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# Mesoscopic Treatment of a Fluid/Liquid Interface. 2. Air/Water Interfacial Tension

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In a previous report, a new model for the thermodynamic description of a fluid/liquid interface was developed. In that model the dual meaning of the interfacial tension as the free energy per unit area of interface, as well as the force per unit length required to increase the interfacial area, is fully exploited. According to that formalism the interfacial tension is the macroscopic observable of the potential energy accumulated within the interfacial layers; it results from the existence of *elastic* fields occurring in each bulk phase near the interfacial boundary. Here that theoretical framework is used to estimate the width of an air/water interface. The present analysis starts from a novel interpretation of the isothermal changes that are required to occur upon a homogeneous water phase so that its chemical potential could be equal to that of the molecules at the interface. As intuitively expected, this results indicate that the interface is slightly more dense than the adjacent bulk. This difference in density is attributed to minor changes in the spatial distribution of the molecules.

## Introduction

To introduce a convenient definition of interfacial chemical potentials, the concept of an *elastic* interfacial field was recently introduced.[1] Such a field can be understood in simple terms establishing an analogy between the actual case and that of a binary system composed by two distinct networks of harmonic springs coupled at the interfacial boundary. These gives rise to distortions of the former structures which are more severe near the matching region. Because the networks are distinct, the extent of the perturbation caused by the interface will be different for each subphase. The interfacial tension results from the additional potential energy stored at the interfacial layers of the original bulk phases due to the presence of the interface.

In a one-component two-phase system, the origin of the interfacial tension can be ascribed to the effective intermolecular interactions between fluid molecules that occur in the liquid and vapor phases. These interactions result from different regions of the electronic potential energy surface that correspond to these bulk phases, and also to their interface. Different effective interactions may occur as a consequence of (i) the position of potential energy minima, (ii) the force constants associated with these minima, and (iii) the possible nonharmonic character of these force constants.

In the case of a gas/liquid interface, the vapor phase is expected to show “spring constants” substantially weaker than those of a condensed phase, because of the strong variation of the effective intermolecular forces with the average intermolecular distance. Thus, the potential energy accumulated in the liquid phase, caused by the possible distortion of its bulk structure at the interfacial level, is much stronger than that of the gas, for which a minor change in the mean intermolecular distance causes negligible differences in its bulk properties. Furthermore, the distortion of the liquid phase in contact with a gas will be larger than its distortion in contact with another (similar) liquid phase. This is basically due to the weak nature of the gaseous network which does not allow this phase to accumulate sizable amounts of “elastic” potential energy. As a result, the air/liquid surface tension can be completely ascribed to the deformation of the liquid network only. The magnitude of the potential energy accumulated at the gas/liquid interface (surface tension) has to be therefore necessarily larger than that which could be possibly stored in liquid/liquid interfaces, as experimentally found.

Because distortions depend on the details of the interaction between molecules, they will vary for different liquids, and there is no reason to favor a priori either contraction or expansion of a liquid at the interface. Recently, Shen[2] observed structural modifications of the water liquid structure at the air/water interface using a special vibrational spectroscopy technique known as sum frequency generation (SFG). According to this author there is some evidence of the formation of an ice-like structures at the interface, which suggests an increase in the intermolecular distance of water molecules in this region.[2,3] A preferential orientation of the water molecules at the air/water interface along with some vibrational signals similar to those of ice were also observed in water/surfactant systems, but the exact water configuration in these systems is still under debate.[3] Using the formalism of ref 1, we report here a very small contraction of the intermolecular water−water distance, regardless of the packing configuration assumed (see below).

## Theoretical Aspects

Assuming the ineffectiveness of gas phase $\beta$ to accumulate sizable amounts of elastic energy at a gas/liquid ($\beta/\alpha$) interface, the surface energy can be completely ascribed to the interfacial sub-phase region $\sigma_A$, located at the uppermost zone of phase $\alpha$, just below the interfacial plane $z = 0$. According to eq 48

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from ref 1, the change in the surface tension of this system is equal to

$$\Delta\gamma^{\sigma_A} = \sum_i g_\alpha{}^2(-\epsilon) h_i(-\epsilon) N_i y_i \delta_{\sigma_A} \tag{1}$$

where $g_\alpha{}^2(-\epsilon)$ is the average elastic field existing in subphase $\sigma_A$ in the presence of the interface, $\epsilon$ is a macroscopic infinitesimal close to 0, $h_i(-\epsilon)$ is the intrinsic contribution of the molecules of i to the free energy of the subphase, $N_i$ is the maximum molar density of component $i$, $y_i$ is the fraction of area occupied by component $i$ in $\sigma_A$, and $\delta_{\sigma_A}$ the average width of sub-phase $\sigma_A$, and $A$ the matrix component.

In the case of a pure component, the series in eq 1 reduces to only one term, namely $i = A$. On the other hand, in a multicomponent system,[1] $\Delta\gamma^{\sigma_A}$ measures the difference between the interfacial tension of the actual system and that corresponding to a “clean” interface made out of unmixed matrix components only. In the case of a one-component system, the reference state corresponds to a virtual interface occurring in bulk phase α, so that $\gamma_0^{\sigma_A} = 0$. $\gamma^{\sigma_A}$ corresponds to the perturbation of the initial bulk phase from $g_\alpha^0(z)$ to $g_\alpha(z)$. In this case, the chemical environment below the interface is the same, although the spatial configuration of the molecules may vary with the distance to the interfacial boundary located at $z = 0$[4−6] (see also Appendix A). Furthermore, because $N_i y_i \delta_{\sigma_A} = n_A^{\sigma_A}/A^{\sigma_A}$, where $n_A^\sigma$ is the number of moles of substance $A$ in subphase $\sigma$, eq 1 reduces to

$$\gamma^{\sigma_A} A^{\sigma_A} = n_A^{\sigma_A} g_\alpha{}^2(-\epsilon) h_A(-\epsilon) \tag{2}$$

Since the theory outlined in ref 1 was developed for a multicomponent system, the interfacial tension was originally expressed as a function of the difference between the activity coefficients of a component in the bulk phase and the interface. However, the required equations can be suitably expressed in terms of a change in the fugacity for the case of a one-component system (see eq 22 in ref 1). Here we consider that, due to the distortion of the network, the molecules included in sub-phase $\sigma = \sigma_A$ will have an average intermolecular energy different to that of the bulk, producing a different local fugacity. Hence

$$RT \ln \frac{\lambda_A^{o\sigma}}{\lambda_A^{o\alpha}} = g_\alpha{}^2(-\epsilon) h_A(-\epsilon) \tag{3}$$

where $\lambda_A^{o\sigma}$ is the standard fugacity of the matrix component $A$ at the interface $\sigma$, and $\lambda_A^{o\alpha}$ is the corresponding standard fugacity of $A$ in bulk phase α. According to eqs 2 and 3

$$\gamma^\sigma = N_A^\sigma RT \ln \frac{\lambda_A^{o\sigma}}{\lambda_A^{o\alpha}} \tag{4}$$

It is difficult to obtain a physical description of the changes in density that occur in the liquid subphase employing thermodynamic arguments alone. However, it is possible to find an equivalent thermodynamic system to evaluate the amount of mechanical effort needed to achieve those changes at constant temperature. For this purpose, we will consider subphase $\sigma$ as an isotropic fluid whose final state can be obtained as a result of an isothermal compression/expansion process starting from the bulk liquid α. In this case, the chemical potential can be obtained from the well-known differential relation

$$d\mu_A = V_A^{\mathrm{L}}(P)\, dP \text{ (one-component)} \tag{5}$$

Here $V_A^{\mathrm{L}}$ is the molar volume of $A$ in the liquid phase and $P$ is the pressure that acts upon the liquid. The functional change of $V_A^{\mathrm{L}}$ with pressure can be described in the case of water by the equation of Fine and Millero:[7]

$$\frac{\xi \mathrm{V}(\xi)}{V(\xi) - V(0)} = B + A_1\xi + A_2\xi^2 \tag{6}$$

where $B$, $A_1$, and $A_2$ are constants, which depend on temperature, whereas $\xi$ is conveniently defined as

$$\xi = P - P_0 \tag{7}$$

Here $P_0$ is the pressure of the bulk under study. Inserting eq 7 into eq 5, and integrating over variable $\xi$

$$d\mu_A = RT \ln\left(\frac{\lambda_A^{o\sigma}}{\lambda_A^{o}} = \int_0^{\xi^\sigma} V_A^{\mathrm{L}}(\xi)\, \mathrm{d}\xi\right) \tag{8}$$

If a pressure change acting upon an isotropic slab of fluid $\sigma$ produces the same change in fugacity as that resulting from the creation of an interface, eqs 8 and 4 can be equalized. Expressing $N_A^\sigma$ in terms of the interfacial molar area $A_A^\sigma$

$$\gamma^\sigma = \frac{1}{A_A^\sigma(\xi^\sigma)} \int_0^{\xi^\sigma} V_A^{\mathrm{L}}(\xi)\, \mathrm{d}\xi \tag{9}$$

To estimate the quantity $A_A^\sigma$(in m$^2$/mol) appearing in the above equation, several packing models can be considered.[8] Use of a cubic model leads to $A_A^\sigma = 8444.69(V_A^{\mathrm{L}}(\xi^\sigma))^{(2/3)}$. According to a spherical model: $A_A^\sigma = 10208.38(V_A^{\mathrm{L}}(\xi^\sigma))^{(2/3)}$. Finally, using the molar area model proposed by Rasmussen,[9,10] we have $A_A^\sigma = \kappa^{\mathrm{R}}(V_A^{\mathrm{L}}(\xi^\sigma))^{(2/3)}$, where $V_A^{\mathrm{L}}(\xi^\sigma)$[in m$^3$/mol] is the molar volume of $A$ in subphase $\sigma$, and $\kappa^{\mathrm{R}}$ is an adjustable constant consistent with $A_A^\sigma = 7225$ (m$^2$/mol) at 25 °C. Hence

$$\gamma^\sigma = \frac{1}{\kappa}(V_A^{\mathrm{L}}(\xi^\sigma))^{-(2/3)} \int_0^{\xi^\sigma} V_A^{\mathrm{L}}(\xi)\, \mathrm{d}\xi \tag{10}$$

where the value of $\kappa$ depends on the packing model selected.

To evaluate the previous equation, we employed the values for the surface tension of water under its own vapor pressure reported by Vargaftik et al.[11] This implies that the bulk pressure, Po, should be equal to the vapor pressure. Furthermore, $\xi$ will only change with temperature, as will $B$, $A_1$, and $A_2$. The values of $B$, $A_1$, and $A_2$ were determined for twelve different temperatures between 273.15 and 647.14K, employing the data of specific volumes from the International Tables of Skeleton reported by Sato et al.[12] Using eq 6, eq 10 can be expressed as a function of these parameters:[13,14]

$$\gamma^\sigma = \frac{1}{\kappa} \frac{\displaystyle\int_0^{\xi^\sigma} \frac{V_A^{\mathrm{sat}}(B + A_1\xi + A_2\xi^2)}{B + (A_1 - 1)\xi + A_2\xi^2} d\xi}{\left[\dfrac{\mathrm{V}_A^{\mathrm{sat}}(B + A_1\xi^\sigma + A_2(\xi^\sigma)^2)}{B + (A_1 - 1)\xi^\sigma + A_2(\xi^\sigma)^2}\right]^{(2/3)}} \tag{11}$$

The value of $V_A^{\mathrm{L}}(\xi = 0)$ corresponds to the molar volume of the saturated liquid $V_A^{\mathrm{sat}}$. The solution of eq 11 allows the estimation of the value of $\xi^\sigma$ that corresponds to equivalent mechanical effort acting over subphase $\sigma$. Additionally, the average density in the interface can be calculated according to

$$\langle V_A\rangle^\sigma = \frac{\int_{P^{\mathrm{sat}}}^{P^\sigma} V_A^{\mathrm{L}}(P)\,\mathrm{d}P}{P^\sigma - P^{\mathrm{sat}}} = \frac{\int_0^{\xi^\sigma} V_A^{\mathrm{L}}(\xi)\,\mathrm{d}\xi}{\xi^\sigma} \tag{12}$$

which, when combined with eq 10, yields

$$\gamma^\sigma = \frac{\langle V_A\rangle^\sigma}{A_A^\sigma}(P^\sigma - P^{\mathrm{sat}}) = \frac{\langle V_A\rangle^\sigma}{A_A^\sigma}\xi^\sigma \tag{13}$$

On the other hand, the quotient between the molar volume and the molar area is an estimation of the thickness of the interface $\langle l\,\rangle^\sigma$ ($\sim \delta_\sigma$) that can be calculated from the relation

$$\langle l\rangle^\sigma = \frac{\langle V_A\rangle^\sigma}{A_A^\sigma} \tag{14}$$

This relation for $\langle l\rangle^\sigma$ is consistent with our model and differs from that proposed by Hansen.[15-16] Taking into account eq 14, eq 12 can be written in the following convenient form:

$$\gamma^\sigma = \langle l\rangle^\sigma \xi^\sigma \tag{15}$$

This simple relation allows the estimation of the thickness of the interface as the slope of the curve $\gamma^\sigma$ vs $\xi^\sigma$.

## Results and Discussion

Figure 1a shows a plot of $\xi^\sigma$ vs $T$ for the cubic and spherical packing models represented by squares and circles respectively, whereas Figure 1b shows the results corresponding to the packing model proposed by Rasmussen (diamonds). In this particular case, the values of $\xi^\sigma$ are positive at all temperatures meaning that the density of the surface (represented in this formalism by the subphase $\sigma$) is always greater than that of the bulk. The behavior of $\xi^\sigma$ with temperature illustrated in Figure 1, parts a and b, appears to be analogous to that of the surface tension which is expected to decrease until the critical point is reached. The mechanical effect of an equivalent surface pressure can be obtained evaluating the pressure of the subphase $\sigma$. This pressure is the equivalent force per unit area that must be applied in order to deform the liquid network of the subphase by means of an isothermal process until it reaches the required surface density (Figure 2, parts a and b). It is interesting to note that for the cubic and spherical models the pressure values are of the order of thousands of bars. Furthermore, in both models, the minimal value corresponds to the critical point. However, in the case of Rasmussen's, the minimum value of the surface pressure corresponds to about 560 K, suggesting that from this point on the main barrier toward further deformation of the network is not the water structure but the change of entropy associated to the temperature increase.

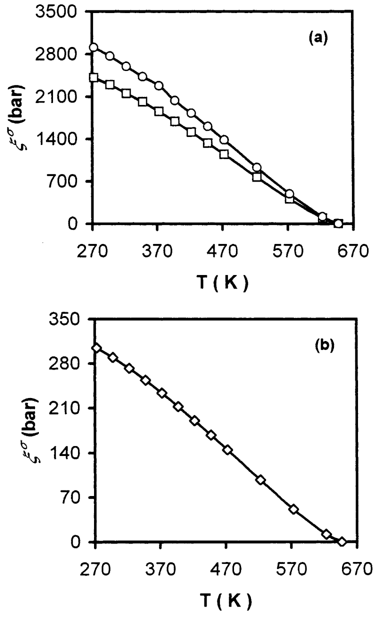

**Figure 1.** Pressure difference ($\xi$) between subphase $\sigma$ and bulk phase α of water at the gas/liquid interface. Results for different approximate packing models are shown: (a) spherical (○), cubic (□), and (b) Rasmussen's model (◇).[9] In Figures 1−5, the lines are only guides to the eye.

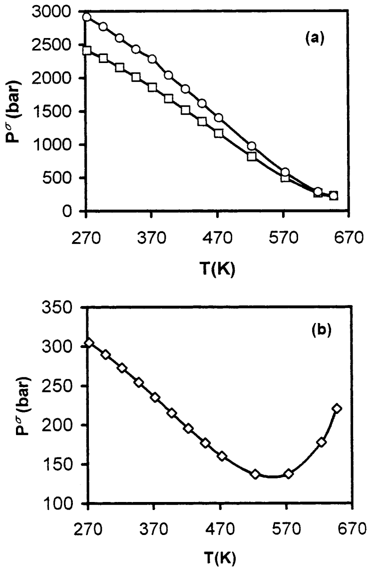

**Figure 2.** Dependence of the pressure of sub-phase $\sigma$ as a function of temperature for (a) spherical (○), cubic (□), and (b) Rasmussen's packing model (◇).

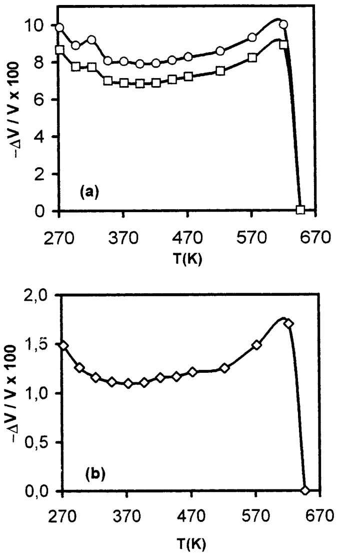

**Figure 3.** Percentile of molar volume decrease of the interfacial water in comparison with its bulk phase. Results for the three packing models tested are shown: (a) spherical (○), cubic (□), and (b) Rasmussen's model (◇).

Figure 3a shows the ratio of variation of the compressed volume of subphase $\sigma$ as a function of temperature for both cubic and spherical models. It is observed that $-\Delta V$ does not change drastically in a fairly wide range of temperatures. Within this range, the suggested preferential arrangement of water may

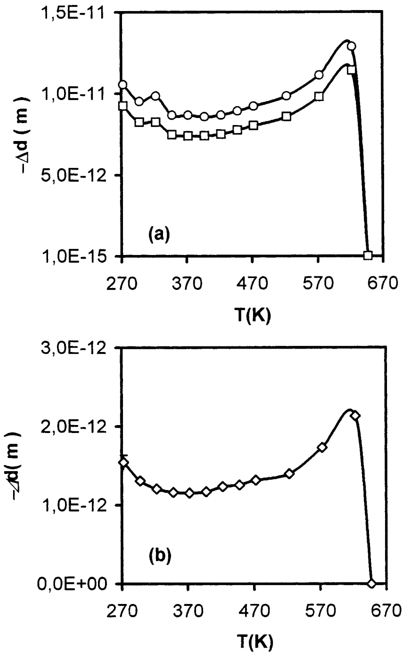

**Figure 4.** Decrease of the mean intermolecular distance as a function of temperature for the three packing models tested. Results for the three packing models studied are shown: (a) spherical (○), cubic (□), and (b) Rasmussen's model (◇).

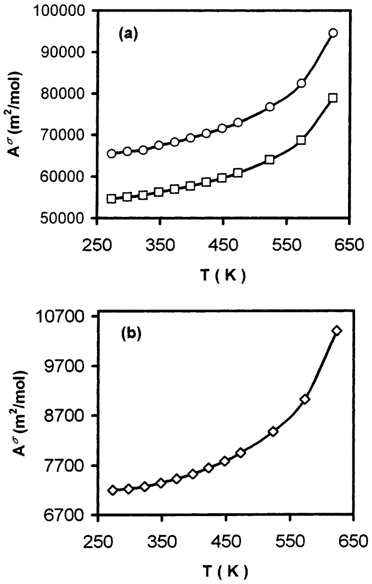

**Figure 5.** Molar interfacial area of water in subphase $\sigma$ as a function of temperature. (a) spherical (○), cubic (□), and (b) Rasmussen's model (◇).[9]

exist as a consequence of the potential energy accumulated in the subphase. An analogous behavior is observed for the Rasmussen model (Figure 3b), and again, the values obtained for this model are 1 order of magnitude lower than those of the cubic and spherical models.

Figure 4, parts a and b, shows the decrease of the intermolecular distance $d$ predicted by the referred packing models. These results indicate that a considerable amount of potential energy accumulated at the interface can be achieved with only a fraction of an Armstrong change in the intermolecular distance (approximately $\sim 1.0 \times 10^{-11}$ m for the cubic and spherical models and $1.5 \times 10^{-12}$ m for Rasmussen's). Thus, minor changes in the spatial configuration of water lead to the macroscopically observed values of the surface tension. Notice that the difference $-\Delta\ d$ between the bulk and the subphase remains approximately constant in a fairly large range of temperatures.

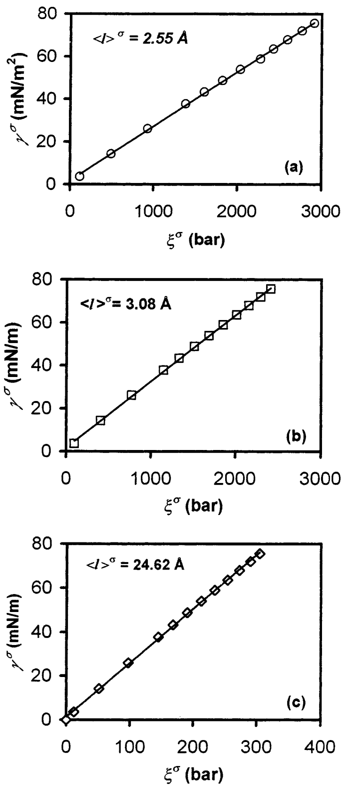

**Figure 6.** Surface tension as a function of pressure for (a) spherical, (b) cubic, (c) Rasmussen's packing models.

Figure 5, parts a and b, illustrates the area per mol of monomolecular planes as a function of temperature. Analogous increasing tendencies are observed in all packing models considered.

Finally, the variations of the interfacial tension $\gamma$ as a function of $\xi^\sigma$ for different packing models are shown in Figure 6. The linear dependence of $\gamma^\sigma$ vs $\xi^\sigma$ appearing in these figures indicates that the width of the perturbed region $\sigma$ produced in the neighborhood of the interface remains almost constant in a wide region of temperature, including those near to the critical point (see eq 15). Widths of 3.08 and 2.55 Å were obtained for the cubic and spherical models, respectively. These values fairly correspond to the width of one monomolecular plane. However, the model of Rasmussen[5] produces a width of 24.6 Å, which roughly corresponds to a thickness of 9 monomolecular planes. This value is of the same order of magnitude as those reported by Yang and Li for the interfacial tension between water and: carbon tetrachloride, dodecane, hexane, octane, and decane,[16] which range from 14.46 to 36.86 Å depending on $T$ and $P$.

## Conclusions

In the past, several authors had suggested a relationship between the variation of the interfacial tension with pressure and the width of the interface using different formalisms.[5,13−17] The present application of a novel thermodynamic model for the fugacity coefficient of a molecule located at the interface along with the use of reported data for the surface tension allowed studying the variation of important macroscopic and microscopic variables for describing the behavior of water at gas/liquid interfaces. The following observations were made: (i) For a wide temperature range and the three models of packing considered, our thermodynamic model predicts a small increase of density at the interface with respect to bulk. (ii) The surface tension diminishes as temperature increases. The minimum value for the cubic and spherical packing models is attained at the critical temperature, whereas that of the Rasmussen area model is obtained at a lower temperature. (iii) For the three packing models considered, the surface excess increases with temperature, although the values corresponding to the model of Rasmussen are 1 order of magnitude smaller. (iv) The thickness of the interface corresponding to the Rasmussen's model (~24 Å) is about an order of magnitude larger than those of cubic and spherical models (~3 Å). The latter models suggest that the interfacial layer of water is one monolayer thick.

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## Appendix I. Concentration Difference Caused by the Presence of a Field in a Liquid Medium

At first glance, eq 3 seems to be in contradiction with the expression of the interfacial tension as a function of the activity, previously deduced in ref 1 for a multicomponent system. This is not the case, as will be seen in the following analogous situation described by Guggenheim concerning the effect of an electric field on the concentration of a pure ideal gas.[4−6] It can be shown that the chemical potentials of an ideal gas inside and outside a given electric field are

$$\mu_i^{\mathrm{in}} = \mu_i^0 + RT\ln\frac{C_i^{\mathrm{out}}RT}{\lambda_i^0} - \frac{\xi_o N_A \epsilon^2\left[\alpha + \dfrac{\mu_{\mathrm{D}}{}^2}{3\xi_o kT}\right]}{2} \qquad \text{(I)}$$

and

$$\mu_i^{\mathrm{out}} = \mu_i^0 + RT\ln\frac{C_i^{\mathrm{out}}\,RT}{\lambda_i^0} \qquad \text{(II)}$$

where $\lambda_i^0$ is the standard fugacity of the ideal gas $i$, $C_i^{\mathrm{out}}$ and $C_i^{\mathrm{in}}$ are the concentrations of the gas outside and inside the electric field, and $\xi_0$, $\mu_{\mathrm{D}}$, and $\epsilon$ are the electrical permittivity, dipole moment and intensity of the electric field, respectively. The condition of equilibrium

$$\mu_i^{\mathrm{out}} = \mu_i^{\mathrm{in}} \qquad \text{(III)}$$

and some arithmetic yields

$$RT\ln\frac{C_i^{\mathrm{out}}}{C_i^{\mathrm{in}}} = \frac{\xi_o N_A \epsilon^2\left[\alpha + \dfrac{\mu_{\mathrm{D}}{}^2}{3\xi_o kT}\right]}{2} \qquad \text{(IV)}$$

An analogous treatment for liquids would not yield a so transparent equation as this one. Yet, this equation suggests that far from conditions of ideality, which is the case of a liquid, the concentration in the bulk may be different from that in the interfacial zone ($C^{\alpha}{}_{A} \neq C^{\sigma}{}_{A}$).

## References and Notes

(1) Castellanos, A; Urbina-Villalba, G.; García-Sucre, M. *J. Phys. Chem.* **2002**, *107*, 875.

(2) Shen, Y. R. *Solid State Commun.* **1998**, *108*, 399.

(3) Gragson, D. E.; McCarty, B. M.; Richmond, G. L. *J. Am. Chem. Soc.* **1997**, *119*, 6144.

(4) Modell, M.; Reid, R. C. *Thermodynamics and its applications*; Prentice Hall: New Jersey, 1974; Chapter 12, p 474.

(5) Gugenheim, E. A. *Thermodynamics, An Advance Treatment for Chemists and Physicists*, 2nd ed.; Wiley-Interscience: New York, 1950; Chapter 12, p 361.

(6) Hill, T. *An Introduction to Statistical Thermodynamics.* Dover Publications Inc.: New York, 1986; Chapter 12, p 209.

(7) Fine, R. A.; Millero, F. J. *J. Chem. Phys*. **1973**, *59*, 5529.

(8) Sugimoto, T.; Shiba, F. *J. Phys. Chem. B* **1999**, *103*, 3607.

(9) Suarez, J. M.; Torres-Marchal, C.; Rasmussen, P. *Chem. Eng. Sci.* **1989**, *44*, 782.

(10) Nath, S. *J. Colloid Interface Sci*. **1999**, *209*, 116.

(11) Vargaftik, N. B.; Volkov, B. N.; Voljak, L. D. *J. Phys. Chem. Ref. Data* **1983**, *12*, 817.

(12) Sato, H.; Saul, A.; Uematsu, M.; Wagner, W.; Watanabe, K. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1439.

(13) Turkevich, L. A.; Mann, J. A. *Langmuir* **1990**, *6*, 445.

(14) Montumura, K.; Iyota, H.; Aratono, M.; Yamanaka, M.; Matuura, R. *J. Coll. Interface Sci.* **1983**, *93*, 264.

(15) Hansen, R. S. *J. Phys. Chem.* **1962**, *66*, 410.

(16) Yang, C.; Li, D. *Colloids Surf. A: Physicochem. Eng. Aspects* **1996**, *113*, 51.

(17) Defay, R.; Prigogine, I.; Belemans, A.; Everett, D. H. *Surface Tension and Adsorption*; Wiley: New York, 1966.