = -\frac{1}{2}\gamma E_e^2 = -\frac{m^2}{2\gamma}$$

The electrostatic interaction energy per unit area, between the two parallel plates, is given by

$$U_{H,p}(H) = -\frac{1}{2S}\sum_{\text{all molecules}}\frac{(m(x))^2}{\gamma} =$$

$$-\frac{1}{2S}\int_{\text{Volume}}\frac{(m(x))^2}{\gamma v}\,dV = -\frac{1}{2\gamma v}\int_{-H/2}^{H/2}(m(x))^2\,dx =$$

$$\frac{\gamma \bar{E}^2}{\left(1 - \gamma\left(C_0 + C_1 \dfrac{\sinh\left(\dfrac{H-2\Delta}{2\lambda}\right)}{\sinh\left(\dfrac{H}{2\lambda}\right)} + ...\right)\right)^2} \frac{H - \lambda \sinh\left(\dfrac{H}{\lambda}\right)}{4v\sinh^2\left(\dfrac{H}{2\lambda}\right)}$$

$$(22)$$

where V is the volume occupied by all the icelike organized water layers, v is the volume occupied by a water molecule, and S is the surface area of a plate. Here, we will assume that the electrostatic energy of the remaining water molecules, located among the headgroups of the surfactant molecules, does not depend on the separation distance H between plates and hence does not contribute to the hydration interaction.

The interaction energy is obtained by subtracting the electrostatic energy at large separation distances, $U_{H,p}(\infty)$. Using the Derjaguin approximation, the hydration interaction energy between two spheres is given by

$$U_{H,s}(z) = \pi a \int_z^\infty (U_{H,p}(H) - U_{H,p}(\infty))\,dH \quad (23)$$

II.E.4. Evaluation of the Local Field. For a tetrahedral coordination of the water molecules, the distance between the two planar sublayers of the same layer of icelike structure is $(1/3)l$, l being the distance between the centers of two adjacent water molecules, while the distance between the centers of two adjacent layers is $\Delta = (4/3)l$. The vertexes of the tetrahedron formed by the four first neighbors of a water molecule have the length $l\sqrt{8/3}$, while the planar projection of the tilted hexagonal lattice has the side $l\sqrt{8/9}$. The volume occupied in this structure by a water molecule is $v = (8/3\sqrt{3})l^3$.

While the field produced by remote dipoles can be treated as screened by a medium with a large dielectric constant ($\epsilon \cong 80$), the screening of the neighboring dipoles is much weaker. In the present treatment, we will simply assume that E^{local} is produced only by the dipoles located within a radius $2l$ from the given site and that the dielectric constant for them is a constant ϵ''. The electric field caused by a neighboring molecule is given by eq 17 (with ϵ'' replacing ϵ'). It is important to emphasize that the local dielectric constant ϵ'' is smaller than ϵ, the bulk dielectric constant of water.

The electric field $E_{i,0}^{local}$ generated at a site of layer i by the other dipoles from the same layer is given by

$$E_{i,0}^{local} = C_0 m_i = \left(3\frac{\left(3\left(\dfrac{1}{3}\right)^2 - 1\right)}{1} + 6\frac{(3(0)^2 - 1)}{\left(\sqrt{\dfrac{8}{3}}\right)^3} + \right.$$

$$\left. 3\frac{\left(3\left(\dfrac{1}{\sqrt{33}}\right)^2 - 1\right)}{\left(\sqrt{\dfrac{11}{3}}\right)^3}\right)\frac{m_i}{4\pi\epsilon_0\epsilon''l^3} = -\frac{3.7663}{4\pi\epsilon_0\epsilon''l^3}m_i \quad (24)$$

The field generated by the neighbors (within a radius $2l$ from the given site) located in the adjacent water layers $i \pm 1$, averaged over the two sublayer sites of layer i, is given by

$$E_{i,\pm1}^{local} = C_1 m_{i\pm1} =$$

$$\frac{\left(2 + 3\dfrac{\left(3\left(\sqrt{\dfrac{2}{3}}\right)^2 - 1\right)}{\left(\sqrt{\dfrac{8}{3}}\right)^3} + 6\dfrac{\left(3\left(\sqrt{\dfrac{3}{11}}\right)^2 - 1\right)}{\left(\sqrt{\dfrac{11}{3}}\right)^3}\right) + \left(\dfrac{2}{\left(\dfrac{5}{3}\right)^3} + 3\dfrac{\left(3\left(\sqrt{\dfrac{2}{3}}\right)^2 - 1\right)}{\left(\sqrt{\dfrac{8}{3}}\right)^3}\right)}{2}$$

$$\times \frac{m_{i\pm1}}{4\pi\epsilon''\epsilon_0 l^3} = \frac{1.8272}{4\pi\epsilon''\epsilon_0 l^3}m_{i\pm1} \quad (25)$$

Only the contributions from the first 26 neighbors (12 from the same layer and 14 from the two adjacent layers) were taken into account. The field produced by the more remote dipoles is neglected, because it is screened by the intervening water molecules.

III. Results

III.1. General Behavior of the Interaction Energy. We will try first to obtain some general information about the interaction energy between two identical spheres of radius a, separated by the distance of closest approach z, at high electrolyte concentrations, using some simple approximations. The following expressions will be used for the interaction energies:

$$U_{vdW,s} = -\frac{A_H a}{12z} \quad (26a)$$

$$U_{H,s} = \pi a \lambda B \exp\left(-\frac{z}{\lambda}\right) \quad (26b)$$

which are rough approximations of the interaction energies obtained with the methods described above for the van der Waals and hydration interactions (we approximate the hydration interaction energy per unit area between two parallel plates at distance x apart by $U_{H,p} = B \exp(-x/\lambda)$). When the double-layer interaction at high ionic strengths is neglected, the interaction energy has an

absolute minimum at $z = 0$ (primary minimum) and a local minimum at some finite z (secondary minimum), separated by a potential barrier. The extrema of the interaction energy are obtained from the condition of vanishing of the first derivative,

$$\frac{dU(z)}{dz} = -\pi aB \exp\left(-\frac{z}{\lambda}\right) + \frac{A_H a}{12z^2} = 0$$

which can be rewritten as

$$F(\xi) \equiv \xi^2 \exp(-\xi) = \frac{A_H}{12\pi B\lambda^2} \quad (27)$$

where $\xi = z/\lambda$. $F(\xi)$ has a maximum at $\xi = 2$, $F(2) = 2^2 \exp(-2)$. Hence, if $B < B^* = A_H/[48\pi\lambda^2\exp(-2)]$, eq 27 has no solution and there is no potential barrier to prevent coagulation. When $B > B^*$, eq 27 has two solutions, the smaller one corresponding to the maximum and the larger one to the secondary minimum of the energy. Another useful value for the preexponential factor B of hydration is obtained from the condition of vanishing of the energy maximum,

$$U(z) = \pi a\lambda B \exp\left(-\frac{z}{\lambda}\right) - \frac{A_H a}{12z} = 0 \quad (28)$$

which, together with eq 27, leads to

$$z_{max} = \lambda \quad (29a)$$

and

$$B = B_0 = \frac{A_H \exp(1)}{12\pi\lambda^2} \quad (29b)$$

Although in this case $U(z_{max}) - U(\infty) = 0$, the secondary minimum can be sufficiently deep for the potential barrier between the latter and the maximum to hinder the coagulation at the primary minimum. By substitution of eq 29b in eq 27, the positions of the two extrema satisfy the equation

$$\xi^2 \exp(-\xi) = \exp(-1) \quad (30)$$

with the solutions $\xi = \xi_1 = 1$ for the maximum (eq 29a) and $\xi = \xi_2 = 3.5129$ for the minimum. Therefore,

$$z_{min} = \xi_2\lambda \quad (31a)$$

and

$$U(z_{min}) = -\frac{A_H a}{12\lambda}\left(\frac{\xi_2 - 1}{\xi_2^2}\right) \quad (31b)$$

By use of some typical values for the parameters, namely, $A_H = 1 \times 10^{-20}$ J, $a = 1000$ Å, and $\lambda = 2.96$ Å, for an absolute temperature $T = 300$ K, the depth of the minimum is about -13.8 kT, and hence the transition from the secondary to the primary minimum is very slow. The depth of the minimum increases as the radius a and the Hamaker constant A_H increase.

We will now examine the consequences of a small increase in the hydration force, by assuming that the preexponential factor becomes $B = B_0(1 + \eta)$, with η small compared to 1. Equation 27 acquires the form

$$F(\xi) = \xi^2 \exp(-\xi) = \frac{\exp(-1)}{(1 + \eta)} \quad (32)$$

Because the perturbation η is small, $F(\xi)$ can be replaced around ξ_1 and ξ_2 by the linear approximations

$$F_1(\xi) = \frac{\xi}{\exp(1)} \quad (33a)$$

$$F_2(\xi) = \frac{\xi(2 - \xi_2) + \xi_2^2 - \xi_2}{\xi_2 \exp(1)} \quad (33b)$$

For the maximum, the linear approximation (eq 33a) inserted in eq 32 provides

$$z_{max} = \frac{\lambda}{1 + \eta} \quad (34a)$$

and

$$U(z_{max}) = \frac{A_H a}{12\lambda}(\eta + \eta^2) \quad (34b)$$

For the values of the parameters employed above, the factor in the front of the parenthesis is about 68 kT, and consequently even a small η produces a large increase of the energy of the maximum.

For the minimum, eqs 33b and 32 lead to

$$z_{min} = \frac{\lambda\xi_2}{\xi_2 - 2}\left(\xi_2 - \frac{2 + \eta}{1 + \eta}\right) \quad (36a)$$

and

$$U(z_{min}) = \frac{A_H a}{12\lambda}\left(-\frac{\xi_2 - 1}{\xi_2^2} + \frac{\eta}{\xi_2^2} + O(\eta^2)\right) \quad (36b)$$

where the terms in η^2 and higher were neglected. The first term represents the depth of the minimum for $\eta = 0$. Because $\xi_2^2 = 12.34$, the increase in the energy of the secondary minimum, when the hydration increases, is about 1 order of magnitude smaller than the corresponding increase of the maximum energy. For small values of η, the increase is negligible compared with the depth of the unperturbed secondary minimum ($\xi_2 - 1 \cong 2.5129 \gg \eta$).

As general conclusions, one can notice the following: (1) if the preexponential factor B is smaller than the critical value B^*, there is no potential barrier which can prevent aggregation; (2) if $B \gg B_0$, the maximum of the interaction energy is large and no aggregation takes place at the primary minimum but can take place at the secondary minimum; and (3) small changes of B around B_0 dramatically affect the value of the maximum, but much less the minimum. Because B is proportional to $(p_\perp/\epsilon')^2$, the behavior of the system is expected to be very sensitive to changes in the ratio $p_\perp/\epsilon'$.

III.2. Numerical Calculations. In what follows, the equations from section II will be employed to calculate the effect of the hydration force on the stability of colloids or emulsions in water in the presence of NaCl and SDS, which represent a common electrolyte and surfactant, respectively.

For the adsorption isotherm, the following values of the parameters will be used: $b_1 = 881$ m³/mol, $b_2 = -1.53$, and $\Gamma_\infty = 5 \times 10^{-6}$ mol/m². These coefficients were obtained from experimental data at high electrolyte concentra-

tions.[17] While the experiments have been carried out for a water−air interface, the coefficients probably provide good approximations also for the present case, because the hydrophobic bonding (the disorganization of water by the presence of surfactant) constitutes the main driving force for adsorption. The equilibrium constant for the association−dissociation at the interface is not known. The only related relevant information is the dissociation constant of the ion pair $NaSO_4^-$, which was estimated to be $K_D = 10^{-0.7} = 0.1995$ mol/dm³.[18] Because the repulsion among the headgroups increases as the dissociation increases (and this provides a positive contribution to the free energy), the dissociation constant is expected to be lower in this case.

A discussion regarding the molecular polarizability is provided in the Appendix. In the present paper, we will use for the molecular polarizability expression A.7, which provides a lower bound for γ, in the absence of saturation effects. When eq A.7 is inserted into eq 15, the decay length acquires the simple form ($C_k = 0$ for $k > 1$)
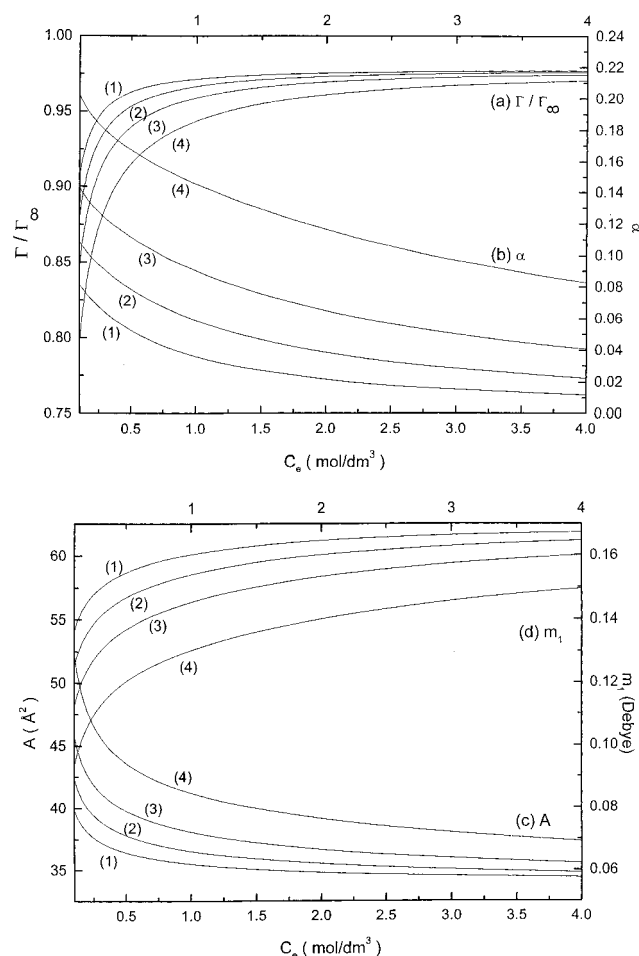
$$\lambda = \sqrt{\frac{3\epsilon_0 \nu(\epsilon - 1)C_1\Delta^2}{\epsilon + 2}} \qquad (37)$$

We will use in the calculations $l = 2.76$ Å (which corresponds to the distance between molecules in the structure of ice I, as compared to about 2.9 Å for molecules in water), and $\epsilon = 80$. For the local dielectric constant, we will assume $\epsilon'' = 1$, which constitutes a lower bound. In a perfect tetrahedral coordination, the average distance between two successive water layers is $\Delta = (4/3)l$, and the decay length of the hydration interaction calculated using eq 37 is $\lambda = 2.96$ Å. It should be noted that the latter value is in the range determined experimentally for the hydration force between phospholipid bilayers.[4] Lower values of λ can be obtained for higher ϵ''. For the distance between the center of the ion pair and the interface (located at the boundary of the first organized water layer), the value $\Delta' = 1.0$ Å was selected.

The model employed for the hydration force implies a continuum, even for low separation distances between particles. It was also assumed that the hydration, double-layer, and van der Waals interactions are additive. The double layer affects the hydration force mainly because of the decrease of the molecular polarizability by large electric fields. However, in the present case, in the vicinity of the surface the electric field due to the double layer is smaller than $\bar{E}$ by an order of magnitude and hence its influence on the hydration force can be neglected at small separation distances.

The magnitude of the hydration force is proportional to the ratio $(p_\perp/\epsilon')^2$, which can vary in a quite large range. The dipole moments of the common salt molecules are of the order of 10 D (e.g., 8.5 D for NaCl and 10.4 D for CsCl);[19] the values are expected to be larger for the ion pairs on the particle surface, because the cations are hydrated. The value of ϵ' is expected to depend strongly on the particular organization of the water molecules absorbed among the headgroups of the surface.

To have some feelings about their order of magnitude, the ratio Γ/Γ_∞, the dissociation constant α, the area per ion pair A, and the average dipole moment of the first water layer m_1 are plotted in Figure 3a−d as functions of electrolyte concentration for $C_s = 0.001$ mol/dm³, $(p_\perp/\epsilon') = 1.0$ D, large distances between particles or droplets ($z \rightarrow$

(17) Feinerman, V. B. *Colloids Surf.* **1991**, *57*, 249.
(18) Davies, C. W. *Ion Association*; Butterworth: London, 1962.
(19) Landolt-Börnstein, Springer, Heidelberg, 1985.

Figure 3. (a) The ratio Γ/Γ_∞, (b) the dissociation constant α, (c) the area per ion pair A, and (d) the polarization of the water molecules near the interface, m_1, as functions of the electrolyte concentration C_e for various values for the dissociation constant: (1) $K_D = 0.05$ mol/dm³; (2) $K_D = 0.1$ mol/dm³; (3) $K_D = 0.1995$ mol/dm³; (4) $K_D = 0.5$ mol/dm³.

∞), and various dissociation constants K_D, ranging between 0.05 and 0.5 mol/dm³. The low dissociation of the surfactant headgroups is a consequence of the low value selected for the equilibrium dissociation constant K_D; however, the results are not significantly modified even when K_D varies with 1 order of magnitude. In what follows, the following values will be used for some of the parameters: $K_D = 0.1$ mol/dm³, $b_1 = 881$ m³/mol, $b_2 = -1.53$, $\Gamma_\infty = 5 \times 10^{-6}$ mol/m², $\lambda = 2.96$ Å, $\epsilon = 80$, $\Delta' = 1.0$ Å, and $C_s = 0.001$ mol/dm³. The other parameters, namely, a, A_H, and the ratio $(p_\perp/\epsilon')$, will be varied.

The values of the interaction energy at the maximum and at the secondary minimum are proportional with the radius a of the particle or droplet and depend strongly on the Hamaker constant A_H and on the hydration repulsion. As shown in the previous section, small modifications in the ratio $(p_\perp/\epsilon')$ (and hence in the hydration repulsion) can lead to a large increase in the potential barrier between the primary and secondary minima, thus affecting the stability of the system.

First, calculations will be presented regarding the interaction energy between two identical spherical particles of radius $a = 100$ Å, Hamaker constant $A_H = 2.0 \times 10^{-20}$ J, and $p_\perp/\epsilon' = 2.6$ D. The interaction energy is plotted as a function of distance for electrolyte concentrations ranging from 0.1 to 4.0 mol/dm³ (Figure 4a). At relatively low electrolyte concentrations, the height of the barrier
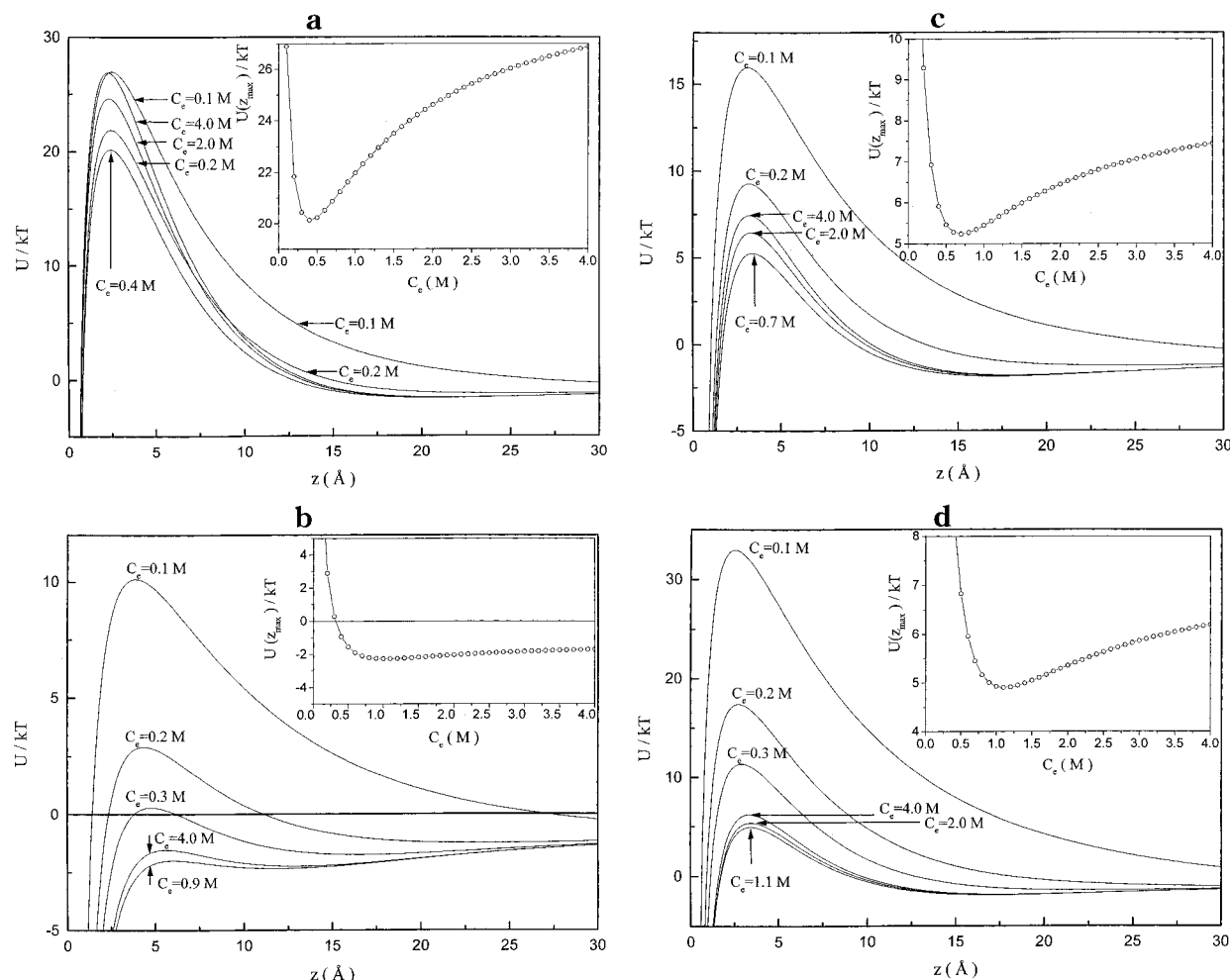
Figure 4. (a) The interaction energy as a function of separation distance, for $a = 100$ Å, $p_\perp/\epsilon' = 2.6$ D, $A_H = 2.0 \times 10^{-20}$ J, and various electrolyte concentrations. In the inset, the maximum value of the interaction energy is plotted versus electrolyte concentration. (b) The interaction energy as a function of separation distance, for $a = 100$ Å, $p_\perp/\epsilon' = 1.3$ D, $A_H = 2.0 \times 10^{-20}$ J, and various electrolyte concentrations. In the inset, the maximum value of the interaction energy is plotted versus electrolyte concentration. (c) The interaction energy as a function of separation distance, for $a = 100$ Å, $p_\perp/\epsilon' = 1.9$ D, $A_H = 2.0 \times 10^{-20}$ J, and various electrolyte concentrations. In the inset, the maximum value of the interaction energy is plotted versus electrolyte concentration. (d) The interaction energy as a function of separation distance, for $a = 200$ Å, $p_\perp/\epsilon' = 1.3$ D, $A_H = 1.0 \times 10^{-20}$ J, and various electrolyte concentrations. In the inset, the maximum value of the interaction energy is plotted versus electrolyte concentration.

ΔU, which is measured with respect to an infinite separation distance, $\Delta U = U(z_{max}) - U(\infty)$, decreases with increasing electrolyte concentration, as predicted by the DLVO theory. However, after reaching a minimum at $C_e = 0.4$ M, the barrier slowly increases with increasing ionic strength (the inset presents the maximum value of the energy as a function of electrolyte concentration). Since in this case the height of the barrier is always higher than 20 kT, the system is stable at any electrolyte concentration.

In Figure 4b, the interaction energy is calculated using $p_\perp/\epsilon' = 1.3$ D. At low electrolyte concentrations, the height of the potential barrier decreases with increasing C_e, because of the screening of the double layer. The increase in the hydration force with increasing C_e, due to the reassociation, is not sufficient to generate a high enough potential barrier to prevent the rapid coagulation. For electrolyte concentrations larger than about 0.25 mol/dm³, the system is unstable.

Figure 4c provides U/kT for $p_\perp/\epsilon' = 1.9$ D. The maximum of the interaction energy decreases with increasing electrolyte concentration and reaches a minimum of 5.26 kT at $C_e = 0.7$ mol/dm³. However, with a further increase of the ionic strength the maximum energy gradually increases and at $C_e = 4.0$ mol/dm³ it becomes 7.45 kT. The

rate of aggregation at 4.0 mol/dm³ is hence decreased by a factor of the order of exp(7.45 − 5.26) = 8.93, as compared to the maximum aggregation rate, obtained at $C_e = 0.7$ mol/dm³. There is therefore a restabilization of the system with increasing electrolyte concentration.

The calculations were repeated for a system with $a = 200$ Å, $A_H = 1.0 \times 10^{-20}$ J, and $p_\perp/\epsilon' = 1.5$ D. As shown in Figure 4d, the minimum potential barrier is reached now at $C_e = 1.1$ mol/dm³. The rate of aggregation is in this case about 3.7 times slower at $C_e = 4.0$ mol/dm³ than at $C_e = 1.1$ mol/dm³.

The matters become more complex for large particles and large Hamaker constants. Figure 5a presents the interaction energy for $a = 1000$ Å, $A_H = 5.0 \times 10^{-20}$ J, and $p_\perp/\epsilon' = 2.45$ D (while keeping the values of the other parameters as before). The maximum of the interaction energy becomes negative at $C_e \sim 0.3$ mol/dm³, reaches a minimum at $C_e \sim 0.5$ mol/dm³, and then strongly increases, becomes again positive at $C_e \sim 1.0$ mol/dm³, and exceeds 30 kT at $C_e = 4.0$ mol/dm³. However, as anticipated in the section where the general behavior was examined, the secondary minimum is extremely deep in this case. The increase of the hydration force with increasing ionic strength has only a moderate effect on the depth of the
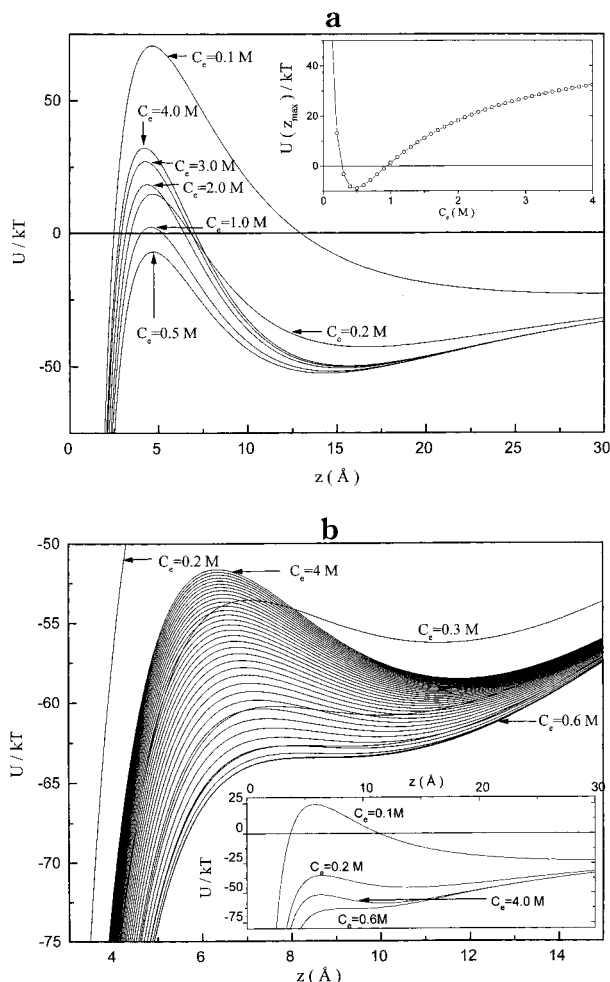
Figure 5. (a) The interaction energy as a function of separation distance, for $a = 1000$ Å, $p_\perp/\epsilon' = 2.45$ D, $A_H = 5.0 \times 10^{-20}$ J, and various electrolyte concentrations. In the inset, the maximum value of the interaction energy is plotted versus electrolyte concentration. (b) The interaction energy as a function of separation distance, for $a = 1000$ Å, $p_\perp/\epsilon' = 1.95$ D, and $A_H = 5.0 \times 10^{-20}$ J for various electrolyte concentrations, in the region where a potential barrier between the primary and the secondary minimum is formed at large electrolyte concentrations. The electrolyte concentration is varied in steps of 0.1 M. The interaction energy is plotted over larger ranges in the inset.

secondary minimum (see eq 36b and Figure 5a). Therefore, the particles will coagulate at the secondary minimum for all the electrolyte concentrations considered, with the exception of a narrow range around $C_e \sim 0.5$ mol/dm³. At concentrations of the order of 0.5 mol/dm³, the particles can overcome the barrier and aggregate at the primary minimum if the frictional losses are small enough.

If the frictional losses are large, an interesting situation occurs at a lower value of $p_\perp/\epsilon'$ than that used in Figure 5a, namely, $p_\perp/\epsilon' = 1.95$ D (see Figure 5b). When $C_e = 0.5$ mol/dm³, there is no potential barrier and rapid coagulation at the primary minimum occurs. However, a relatively large potential barrier of the order of 10 kT between the primary and the secondary minima ($\Delta U = U(z_{max}) - U(z_{min})$) is established at very large electrolyte concentrations ($C_e > 4$ mol/dm³). In this case, the aggregation occurs at the secondary minimum.

There is some experimental evidence that for some colloidal systems, the rate of aggregation has a maximum and then decreases with increasing electrolyte concentration. In the experiment of Alfridsson et al.,[2] the rate constant of aggregation for a suspension of charged

paraffin particles (in the presence of a long-chain carboxylic acid, C_{22}) increased with the concentration of NaCl at low ionic strength, reached a maximum at about 0.5 mol/dm³ NaCl, and then decreased for higher electrolyte concentrations.

There are also colloidal systems (e.g., silica) whose stability at any electrolyte concentration can be explained by a large hydration repulsive force.[1] It is interesting to note that there are also systems whose stability depends on the nature of the electrolyte. Healy et al.[12] reported that amphoteric latex particles coagulated when the concentration of $CsNO_3$ exceeded 0.8 mol/dm³. However, they remained stable even when concentrations up to 3.0 mol/dm³ of KNO_3 or $LiNO_3$ were employed. The effect was qualitatively interpreted in terms of a "hydration barrier"; to allow close particle–particle aggregation, the cations adsorbed on the surface should be dehydrated. In the present paper, the hydration force is considered as originating from the ability of the ion pairs formed on the surface to polarize the water layers. The cation Cs^+ can be easily dehydrated because its heat of hydration is relatively low. In contrast, the cations Li^+ and K^+ have higher heats of hydration and it is difficult to dehydrate them. As a result, the dipole moment of Cs is smaller than those of Li and K, and hence the hydration repulsion is weaker for the former cation. As our calculations indicate, changes of the order of 10% in the ratio $p_\perp/\epsilon'$ might be sufficient to convert an unstable system into a stable one at high electrolyte concentrations. A detailed treatment of the problem will be presented in a forthcoming paper.

IV. Conclusions

The surface charge is responsible for the double-layer repulsion, which is attenuated by increasing the ionic strength. However, the ion pairs formed through the association–dissociation of the charges with the counterions induce a repulsive hydration force that increases with ionic strength. At the same surface density of ion pairs, the magnitude of the hydration force is related to the dipole moment, normal to the surface, of the surface ion pair, and to the local dielectric constant in the vicinity of the headgroups. A small value of $p_\perp/\epsilon'$ corresponds to a system which coagulates when the electrolyte concentration exceeds a critical value, as predicted by the DLVO theory. If $p_\perp/\epsilon'$ is large, the colloidal or emulsion system can remain stable at any ionic strength.

At intermediate values of $p_\perp/\epsilon'$ and for small particles or droplets and low van der Waals forces, the increase in the hydration force with electrolyte concentration can reduce the rate of aggregation by 1 order of magnitude; for large particles or droplets, the increase in hydration force with the ionic strength can increase the maximum interaction energy by more than 30 kT. In the latter case, the coagulation at the primary minimum can occur at intermediate electrolyte concentrations but at large electrolyte concentrations can be prevented by the increase of the hydration repulsion with increasing ionic strength. The particles can however aggregate at the secondary minimum, which is deep.

Appendix: Evaluation of the Molecular Polarizability

We considered two models for the evaluation of the molecular polarizability in the condensed phase.

One of the models follows the Lorentz–Debye theory, as summarized by Jackson[20] and Frenkel.[21] In a constant macroscopic field E_0, the macroscopic polarization P is

given by

$$P = \epsilon_0(\epsilon - 1)E_0 \tag{A.1}$$

where ϵ is the macroscopic dielectric constant.

The effective field E_e is the sum between the macroscopic field E_0 and the internal field E_{int}, due to the other molecules of the medium. The latter can be calculated by adding the individual contributions of the other molecules close to the selected one, E^{local}, and subtracting the contribution from the same molecules treated in an average continuum approximation described by the polarization P:

$$E_{int} = E^{local} - E_P = E^{local} + \frac{P}{3\epsilon_0} \tag{A.2}$$

The field E^{local} at a site of an icelike lattice generated by the dipoles located at the other sites of the lattice, assuming that all the water molecules have the average dipole moment m, normal to the layer, is given by

$$E^{local} = m(C_0 + 2C_1 + ... + 2C_k + ...) \tag{A.3}$$

where the coefficient C_k accounts for the contribution of the dipoles of layer $i \pm k$ to the E^{local} at a site of layer i. The average dipole moment m is proportional to the effective field; hence,

$$m = \gamma E_e = \gamma \left(E_0 + \frac{P}{3\epsilon_0} + m(C_0 + 2C_1 + 2C_2 + ...) \right) \tag{A.4}$$

where γ is the molecular polarizability.

Since m is related to the macroscopic polarization P via $m = Pv$, where v is the volume of a water molecule, eqs A.1 and A.4 provide the following expression for the macroscopic dielectric constant:

$$\epsilon = \frac{1 - \gamma(C_0 + 2C_1 + 2C_2 + ...) + \dfrac{2\gamma}{3\epsilon_0 V}}{1 - \gamma(C_0 + 2C_1 + 2C_2 + ...) - \dfrac{\gamma}{3\epsilon_0 V}} \tag{A.5}$$

(20) Jackson, J. D. *Classical Electrodynamics*; John Wiley & Sons: New York, 1975.
(21) Frenkel. J. *Kinetic theory of liquids*; Clarendon Press: Oxford, 1946.

The polarizability of a polar molecule has two components: an electronic polarizability, γ_e, due to the displacement of electrons, and an orientational polarizability, γ_d, due to the rotation of the permanent dipole in an electric field. In the vapor phase, assuming that the molecule can rotate freely, the orientational polarizability is given by the Langevin function. Therefore, for low effective electric fields ($pE_e \ll kT$)

$$\gamma = \gamma_e + \gamma_d \cong \gamma_e + \frac{p^2}{3kT} \tag{A.6}$$

where p is the permanent dipole moment of the molecule.

For vapors, the local field vanishes because of the spherical symmetry and eqs A.5 and A.6 provide good agreement with experiment. However, for liquids one can no longer use eq A.6 for the polarizability in the Lorentz−Debye model. Indeed, for liquid water, eq A.5 diverges for values of γ about 4 times smaller than the value of γ for its vapor, which at 300 K is $\gamma = \gamma_e + \gamma_d = 32.3 \times 10^{-40}$ C^2 m^2 J^{-1}. One can regard eq A.5 as the definition of the molecular polarizability and calculate γ in terms of the macroscopic dielectric constant ϵ. The lower value of the polarizability in liquid than in vapor can be explained in the framework of the Lorentz−Debye model by the hindered rotation of the permanent dipole moment by the neighboring molecules in the condensed state.

In contrast, the Onsager−Kirkwood model provides a polarizability in polar liquids larger than that in vapors.[21] This is a result of the increase of the dipole moment by the strong electric field, which is generated when a molecule with a permanent dipole moment is introduced in a polarizable medium (Onsager), and the correlation between the orientations of neighboring molecules (Kirkwood).[21]

In the present paper, we will use for the molecular polarizability the following expression (obtained from eq A.5):

$$\gamma = \frac{\epsilon_0 V}{\dfrac{\epsilon + 2}{3(\epsilon - 1)} + (C_0 + 2C_1 + 2C_2 + ...)\epsilon_0 V} \tag{A.7}$$

which provides a lower bound for γ in the absence of saturation. In a nonuniform field, we consider that $m = \gamma E^t$, where E^t is the total field acting on a molecule.