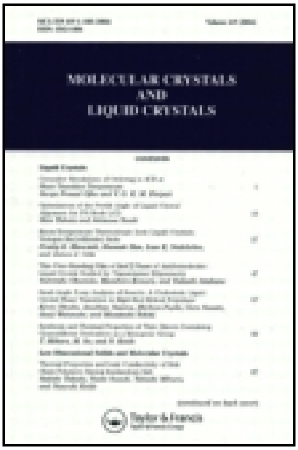

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Interactions Between Micelles in Nematic Lyomesophases

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Interactions Between Micelles in Nematic Lyomesophases

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Interactions between micelles are analyzed, taking into account Coulombian repulsion, van der Waals attraction and excluded volume, including the water solvation shell bound to the micelles. Curves of interaction energy and force are obtained as a function of the distance between micelles for planar and cylindrical micelles for specific nematic lyomesophases, having the fraction α of ionized polar groups as parameter. It is verified that for both geometries the attractive interaction is always larger than Coulombian repulsion for $\alpha \lesssim 0.1$; the high ionic strength of the medium leads to screening of the micelles since α values are smaller than this limit. Therefore, the systems are in flocculation conditions, with behavior determined by the interplay of the net attractive interaction, the amount of bound water giving the length of the excluded volume interaction and thermal agitation. Possible formation of aggregates of micelles is discussed in view of the results obtained.

I. INTRODUCTION

The problem of the interactions between micelles in an aqueous solvent has analogies with the problem of interactions between colloidal particles in an ionic bath, since the micelles may be charged in the surface, where the polar heads are located.

The DLVO theory[1,2] for the stability of lyophobic colloids takes into account the balance between van der Waals attractive and Coulombian repulsive forces acting in colloidal particles in an ionic bath. This theory, in its original form, has been developed for the cases of flat plates and spherical particles considering fixed surface potential (or charge) and punctual ions; a correction for finite ion size was soon introduced by Stern.[2] The problem has been extended to cylindrical particles,[3] also for fixed surface potential (or charge).

Initially the van der Waals interaction was treated considering the Hamaker constant as an adjustable parameter but afterwards a great advance has been given by the Lifshitz theory; the hypothesis of fixed surface potential (or charge) has also been abandoned in favor of a self-consistent solution, specially adapted for biological problems, both for planar geometry[4] and cylindrical particles.[5] A revision of the applicability of DLVO theory to colloids[6] and a review about intermolecular interactions of short and long range[7] have been made some years ago. More recent computational methods, giving a more exact solution to the double layer problem, have been applied only to the spherical geometry.[8,9]

In lyophobic colloids the stability is governed by the charge of the particles and DLVO theory has been fundamental to understand the flocculation process in colloids, which corresponds to the spontaneous formation of aggregates of particles in the solution, initially homogeneous, when the ionic strength is increased. Addition of small amounts of salt can provoke flocculation and the effective quantity depends drastically on the nature and valency of the electrolyte.

The stability of colloids that have water affinity needs additional considerations about solvation water (water molecules bound to the colloid or to the ionic double layer surrounding it). In lyophilic colloids the stability is governed by two factors: charge and solvation. Therefore, they do not present, as a rule, the flocculation phenomenon under the influence of addition of small quantities of electrolyte. In special cases, however, very similar phenomena are observed when small quantities of alcohol have been added to the solution and in several cases[2] the physical properties of lyophilic colloids are influenced by electrolytes in the same form as in lyophobics.

Due to these analogies, we found it worthwhile to analyze interactions between micelles in nematic lyomesophases in terms of DLVO theory, with consideration of the additional solvation interaction and of the question of bound and free water, fundamental for lyomesophases. We shall discuss also possible criticisms and limitations of the present approach.

Finally, we shall discuss the possible formation of aggregates of micelles in nematic lyomesophases, proposed previously from X-ray diffraction results in nematic lyomesophases.[10,11]

II. THEORY

II.1 Coulombian repulsion

The Coulombian interaction is treated in the context of an electrical or electrochemical double layer, whose theory has been developed by Debye-

Hückel (DH) and Gouy-Chapman (GC), and is applicable whenever there is a border between two phases, one of which contains free ions. This problem occurs in various fields, from semiconductors to colloidal particles and biological membranes. The basic method applied in both theories consists in the application of a Boltzmann distribution to obtain the ion concentration, which corresponds to a mean field approximation. DH theory introduces also a linear approximation, whose applicability has been discussed rather completely.[6,8]

The deviations of the ionic distribution from the average concentration occur within a characteristic distance known as Debye screening length, defined as

$$l_D = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon kT}{N_0 8\pi e^2 I}},$$

where ε = the dielectric constant of the solvent medium
T = the absolute temperature
k = the Boltzman constant
N_0 = the Avogadro's number
I = the ionic strength in moles/liter, given by

$$I = \frac{1}{2}\sum_j n_j v_j^2$$

n_j = the concentration of ions of type j and valency v_j.

In this paper the calculation of the Coulomb repulsion for the planar geometry has been made by two methods: the classical GC theory for constant potential at the surface with correction for the Stern layer of adsorbed counter-ions and by an adaptation of the self-consistent method, taking the fraction α of ionized polar groups as parameter.

In classical DLVO theory the repulsive potential between two plates separated by 2b is given by[2]

$$V_r = \left(\frac{\kappa}{v^2}\right) f(u,z)$$

where

$$u = \frac{ve\psi_b}{kT}; \qquad z = \frac{ve\psi_0}{kT}$$

ψ_0 and ψ_b are the potentials at the surface of the particle and at distance b.

Verwey and Overbeek give[2] tables with values of $f(u, z)$ and u as a function of κb for known values of z, obtained from the condition

$$\sigma = \frac{\varepsilon\kappa}{4\pi}\psi_o$$

where σ is the charge per unit area.

It is also possible to calculate directly the repulsive force per cm^2 by the relation[2]

$$F_r = 2nkT(\cosh u - 1)$$

It has been recently commented[12] that the force result for planar geometry, derived originally for constant potential with approximations, is exact and of general validity.

The self-consistent treatment[4,5] is specially adaptable to biological problems, when the polar groups are nonionic with well known dissociation constants; the fraction α of dissociated ionic groups is then treated as a self-consistent function of the electrical potential. For the planar geometry, Ninham and Parsegian[4] give analytic expressions for the degree of dissociation α and for the variable $\xi = \exp(u)$ for several limiting cases. For monovalent ions and b $\gtrsim l_D$, when α is practically constant, the following expression applies:[4]

$$\xi = 1 - \frac{\kappa\alpha}{nS}\exp(-\kappa b)$$

where S is the surface area per polar group.

For the cylindrical geometry an intermediary approach between those of constant charge at the surface and the self-consistent method has been adopted, that also considers α as a parameter. For two long parallel cylinders with radius R and distance between axis D, the zero order approximation for the electrostatic potential was given by Brenner and McQuarrie[5] as

$$\psi^{(o)}(r) = A_o^{(o)}\left\{K_o(\kappa r) + \sum_{n=-\infty}^{\infty} K_n(\kappa D)I_n(\kappa r)\cos(n\theta)\right\}$$

where θ is the polar angle of a coordinate system placed at one of the cylinders, I_n and K_n are the modified Bessel functions of first and second kind respectively and order n.

Applying the boundary condition, the discontinuity of the normal component of the electric field at the cylinders surface, the constant $A_o^{(o)}$ is obtained in terms of the charge density σ. So, $A_o^{(o)}$ can be written:

$$A_o^{(o)} = \frac{4\pi e\alpha}{\varepsilon S\kappa}\{K_1(\kappa R) - K_o(\kappa D)I_1(\kappa R)\}^{-1}$$

In the expression for the Gibbs free energy of the system, only the electrostatic term (in this approximation) depends on D. With this consideration, a straightforward calculation gives for the repulsive force per unit length of the cylinder

$$F_r(D) = 2\pi R\frac{e\alpha}{S}\frac{\partial}{\partial D}\psi^{(0)} = 2\pi R\frac{e\alpha}{S}\{a\cdot b + c\}$$

where $a = -\dfrac{4\pi e\alpha}{\varepsilon S}I_1(\kappa R)K_1(\kappa D)\{K_1(\kappa R) - K_0(\kappa D)I_1(\kappa R)\}^{-2}$

$b = K_0(\kappa R) + K_0(\kappa D)I_0(\kappa R)$

$c = -A_0^{(0)}I_0(\kappa R)\kappa K_1(\kappa D)$

This force can be well fitted by a function

$$F_r(D) = \frac{\gamma e^{-\kappa D}}{\sqrt{\kappa D}}$$

where γ is a force parameter. From this expression it is possible to write down the electrostatic potential energy of the system as:

$$V_r(D) = \frac{\sqrt{\pi}\gamma}{\kappa}\,erfc(\sqrt{\kappa D})$$

where *erfc* is the complementary error function.

II.2 Van der Waals attraction

The basic energy interaction between two atoms separated by distance r is

$$V_a = -\frac{C_6}{r^6}$$

and the Hamaker constant is defined as $H = n^2\pi^2C_6$, where n is the number of atoms per unit volume.

Assuming a pairwise summation of interactions, it is possible to obtain the following analytic expressions for two interacting condensed bodies: –for plates[2] of thickness: l:

$$V_a(b) = -\frac{H}{48\pi}\left[\frac{1}{b^2} + \frac{1}{(b+l)^2} - \frac{1}{(b+l/2)^2}\right]$$

–for cylinders:[5]

$$V_a(D) = -\frac{2H}{3D}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\frac{\Gamma^2(m+n+1/2)}{m!n!(m-1)!(n-1)!}\left(\frac{R}{D}\right)^{2(m+n)}$$

Lifshitz theory has shown the deficiencies of the additive method, particularly for polar media. This theory does not depend on arbitrary parameters, being based on measured dielectric properties; the theory has been generalized to include a third medium between the two interacting bodies but this form is of difficult application.[7]

In this paper we adopt the simpler additive method, but using the Hamaker constant determined by rigorous methods. The Hamaker constant for interaction between two bodies in the presence of a third medium has been calculated rigorously for the hydrocarbon-water case[13] resulting in a value in the interval $(3.4 - 6.8)10^{-14}$ erg.

Deviations due to non-additivity of the interactions are expected to give errors of 20-30%, which are not so important in view of the imprecision of the value of H itself.

II.3 Solvation Interaction

The solvation interaction, not included in classical DLVO theory, is of more difficult theoretical treatment.

The presence of bound water increases the effective size of the particles in a repulsive interaction of excluded volume. In a first approach to this problem, we consider the plate thickness increased by Δl and the cylinder radius increased by ΔR in a rigid body excluded volume interaction of hard core type.

III. RESULTS AND DISCUSSION

Calculations have been performed for two typical nematic lyomesophase systems:

SDS (Na decyl sulfate/water/decanol/Na_2SO_4 with wt.% 36/54/5/5);
LK (K laurate/water/KCl with wt.% 34/63/3)

These systems have been chosen because X-ray diffraction results[10,11] evidence a rather small width for the diffraction peak, indicating the existence of some degree of positional order, corresponding to aggregates of about 10 plates for SDS[10] and 25 cylinders for LK.[11]

The ionic strengths I and Debye screening lengths l_D for the two systems are shown in Table I, considering the contributions of amphiphile counterions and dissociated salt.

As l_D is of the order of ionic bonds, it can be concluded that the counterions are brought back to the surface of the micelles, that are almost totally screened by a Stern layer of adsorbed counter-ions. In this condition, it is fundamental to make the Stern correction,[2] considering the potential after the Stern layer instead of the potential at the particle surface; at the Stern-

Table I

Ionic strength I and Debye screening length l_D for two nematic lyomesophases.

		I(moles/liter)	l_D (Å)
SDS	Na amph	1.28	2.69
	Na salt	1.30	2.67
	Na total	2.58	1.89
LK	K amph	1.16	2.82
	K salt	0.63	3.83
	K total	1.79	2.27

Gouy Chapman interface the system can be considered as weakly charged and the theory can be applied even for such high values of I.

The hypothesis of counter-ions totally bound to the micelles is usually assumed in the hexagonal phase;[14] we see by the results of Table I that the presence of salt is not necessary to induce a high screening and that the ionic strength due to the counter-ions is enough to give a picture of highly screened micelles.

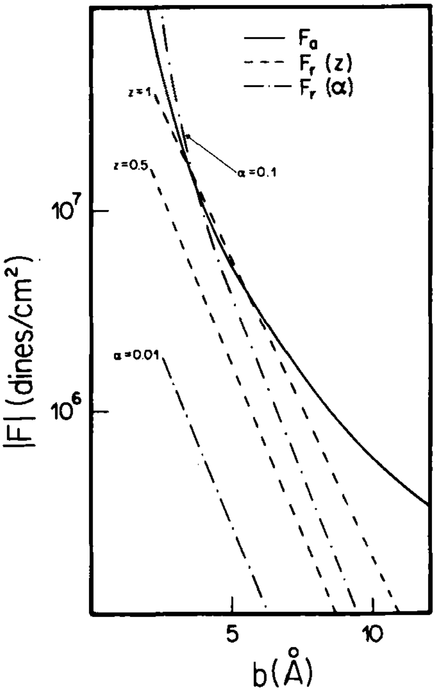

FIGURE 1 Absolute values of the attractive force (F_a) and repulsive force (F_r) as a function of the half-distance between two plates, for different values of the parameters z and α. Hamaker constant H = 5×10^{-14} erg.

The attractive interaction between plates has been calculated admitting $l = 28$ Å and $H = 5.10^{-14}$ erg. For the repulsive interaction, admitting a surface area per polar group of 40 Å^2, one would expect $z \lesssim 0.2$. Results for the interacting forces per unit area can be seen in Figure 1, for the minimum z values given in the tables of Verwey and Overbeek[2] ($z = 0.5$ and $z = 1$), which correspond therefore to upper limits for the interaction force, and for $\alpha = 0.1$ and 0.01.

It is seen that due to the high degree of screening the system has $|F_a| > |F_r|$ and, therefore, is in flocculation conditions. Even if by local fluctuations $|F_r| > |F_a|$, this occurs for such small plate separation that the potential barrier due to Coulombian repulsion will coincide with the repulsive excluded volume interaction, which shall include the bound water layer.

For the cylindrical geometry the interacting forces per unit length as a function of the interaxial distance D computed for several values of α and the limiting values of H are displayed in Figure 2.

For dissociation constants (α) greater or equal to 0.1, there are equilibrium points between the forces, i.e., the total force vanishes. At the interval $0.1 \le \alpha \le 1$ the equilibrium points are placed between 50 and 58 Å (for $H = 3.4 \times 10^{-14}$ erg) and at the interval $0.15 \le \alpha \le 1$ between

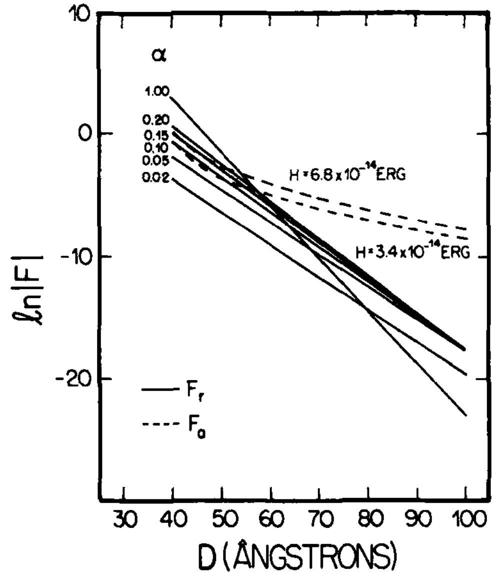

FIGURE 2 Natural logarithm of the absolute value of the attractive force in CGS units (dashed curves) for two values of the Hamaker constant (H) and repulsive force in CGS units (solid curves) for different dissociation constants ($0.02 \le \alpha \le 1$), as a function of the interaxial distance (D) between two cylinders.

45 and 51 Å (for H = 6.8×10^{-14} erg). Fixed the Hamaker constant, for $\alpha \rightarrow 0$, the equilibrium distance tends to the cylinder diameter (corresponding to the excluded volume interaction). This result indicates that equilibrium distances greater than 60 Å are not to be expected in this simplified picture of two interacting cylinders. Modifications in the location of the equilibrium points could be expected in a many body interacting problem.

For $\alpha \lesssim 0.1$ there is no equilibrium point between the two forces; the attractive force is bigger than the repulsive one and the system flocculates, with segregation of the free water unbounded to the micelles. This flocculation condition obtained for the two micelle system can reasonably be extended to the whole system.

It is verified, therefore, that for both geometries the attractive interaction is always larger than the repulsive interaction for $\alpha \lesssim 0.1$ and the high ionic strength of the medium leads to screening of the micelles since α values are smaller than this limit. Therefore, the systems are in flocculation conditions, with behavior determined by the interplay of the net attractive interaction, the amount of bound water giving the length of the excluded volume interaction and thermal agitation.

This must be the case for lyomesophases in general, since it is known[14] that the range of existence of these phases depends critically in the capability of the amphiphile to bind all the available water. Inhomogeneous distribution of amphiphile and water is known to occur, for instance, in dilute gel phases[15] and lamellar crystallites dispersed in the excess water are present in coagel phases;[15] also phospholipid/water systems are known to incorporate[16] water between the bilayers only up to 40 wt.% of water.

The way in which alcohol and salt enhance the range of existence of lyomesophases, leading to the nematic lyomesophases with high water content is not completely understood, but may possibly be related to a decrease in size of the micellar units, which leads to smaller attractive energies.

Since nematic lyomesophases are apparently homogeneous and do not present macroscopic flocculation, it is worthwhile to consider the total energy of the system in units of kT to better understand the interactions.

The total energy for the case of two cylinders is plotted in Figure 3 for different values of α, with H = $3.4 . 10^{-14}$ erg, in units of kT (T = 298 K) per centimeter. For $\alpha > 0.1$ there are equilibrium points at the potential well, however, with energy smaller than kT; for $\alpha < 0.1$ the attractive interaction dominates. In Figure 4 it is plotted the total energy for $\alpha = 0.02$ and the two limit values for the Hamaker constant. Assuming for the micelle length the value of 10^3 Å, at 50 Å of interaxial distance the total energy of the system is located between 0.64 kT and 1.35 kT; for $\alpha = 0$ the

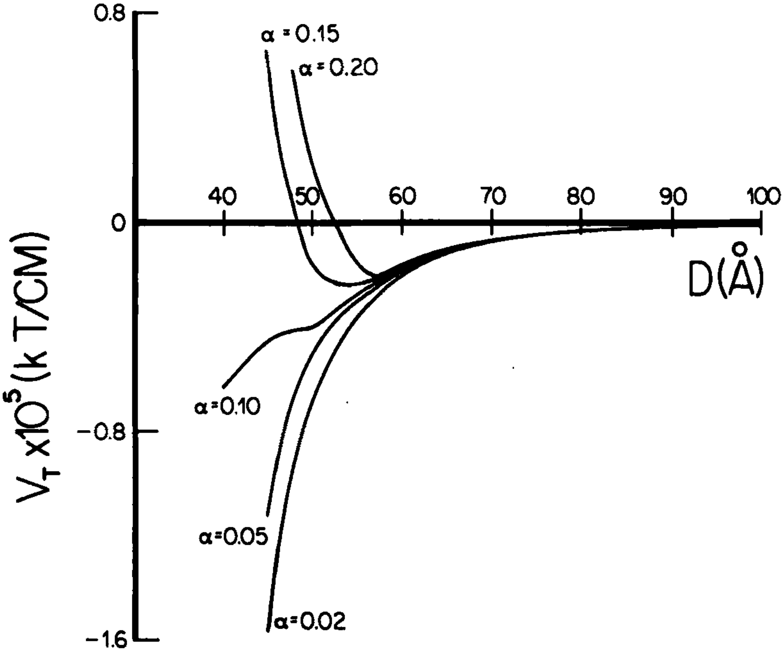

FIGURE 3 Total potential energy of two parallel cylindrical micelles immersed in an ionic bathing medium as a function of the interaxial distance (D) for different dissociation constants ($0.02 \leq \alpha \leq 1$). Hamaker constant used H = 3.4×10^{-14} erg.

total energy coincides with the attractive energy and is located between 0.68 *kT* and 1.37 *kT*.

Therefore, for a type I nematic phase made of cylinders with a diameter of 34 Å a distance between cylinders center of ~50 Å corresponds to attractive energies of ~*kT* at room temperature for cylinder lengths of ~1000 Å; with a solvation shell of three water molecules per micelle thermal agitation may prevent flocculation. For longer cylinders more bound water would be necessary to avoid flocculation.

In the case of highly screened plates, V_r decays much more rapidly than V_a and for $b > 10$ Å we have $E \simeq V_a$. Figure 5 shows V_a for large values of b in units of $kT/\text{Å}^2$; the attractive energy depends on the area of the plates.

For a type II nematic phase made of plates 28 Å thick a distance between plate centers of ~40 Å corresponds to attractive energies of the order of *kT* at room temperature for plate diameters of ~80 Å; with a solvation shell of two water molecules per plate thermal agitation may prevent flocculation. For larger plates more bound water would be necessary to avoid flocculation.

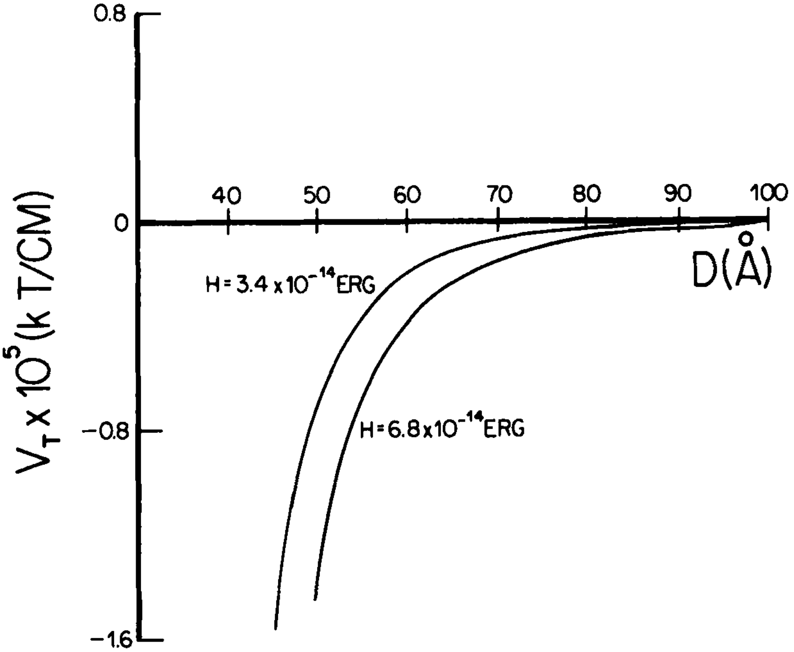

FIGURE 4 Total potential energy of two parallel cylindrical micelles immersed in an ionic bathing medium as a function of the interaxial distance (*D*), for the two limit values of the Hamaker constant. Dissociation constant $\alpha = 0.02$.

The picture that emerges from the obtained interaction energies between micelles in nematic lyomesophases made of finite micelles is that flocculation in an irreversible way is avoided by thermal agitation, but at the same time the net interaction at intermediate distances is of attractive character, giving support to the idea of formation of aggregates of micelles[10,11] in a fluctuating mode.

It shall be mentioned that the pertinent criticism[7] that exists for proposals of applying DLVO theory to explain phase separations in anisotropic systems refers to attempts of attributing to the secondary minimum of the potential curve at large κD (or κb) values the interpretation of equilibrium distance in systems where there is a potential barrier preventing flocculation; this is not at all the case considered here.

Certainly a complete treatment of statistical mechanics is necessary to analyze the many body systems as a whole. However, to discuss the flocculation conditions connected with the existence of the potential barrier at $\kappa r \sim 1$, which prevents close approach of the particles, DLVO theory is enough to give a right answer defining whether the net pair interaction is of essentially attractive character.

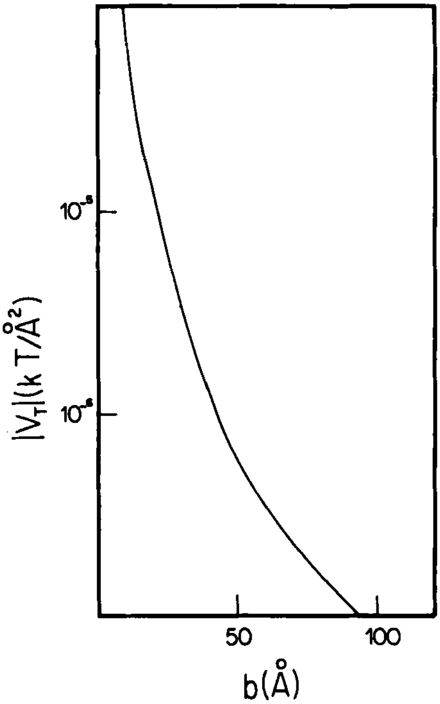

FIGURE 5 Absolute value of the total potential energy of two plates separated by distance 2b. Hamaker constant $H = 5 \times 10^{-14}$ erg.

There are, however, some limitations to the present approach, particularly in relation to two points: solvation interaction and ion mobility.

The solvation interaction acquires an oscillatory character for small distances due to the granulation of the solvent, which can no more be considered continuous at molecular distances;[17] the micelles are neither rigid nor permanent entities. There is a graduation between the so-called bound water and the free water. All these effects mean that the solvation interaction needs to be treated in a much more detailed way to allow a real evaluation of the interaction energies at small distances. However, the main conclusion of this work shall not be changed by improvements in the solvation interaction.

Although the ions are brought back to the vicinities of the micelle, they are not immobile. If they have chaotic movements, the average effect after a few Å will not be sensitive to their movements. However, if defined ion current exists at the micellar surface, important contributions to the micelle interactions are being neglected. Although there are not indications at present that this is the case, this is a point that remains open for discussion.

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