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Deformation of fluid interfaces under double-layer forces stabilizes bubble dispersions

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A theoretical study of the colloidal interaction between two identical fluid drops (i.e., gas bubbles) forms the basis for the proposal of a possible mechanism by which salt inhibition of bubble coalescence occurs. Recent speculations attempting to describe this phenomenon were founded on the assumption that electrostatic double-layer forces are not relevant. In complete contradiction to this claim, the present results indicate that double-layer forces between the deformable bubble interfaces infer precisely the same behavior observed with salt addition: bubble coalescence is predicted to occur in water or in low electrolyte solutions, but is hindered once the electrolyte concentration is increased sufficiently. In other words, low-salt solutions favor large bubbles, high-salt solutions favor small bubbles. In this symmetric system, assuming fixed but physically appropriate conditions, a given bubble size determines a critical electrolyte concentration above which coalescence is not possible. [S1063-651X(96)05212-9]

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INTRODUCTION

In the recent literature there has appeared a resurgence of interest in the peculiar phenomena of gas bubble coalescence in aqueous media [1–6]. Despite being familiar to workers in the flotation field [7], the fact that salt solutions under sufficient concentrations will increase the stability of bubble dispersions has eluded quantitative explanation for an embarrassing length of time. Although speculation on the precise mode of action taken by salts in hindering coalescence has proceeded nonetheless [1–6,8,9], agreement between authorities in this field has not yet been reached. One early proposal that viscosity changes in the aqueous medium affecting hydrodynamic forces between colliding bubbles has been dismissed as a likely mechanism without contention [2], while recently some weak correlation has been noted between *those* salts that both inhibit coalescence and induce surface tension changes [4–6]. However, no physical mechanism was proposed. In a remarkably simple experiment Craig, Ninham, and Pashley [1,2] have added to the puzzle the latter feature that some salts do in fact have negligible influence relative to water (Ref. [2] documents a large variety of different salts tested).

In their summary, Craig, Ninham, and Pashley [1,2] conclude that their findings ‘‘can only be explained by the local influence of ions on water structure in a way related to the hydrophobic force’’ [10,11]. A long-range attractive force is conjectured necessary in order to oppose any repulsive hydrodynamic forces existing between colliding bubbles so that coalescence can occur in pure water. Local water structuring is conjectured in order to distinguish between salt species in reducing this hydrophobic force in salt concentrated solutions. In deducing the existence of a long-range attractive force, these authors have superposed all their observations. Prominent among these is the different attitude taken by different salts, as well as sugars, to coalescence prevention. The authors also state that electrical double-layer forces cannot be responsible for coalescence inhibition ‘‘because increased salt concentration is supposed to screen double layer repulsion not increase it’’ [2].

Because of this persistent quandary it would seem an opportune occasion to reason once more through some of the known facts about coalescence hindrance by salts. It has been found that for those salts that do inhibit coalescence the effectivity behavior scales with the Debye parameter $\kappa = \sqrt{\Sigma_i z_i^2 e^2 c_i N_A / \varepsilon_0 \varepsilon_r kT}$ (here z_i is the valency of the ith ion type with concentration c_i, e is the unit electron charge, T is temperature, k is Boltzmann's constant, N_A is Avagadro's number, ε_0 is the permittivity of real space, and ϵ_r is the relative permittivity of the electrolyte). This is very strong evidence for and very characteristic of electrostatic double-layer phenomena [12]. In comparison, that some sugars also affect coalescence should be considered carefully since the extent of their influence is markedly different from that of salts [2]. These results might very well suggest that a *separate* and less effective mechanism is at work. It is somewhat surprising that Craig, Ninham, and Pashley [2] rule out an electrostatic effect; their results indeed would be interpreted as an increased repulsive force with added salt, which they claim contradicts classical Derjaquin-Landau-Verwey-Overbeek (DLVO) theory. In fact, as is well known to students of electrostatic double-layer theory, for the case of the constant potential surfaces under scrutiny, the electrostatic double-layer force is reduced in range asymptotically (the exponential decay length scales inversely with concentration), but *increases* with salt concentration when the surfaces are separated by finite distances (see Fig. 1 and Ref. [12]), all other things equal. Consequently, it is not at all clear to this author that a prosaic mechanism of electrostatic origin should yet be ruled out.

In searching for an explanation for the salt effect it would seem appropriate at this point to readdress the problem in the form of two questions, rather than one as Craig, Ninham, and Pashley have intimated. Rather than seek a mechanism that accounts for the inhibition effect of some salts and the indif-

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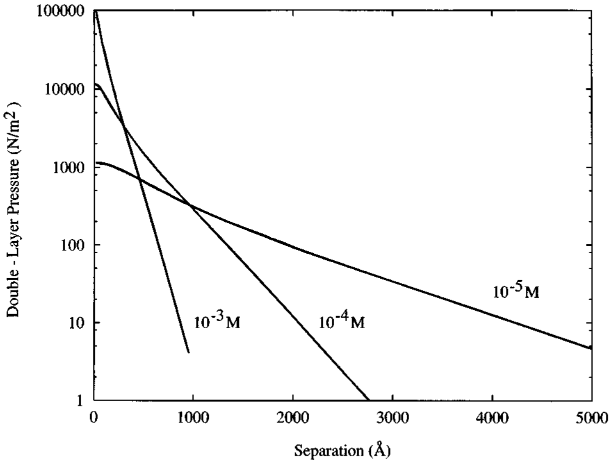

FIG. 1. Plots of repulsive double-layer forces based on Eqs. (4) and (7), between two identically charged rigid planes assuming constant surface potential conditions. The relative dielectric permittivity of the medium is taken to be that of water, 72.8. The surface potential is fixed at $\psi_0 = 100$ mV. Molar concentrations of $10^{-5}M$, $10^{-4}M$, and $10^{-3}M$ of a univalent electrolyte were used in the calculations; corresponding curves have been labeled.

ference of others, more progress might be made if one could first establish a possible fundamental mechanism for salt inhibition and subsequently question why certain specific salts do not conform to the general theory. In this paper we shall take this avenue of approach and address the first aspect.

The reader might raise objections to the results displayed in Fig. 1, pointing out that the surface potential value assumed in the calculation is not appropriate for the gas-water interface and a van der Waals attractive force has not been included. However, the calculations have also assumed two charged planar rigid surfaces. For relevance to bubble interactions, all appropriate features of the bubble surface must be taken into account.

In a recent communication examining the fundamental nature of colloidal interaction between a fluid drop and a rigid macroscopic solid [13], it was found that, as a function of surface separation, repulsive double-layer interactions exhibit a divergence from classical DLVO behavior appearing suddenly at a critical separation as a result of deformation of the fluid interface. The surface conditions studied were of constant charge. However, as stated above, the air-water interface is generally accepted to be constant potential. Consequently, to make any valid statements on how two bubbles interact we must first make the appropriate adjustment to the electrostatic boundary condition.

As we shall see, the physical difference between the constant charge and constant potential systems has important ramifications for deformable fluid interfaces. We have already explored some of these implications in more generality in a recent paper on fluid-solid interactions [14]. However, we devote this paper to the specific case of identical fluid drops, i.e., gas bubbles, immersed in an electrolyte, in an attempt to explore the possibility of a mechanism for bubble coalescence inhibition based on classical colloidal interaction theory.

In the next section, we outline briefly the theoretical procedure required to calculate the force between two bubbles.

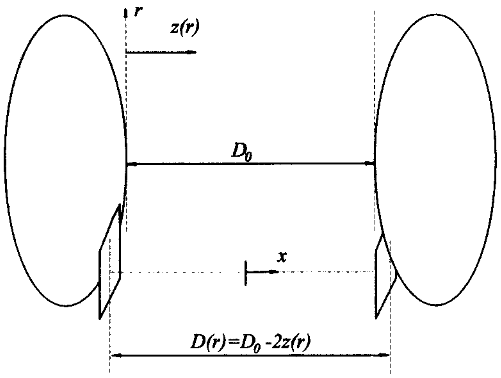

FIG. 2. Schematic figure depicting the geometry of the two-bubble problem. Coordinate axes and variables are shown.

Results of these calculations are given in the last section. There we also discuss how these results reflect on the bubble coalescence phenomena, expanding on the above discussion.

A THEORETICAL MODEL OF BUBBLE INTERACTIONS

The problem is one of solving for the interfacial shape of two fluid drops or gas bubbles interacting through surface forces. Fluid densities do not enter into discussion here as we shall ignore the force of gravity. Thus the fluids concerned could be either gas or liquid, in general. Electrothermodynamic surface stresses that are set up influence the droplet shapes. Neither the surface forces nor the position of the interfaces that determine them are known *a priori*. Consequently, the task at hand is highly nonlinear: the magnitude of the stress and the location of the surfaces must be determined self-consistently. Although the general approach has been described in some detail in other papers [13–15], we present a summary here.

By symmetry we need only solve for the position of one surface $z(r)$ (see Fig. 2), which is a solution of the augmented Laplace equation [16]

$$\gamma\left(\frac{z''(r)}{(1+z'^2)^{3/2}}+\frac{z'(r)}{r\sqrt{1+z'^2}}\right)=-\Delta P_0+\Pi_{\mathrm{DLVO}}[D_0-2z(r)]. \tag{1}$$

The aforementioned gravity or bouyancy term, which should normally appear in Eq. (1) because of density differences, is ignored for simplicity (its presence serves only to reduce the symmetry).

We make two simplifying approximations. The first is one assumption made in the familiar Derjaguin approximation valid for bodies of low curvature at relatively small separations [17]: the normal stress due to colloidal surface forces Π_{DLVO} as a function of r is approximated by the pressure between equivalent plane parallel surfaces at the corresponding surface separation $D(r)=D_0-2z(r)$ [$z(r)<0$; Fig. 2]. Second, the value of ΔP_0, the pressure excess, a value set by a fixed bubble volume constraint, is presumed to be constant throughout the interaction and equal to its value in the absence of surface forces

$$\Delta P_0 = \frac{2\gamma}{R}, \tag{2}$$

where R is the radius of an undeformed sphere of gas with the correct volume. The first assumption is generally acceptable provided that the separation between the interacting surfaces is much smaller than the mean radius of curvature of the two bodies. The second assumption has not yet been validated analytically. However, as we know that surface forces do not induce any significant *macroscopic* changes to droplet shapes [13–15], we do not expect this assumption to be unreasonable. In ongoing work we investigate the effect of avoiding these two approximations [18]. Except under very-high-salt conditions, the normal stress due to colloidal forces is reasonably well approximated by a simple superposition of electrical double-layer and van der Waals interactions [19]

$$\Pi_{\mathrm{DLVO}} = \Pi_{\mathrm{vdW}} + \Pi_{\mathrm{EDL}}. \tag{3}$$

For a univalent electrolyte ($z=1$) at a number density concentration n, the double-layer pressure between two infinite flat plates is given by

$$\Pi_{\mathrm{EDL}} = 2nkT[\cosh(e\beta\psi_s) - 1], \tag{4}$$

where $\psi_s = \psi$ at the symmetry plane and ψ is the solution of the nonlinear Poisson-Boltzmann equation

$$e\beta\psi''(z) = \kappa^2 \sinh(e\beta\psi) \tag{5}$$

subject to the boundary conditions of fixed surface potential ψ_0 at the bubble surfaces and of mirror symmetry:

$$\psi(\text{surface}) = \psi_0, \quad \psi'(\text{symmetry plane}) = 0. \tag{6}$$

An analytic solution exists, expressed in terms of elliptic functions [20,21]; its form is

$$\sinh[e\beta\psi(x)/2] = \sinh[e\beta\psi(0)/2]\mathrm{nc}(\kappa x/\xi, \xi), \tag{7}$$

where x is the coordinate variable measuring the distance from one surface to the other. The origin $x=0$ is placed at the symmetry plane (Fig. 2). $\xi = \mathrm{sech}[e\beta\psi(0)/2]$ is the modulus of the elliptic function $\mathrm{nc}(z,\xi)$ [22].

Between two like bodies separated by a third continuous medium there exists an attractive van der Waals force. Per unit area between planar bounded continua, this force has the form

$$\Pi_{\mathrm{vdW}} = -\frac{A}{6\pi D(r)^3}, \tag{8}$$

where A is the Hamaker constant and $D(r) = D_0 - 2z(r)$.

The net force between the bubbles is defined as the induced surface stress integrated over the symmetry plane

$$F = 2\pi \int_0^\infty \Pi_{\mathrm{DLVO}}[D(r)] r\,dr. \tag{9}$$

Solving Eq. (1) for the profile shape $z(r)$ can be effectively executed directly until $z'(r)$ becomes undefined. It has been found [23], however, that integrating Laplace's equation to obtain the entire drop shape can be achieved most easily after the profile is parametrized with respect to its slope dz/dr. Here we do not assume the drops to be supported by any solid interface as was the case in other work [13–15]. Thus, using the parametrization $dz/dr = \tan\phi$, so that $z = z(\phi)$ and $r = r(\phi)$, we can rewrite Eq. (1) as two first-order differential equations

$$\frac{dz}{d\phi} = \frac{-r\sin\phi}{r\Delta\wp/\gamma + \sin\phi}, \tag{10}$$

$$\frac{dr}{d\phi} = \frac{-r\cos\phi}{r\Delta\wp/\gamma + \sin\phi}, \tag{11}$$

with $\Delta\wp = -\Delta P_0 + \Pi_{\mathrm{DLVO}}$. Boundary conditions for (10) and (11) are

$$\frac{dz}{d\phi} = 0, \quad \frac{dr}{d\phi} = \frac{2\gamma}{\Delta P_0} \quad \text{at } z=0 \text{ or at } \phi = 0. \tag{12}$$

Equations (10) and (11) can be integrated numerically using boundary conditions (12) for the full range of $\phi \epsilon (0,\pi)$. Results shown below were obtained using this system of equations, solved by the Runge-Kutta technique, and subsequent force integration [Eq. (9)] performed using Gaussian quadrature.

In the numerical results shown in Figs. 3–6, we have utilized a single realistic value of surface potential $\psi_0 = -34$ mV taken from the literature [24,25]. However, we are aware of other measured values [26] and reports of different surface potentials for bubbles of different size [27]. Different surface potentials will not affect the qualitative behavior described in this paper. They will, however, affect the quantitative predictions. To achieve the best quantitative accuracy calls for a greater focus of attention on the experimental determination of bubble potentials. The Hamaker constant is given the value of $A = 3.7 \times 10^{-20}$ J and can be assumed constant with respect to salt at these concentrations [17]. The surface tension of the air-water interface is kept constant at $\gamma = 72.8$ mN/m. For the salt concentrations studied variations in surface tension are not expected to occur [6].

DEMONSTRATION OF SALT-INDUCED REPULSIVE FORCES

A modification to the charge boundary condition—constant charge to constant potential—is misleadingly trivial. As our early remarks indicate, it actually leads to markedly different physical behavior at short separations. Under constant charge conditions, the electroneutrality constraint forces a requisite number of surface counterions to remain present in the vanishing gap between two similarly charged surfaces in order to balance their charge, while any excess salt tends to favor the bulk. A fixed two-dimensional density of counterions leads to a diverging three-dimensional density, which, according to the contact theorem [17], implies that the pressure between the plates diverges [28], a consequence of entropy considerations. In contrast, when two identical planar surfaces interact at constant potential, their surface charges, which now vary with separation, tend to zero by symmetry. Consequently, there is no electroneutrality constraint on the counterions in the system, which gives greater freedom for transfer to the bulk in preference to the gap; entropy can be gained in this process. The contact theorem (which is still valid) implies that the pressure tends at most to a constant and thus the interaction free energy to a constant linearly with separation. This constant will now depend on the amount of electrolyte present. In the case of constant surface charge, therefore, the double-layer stress acting on a fluid interface increases without bound with decreasing separation, while in the latter case the stress attains a finite maximum at zero separation, monotonically dependent on bulk concentration. From this one can immediately identify the error made by Craig, Ninham, and Pashley [2]. For constant charge surfaces, in the limit of small separations the double-layer pressure diverges at a fixed rate, *independent of bulk salt concentration.* At large distances the decay of the force becomes more rapid with added salt. From these two limiting features and the fact that the force is a monotonic function of separation, one can deduce that the force is reduced everywhere by salt addition. The statement made by Craig, Ninham, and Pashley thus refers to constant charge surfaces, but is not pertinent to the case of constant potential, *bubble* surfaces.

The shapes of immiscible fluid, i.e., bubble, surfaces are determined by a balance of surface pressures acting on the two sides of the fluid interface and the interfacial tension of that interface. For finite volume gases in isolation in a continuous liquid, the gas pressure is in excess, balanced by the Laplace pressure Eq. (2). Obviously, in the presence of an external source of stress changes to the interfacial curvature result. In the present case, the combination of a repulsive electrical double layer and an attractive van der Waals force is such a source of external stress for which curvature changes have consequences for interacting bodies.

What is relevant here is the balance between the additional external stresses and the excess gas pressure difference under ambient conditions. In the absence of van der Waals forces, one can employ the comparison between ΔP_0 and the maximum in the double-layer pressure found at contact (Fig. 1), as a qualitative guide to determining the interaction behavior of the two bubbles. If the maximum double-layer surface force is lower than ΔP_0, then limited deformation of the fluid interfaces occurs. For a given constant surface tension the local radius of curvature at the point where the axis of symmetry intersects the bubble surface increases from $2\gamma/\Delta P_0$ to $2\gamma/\Delta\wp$, where $\Delta\wp=\Delta P_0-\Pi_{\mathrm{DLVO}}^{\mathrm{max}}$. For a low enough surface potential the repulsive force is not sufficiently strong to prevent the surfaces from coming into contact. However, what Fig. 3 makes explicit is that the repulsive double-layer stress *can* rise to a sufficient magnitude when the salt concentration is increased (the feature demonstrated in Fig. 1), to induce an effective force barrier between the bubbles as a function of their minimum separation, preventing any further approach. The barrier is, of course, a consequence of bubble deformability, which impels exposure of a larger area of bubble surface to the repulsive interaction, at essentially the same separation. We have considered fluid surface deformation in more detail elsewhere [13–15]. However, the reader will readily agree that this feature of deformation, in *association with* the behavior of the double-layer force depicted in Fig. 1, is sufficient to account for bubble coalescence inhibition, far more convincingly than *only* the double-layer behavior itself. The double-layer behavior is incidental, deformation is effectual. Here we see in theory precisely that feature found in experiments, namely, that increased salt concentration leads to a significant repulsive force. This is the key point we impart in this paper.

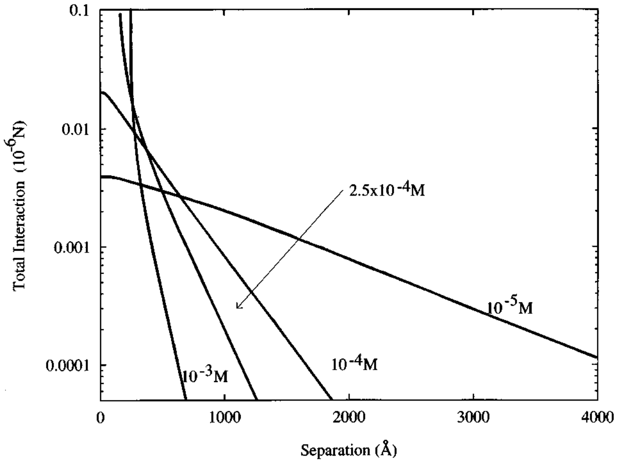

FIG. 3. Plots of the total (repulsive) double-layer force between two identical, charged fluid drops or bubbles under constant surface potential conditions. The curves are based on Eq. (9) with the surface pressure containing only the repulsive double-layer contribution Eq. (4). The abscissa denotes the minimum separation between the two drop surfaces D_0. The relative dielectric permittivity of the medium is taken to be that of water, 72.8. The surface potential is fixed at a literature value for the air-water interface $\psi_0=-34$ mV [24,25]. Molar concentrations of $10^{-5}M$ ($\sigma_\infty=-4.22\times10^{-5}$ e/Å^2), $10^{-4}M$ ($\sigma_\infty=-1.33\times10^{-4}$ e/Å^2), $2.5\times10^{-4}M$ ($\sigma_\infty=-2.11\times10^{-4}$ e/Å^2), and $10^{-3}M$ ($\sigma_\infty=-4.22\times10^{-4}$ e/Å^2) of a univalent electrolyte were used in the calculations; corresponding curves have been labeled. For this figure an ambient pressure difference of $\Delta P_0=1000$ Pa has been used, corresponding, assuming a surface tension of $\gamma=72.8$ mN/m, to a bubble radius of 0.145 mm.

Of course, between two bubbles interacting across an aqueous medium there is always an attractive dispersion

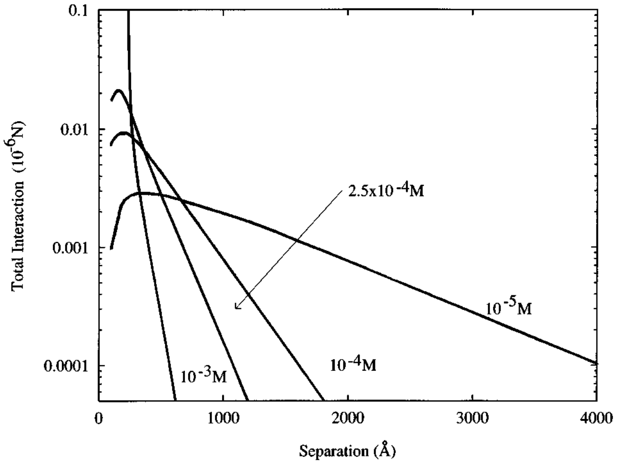

FIG. 4. Same as for Fig. 3, except that the surface pressure now contains both the repulsive double-layer contribution Eq. (4) and the attractive van der Waals force Eq. (8). The literature value of the Hamaker constant is used: $A=3.7\times10^{-20}$ J [17].

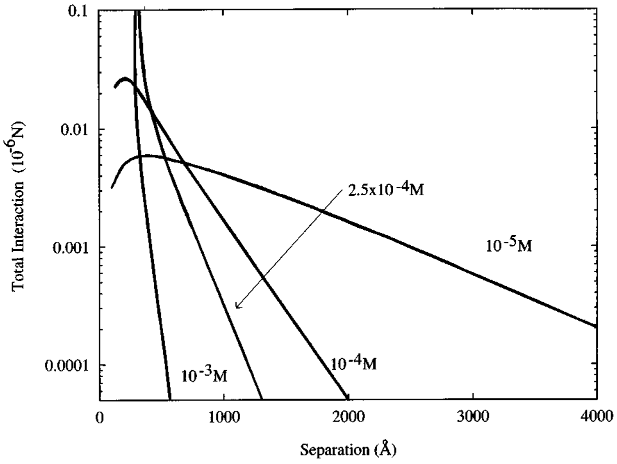

FIG. 5. Same as in Fig. 4, except that an ambient pressure difference of $\Delta P_0 = 500$ Pa has been used. Assuming a surface tension of $\gamma = 72.8$ mN/m, this corresponds to a bubble radius of 0.291 mm.

force. In Fig. 4 we have included a nonretarded and unscreened van der Waals force in the Hamaker approximation, using the literature value for this system's Hamaker constant [17]. For the rest of the discussion, it is appropriate as well as useful, now that dispersion forces are present, to consider contact being synonymous with coalescence.

Between rigid planar bodies, the van der Waals force has the obvious effect of introducing a repulsive maximum at some finite separation rather than at contact. At shorter distances the total surface force rapidly becomes attractive. What is important for the present discussion is that this new peak is substantially lower than the maximum found with constant potential double-layer forces alone. It is not difficult to infer the consequences of this. Obviously, under otherwise identical conditions, deformation is reduced and the effectively infinite barrier is deferred to higher concentrations. Yet it is important still to recognize that in these latter cases, although a net attraction is present in principle, it is not experienced *in practice*, as deformation of the fluid surfaces occurs too readily in competition with any separation decrease.

Whether the barrier appears at all will depend upon the ambient pressure difference and salt concentration. Recall that for a constant surface tension a given value of ΔP_0 corresponds to a given bubble size, via Eq. (2). In Fig. 5, shown are the total interaction vs minimum separation results for a larger bubble. Given the statements above, it is not surprising that the effective barrier appears at a lower salt content compared to the case of Fig. 4. At an arbitrary, fixed salt concentration the total force behavior can therefore appear very different for different bubble sizes. In Fig. 6 we show the total force vs separation profile for the symmetric system assuming different bubble radii. Above a critical bubble size, set by this salt concentration, deformation of the fluid interface once again dominates separation changes. Only for small bubbles is contact, i.e., coalescence, possible. Further variations in bubble size and electrolyte concentration, as well as uniform surface potential and uniform surface tension, lead to qualitatively similar results, which by now can be anticipated.

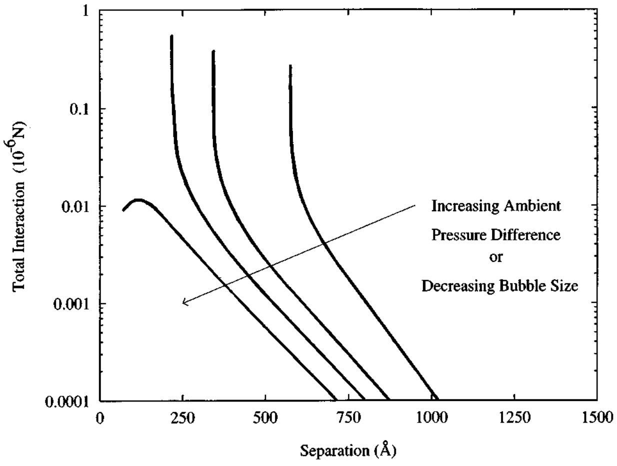

FIG. 6. Plots of the total force between two identical, charged fluid drops or bubbles under constant surface potential conditions. The curves are based on Eq. (9) with both repulsive double-layer and attractive van der Waals contributions. The abscissa denotes the minimum separation between the two drop surfaces D_0. The relative dielectric permittivity of the medium is taken to be that of water, 72.8. The Hamaker constant $A = 3.7\times10^{-20}$ J. The surface potential is fixed at a literature value for the air-water interface $\psi_0 = -34$ mV [24,25]. A fixed molar concentration $5\times10^{-4}M$ ($\sigma_\infty = -3.0\times10^{-4}\ e/\text{Å}^2$) of a univalent electrolyte has been used. In this figure four different values of ambient pressure difference are considered: $\Delta P_0 = 100$, 500, 1000, and 2000 Pa, corresponding to bubble radii of 1.45, 0.291, 0.145, and 0.073 mm, respectively.

FINAL REMARKS

The continuum model employed is inadequate for a study of salt-specific effects. This has proved to be a source of frustration that has hampered workers in the classical colloidal force field, who have yet to understand completely the complex molecular interaction between water, ions, and surfaces and so understand what happens close to an interface or between surfaces [29]. Considerations of bare ion size, the molecular nature of water, and the consequent hydration properties of specific ions are all features that are consequently absent from the present model. Furthermore, no account can be taken of any variation in surface tension with bulk electrolyte concentration [4–6] or more importantly any high-order, self-consistent change in surface tension that may occur as a function of surface separation [30]. Although it is not certain that such effects will occur at the concentrations studied here, it is correct, nevertheless, to point them out for possible future examination.

Notwithstanding these limitations, it is gratifying to know that the model calculations have sufficient validity to deduce a number of important features. Foremost is the aforementioned salt-induced repulsion. Other things being equal, increases in salt lead to increased electrostatic repulsion between interacting bubbles, which eventually, because of surface deformation, induces an effective repulsive barrier that prevents the bubbles from attaining a primary force minimum and presumably coalescence. Furthermore, results shown in Fig. 6 suggest that high salt concentrations infer a limit to the size of bubbles that can achieve coalescence. That is, presuming that large bubbles form by the coalescence of smaller bubbles, the theory predicts that there is a limit to the maximum bubble size thus formed. Based on the information shown in Figs. 4–6, this limiting bubble size is predicted to decrease with increasing salt concentration. Both of these features predicted by the model are characteristically found in experiments. What is still lacking, however, is quantitative agreement between the theoretical predictions of critical salt concentrations and the experimental observations of the amount of salt needed to inhibit coalescence: a discrepancy of some two orders of magnitude. One obvious difficulty is knowing the exact surface potential to use. Agreement between theory and experiment would necessitate a surface potential value of the order of -10 mV. At low salt concentrations, this would suggest a very weak electrical double-layer force, with the total interaction dominated by the long-range dispersion force, thus accounting for coalescence in the case of pure water.

Most, if not all, of the recent experimental studies of bubble interactions have been conducted in dynamic circumstances. This complicates matters greatly since nontrivial hydrodynamic forces are present [31]. Some indications of equilibrium effects can be surmised from the interesting observations of Hofmeier, Yaminsky, and Christenson [5], who describe the mechanisms of bubble ''feeding'' in pure water and ''bouncing'' in salt solutions during the emergence of a bubble stream from a single capillary. In our view, these features are undoubtedly connected to the phenomena described herein. However, for true assurance of compatibility with the mathematical model, equilibrium measurements must still be performed.

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