Interfacial Energy and the Law of Corresponding States 2: Associated Fluids

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A mesoscopic model for the liquid/vapor interface previously developed for nonpolar fluids [*J. Phys. Chem. A* **2003**, *107*, 875; **2003**, *107*, 883] is extended to the case of polar associated compounds. The interfacial energy is factorized in two terms: one corresponding to association depending on the hydrogen bonds density, the other corresponding to the nonpolar contribution. This last term is treated in the framework of the corresponding states formalism similar to the one used in the case of nonpolar fluids [*J. Phys. Chem. B* **2004**, *108*, 5951]. The model yields a generalized behavior of the association factor as a function of the dielectric constant for the treated fluids. The calculated surface tension shows a mean error of about 1% for seven compounds having different multivalent H-bond characters.

Introduction

It is well-established that surface tension is an important physical quantity in the study of emulsion stability. In general, there are differences in the dielectric nature of the liquids participating in an emulsion. For instance, this occurs for water/oil emulsions (w/o), which are of great industrial use. Emulsions are thermodynamically unstable systems, since the situation of lower energy corresponds to the separation of the two liquids. To delay this process, one makes use of amphyphilic molecules called surfactants. These molecules act in the interface to diminish the surface tension. At the same time, the surfactants may strongly modify the interaction potential between drops. In the case of nonionic surfactants, the polar heads are in general formed by segments having a strong tendency to form hydrogen bridges in aqueous solutions. Once the nonionic surfactant is submerged in the aqueous subphase, a sizable change may be expected in the surface tension. Although this is an experimental fact, a sufficiently elaborate theoretical explanation for it has not yet been given. We try to do this in the present paper by studying the influence of molecular association on the surface tension of pure liquids.

The surface tension of pure compounds with a tendency to form hydrogen bonds is usually larger than that of compounds having similar geometric configuration, yet being of nonpolar nature (homomorphe[4]). Starting from the quasi-chemical model, Durov[5] has developed a theory for solutions of polar fluids giving rise to hydrogen bridges in order to study the association equilibrium in these systems. In this work, a connection was established among thermodynamics, dielectric, optical, and kinetic properties. In typical systems such as the *n*-alkanols, it was found that the association contribution predominated on both the dispersive and dipolar ones,[6,7] and the permittivity patterns were very well described. Also, from dielectric measurements, the aggregate distribution and the mean number

of associations were determined, and as could be expected, the mean degree of associations diminishes with temperature.

There are few theoretical models for the treatment of the surface tension of associated polar compounds (APC). This may be related to the fact that the polar functional groups strongly modify the intermolecular interaction, producing local perturbations that are not present in nonpolar compounds (NPC). Rice and Teja[8] have applied a method of corresponding states for several alcohols using ethanol and pentanol as reference fluids, obtaining for the surface tension an absolute mean error of 3.5%. Yet, this method does not allow the treatment of molecules in which occur several H-bonds, such as water, multifunctional alcohols, and so forth. Lu et al.[9] have developed an application of the density functional theory taking into account the van der Waals ideas and integrating plane by plane in the neighborhood of the interface. These authors assumed a fluid model in which the residual Helmholtz free energy is evaluated by considering contributions coming from rigid spheres, chains, dispersions (Lennard-Jones), dipole−dipole, to the intermolecular potential

$$-\frac{2}{3kT}\frac{\mu_i^2\mu_j^2}{(4\pi\epsilon_0)^2 r^6} \tag{1}$$

where μ_i is dipolar moment of molecule *i* and ϵ_0 the vacuum permittivity, and finally a term taking into account the intermolecular association (SAFT). This method yields values of surface tension for water at different temperatures with a mean error of about 4.5%, and it yields an error of 2.9% for 14 other compounds treated in a large range of temperatures of about 300 K.

With exception of the work of Escobedo and Mansoori,[11] the general trends consist of separating the surface tension in nonpolar and polar terms. One of the initiators of this procedure is Prausnitz[4] that separates the second virial coefficient of a polar compound into two parts: one contribution depending on the geometry that corresponds to a nonpolar analogous compound of the same size and shape (homomorphe) and another

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contribution depending on the reduced dipolar moment

$$\mu_R = \frac{10^5 \mu_i^2 P_C}{T_C^2} \qquad (2)$$

Interfacial Energy For Associated Polar Fluids

To extend the corresponding states scheme for nonpolar compounds[3] to the case of APC, we start by recalling the definition of interfacial free energy proposed in the mesoscopic model previously published.[1] According to this model, the surface tension of a gas/liquid interface of a pure component is given by the contribution of the liquid subphase σ_A (see eq 48 of ref 1) and is given by

$$\Delta\gamma_A^\sigma = \sum_i g_\alpha^2(-\epsilon)h_i(-\epsilon)N_i y_i \delta_{\sigma_A} \qquad (3)$$

where $g_\alpha^2(-\epsilon)$ is an average elastic field that attenuates in the liquid phase α as the depth in the direction of $-z$ increases, ϵ is a macroscopic differential near zero, and $h_i(-\epsilon)$ is the intrinsic contribution of the molecule i to the free energy of the plane located in the subphase σ_A. $h_i(-\epsilon)$ multiplied by the field yields the contribution associated to the molecule i to the potential energy stored in the considered plane).[1]

When the component i refers to a pure compound A, we have $N_A y_A \delta_{\sigma_A} = n_A^{\sigma_A} A/A_A^{\sigma_A}$, and eq 3 reduces to the form[2]

$$\gamma_A^{\sigma_A} A_A^{\sigma_A} = g_\alpha^2(-\epsilon)h_A(-\epsilon)n_A^{\sigma_A} \qquad (4)$$

In this case, h_A is a function of z only, since the chemical environment is not perturbed by other components, and h_A will only be affected by the space configuration of the molecules of A.

It can be shown that this interfacial energy fulfills the law of corresponding states using a model of the surface area A^σ proportional to the van der Waals area, which in turn depends on a parameter ϵ_e that we called empty fraction, and that for pure fluids takes values near 0.5. For the case of APC, the reduced representation of the interfacial energy can be written in a analogous way, as was done in the case of NPC[3]

$$\frac{\gamma_P A_P^\sigma}{RT_{C_P}} = \frac{h_P g_P^2}{RT_{C_P}} \qquad (5)$$

where the subindex P refers to polar fluids. The way in which the above reduced interfacial energy shows a generalized pattern of variation as a function of temperature may be expected to differ from that already found for the NPC fluids.[2] In fact, in the APC fluids, ordering occurs because of the formation of H-bonds, and this ordering not only occurs in one layer of coordination but may reach supramolecular dimensions. Then, in this case, the liquid network for APC fluids is expected to be harder than that for NPC fluids. Also, in the case of APC fluids, an increase in temperature not only will modify the intermolecular mean distance, as is the case for NPC fluids, but still may modify the density of H-bonds.

According to the arguments given in ref 1, there is a direct relation between the energy of deformation in the interface and the surface tension, which leads us to the conclusion that the fluids with a larger degree of association will have a larger capacity to store deformation energy by unit volume, and as a consequence a larger surface tension. Also, a clear dependence may be expected between the surface tension and the distribution of size of the molecular aggregates in associated fluids.
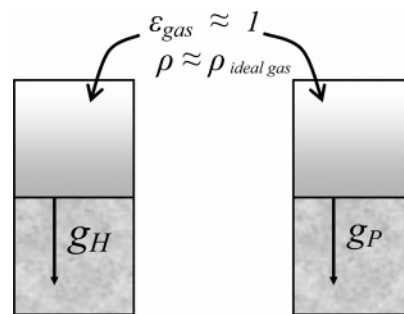

Figure 1. Schematic illustrations of the elastic fields g_P and g_H resulting from the perturbation produced (for low values of T_r) on the liquid phases corresponding to an APC and the corresponding homomorphe fluids, respectively.

To study the contribution to the surface tension due to the molecular association, we factorize the reduced energy of an APC fluid (following the arguments given by Prausnitz[4]) according to the form

$$\frac{h_P g_P^2}{RT_{C_P}} = \frac{T_{C_H} h_P}{T_{C_P} h_H}\left(\frac{g_P^2}{g_H^2}\right)\left(\frac{h_H g_H^2}{RT_{C_H}}\right) \qquad (6)$$

Here, the subindex H stands for the homomorphe of the APC fluid. The right-hand last factor in the above expression can be treated following the same method used for NPC fluids.[3] The second factor in the right-hand side of eq 6 may be treated by considering the elastic fields g_P and g_H as resulting from the perturbation produced on the liquid phase by the adjacent phase (Figure 1). The perturbation either on the APC fluid or on the corresponding homomorphe fluid may be expected to depend on the density and the dielectric response of the adjacent phase. In liquid/vapor equilibrium and for low values of T_r, the density of the vapor phase has a pattern of variation similar to that of an ideal gas, and the function of dielectric response is similar to that of the vacuum. Under these conditions, the particular traits of a fluid associated to the intermolecular interaction potential are erased in the vapor phase. Therefore, in the liquid/vapor equilibrium, the fields g_P and g_H must have the same magnitude independent of the compound considered, provided that the reduced temperature T_r be the same. Yet, the responses h_P and h_H (see eq 3) of the APC and the homomorphe fluids to the fields g_P and g_H could largely differ (see Figure 1). Therefore, in the mentioned conditions, we have $(g_P^2/g_H^2) \approx 1$, and eq 6 reduces to

$$\frac{h_P g_P^2}{RT_{C_P}} = \frac{T_{C_H} h_P}{T_{C_P} h_H}\left(\frac{h_H g_H^2}{RT_{C_H}}\right) = \Phi_D \frac{h_H g_H^2}{RT_{C_H}} \qquad (7)$$

where Φ_D is a function of the ratio h_P/h_H. Such a ratio may be expected to be directly related to the ratio between the corresponding dielectric responses, since the presence of molecular aggregation may be expected to affect in a similar way both types of response.

Since the dielectric constants of the APC fluids are larger than those of the NPC fluids, and, in the first case, the dependence of the dielectric constant on temperature in the region of low T_r is much stronger, one may expect a sizable dependence of the function Φ_D with the dielectric constant of the APC fluid under consideration for low T_r. This allows us to write a generalized correlation for the surface tension of polar

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TABLE 1: Results from Fitting Eq 8 to the Experimental Values of the Surface Tension for Seven Compounds[a]

compound	μ (debye)	μ_R	ϵ_C	ω_H	ϵ_e	AD
water	1.85	180.68	4.885	0.011	0.3333	0.55
ethanol	1.69	66.40	0.7193	0.153	0.2308	0.37
n-propanol	1.68	50.64	0.6841	0.199	0.2308	0.44
2-propanol	1.66	50.77	0.6841	0.183	0.2188	0.71
n-butanol	1.65	37.46	0.6885	0.251	0.1597	1.03
ethylene glycol	2.28	96.21	1.3912	0.199	0.5283	3.06
2-methoxyethanol	2.15	71.85	0.7702	0.251	0.3750	1.39

[a] The average deviation was calculated using the following formula: $\text{AD} = (\sum_N |\gamma_{\text{calcd}} - \gamma_{\text{exptl}}/\gamma_{\text{exptl}}| \times 100)/N$, where N is the number of experimental points for each compound.
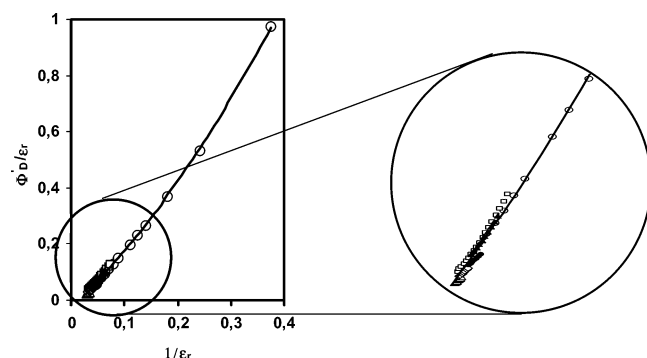
Figure 2. Pattern of variation of Φ'_D/ϵ_r with $1/\epsilon_r$. The values of the dielectric constant for different temperatures were taken from refs 12−17.

fluids, analogous to eq 26 of ref 3

$$\frac{\gamma_P A_P}{RT_{CP}} = \Phi_D \left[\left(\frac{\gamma A_W}{RT_C} \right)^{(0)} + \omega_H \left(\frac{\gamma A_W}{RT_C} \right)^{(1)} \right] \quad (8)$$

where ω_H is the acentric factor of the homomorphe. This factor is assigned as suggested by Prausnitz,[4] e.g., we assign to water the acentric factor of methane because this is the smallest hydrocarbon molecule, while the −OH group is substituted by a methyl group, in the alcohols such as 2-propanol, assigning to isobuthane as its homomorphe. The terms $(\gamma A_W/RT_c)^{(0)}$ and $(\gamma A_W/RT_c)^{(1)}$ of eq 8 are calculated by employing the regression parameters reported in ref 3 (see Table 1 in that reference). Regarding the van der Waals surface area, A_p, this is calculated by employing the liquid volume of its homomorphe, follow by the value of the empty fraction (ϵ_e) parametrized with eq 8.

Results

To evaluate eq 8 according to the corresponding states scheme, we introduce a new variable that we call reduced dielectric constant ($\epsilon_r = (\epsilon/\epsilon_C)$), where ϵ is the dielectric constant at low values of T_r, and ϵ_c is a value of reference corresponding to a region nearby the critical point of the APC fluid. For water,[12] we have taken the value $\epsilon_c = 4.885$, while for other studied compounds, the corresponding values were obtained by parametrizing eq 8 (see Table 1). In Figure 2 is represented a pattern of variation of $\Phi'_D = \Phi_D(T_{C_H}/T_{C_P})$ with $1/\epsilon_r$. The values of the dielectric constant for different temperatures were taken from refs 12−17. According to this figure, we conclude that the APC fluids studied here fulfill, within a good approximation, a general relation within the corresponding states scheme for values of T_r between 0.4 and 0.7. On the other hand, in Figure 3 is illustrated a quadratic dependence of ϵ_c as a function of the reduced dipolar moment, similar to what occurs for the dipole−dipole interaction (see eqs 1 and 2).
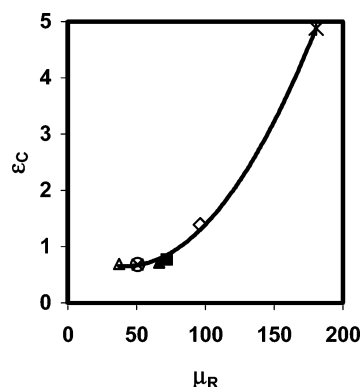
Figure 3. Quadratic dependence of ϵ_c as a function of the reduced dipolar moment for water (∗), ethylene glycol (◇), 2-methoxyethanol (■), ethanol (▲), *n*-propanol (○), 2-propanol (×) and *n*-butanol (△).
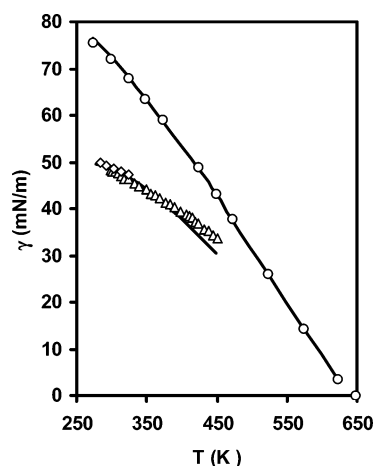
Figure 4. Surface tension as a function of temperature for the cases of water and ethylene glycol. The continuous curves are obtained using eq 8, and the small circles correspond to data for the case of water obtained from reference 19. The small triangles and rhomboids correspond to data for the case of ethylene glycol obtained, respectively, from refs 20 and 21.

In Figure 4, we represent the surface tension as a function of temperature for the cases of water and ethylene glycol. The continuous curves are obtained using eq 8, and the small circles correspond to data for the case of water obtained from ref 19. The small triangles and rhomboids correspond to data for the case of ethylene glycol obtained respectively from refs 20 and 21. We note that the agreement between eq 8 and the experimental data is better for water than for ethylene glycol. According to the argument given in the Introduction on the relation between the surface tension and the density of H-bonds, we may conclude from the shape of the curves appearing in Figure 4 that the density of H-bonds in ethylene glycol decays more slowly when the temperature increases than in the case of water. Also, in the case of ethylene glycol, the density of H-bonds decays more slowly than the estimate of eq 8. Both of the above interpretations are consistent with the fact that as result of an auto-association effect the H-bonds in ethylene glycol are stronger than those in water.[18]

The patterns of variation for the surface tension as a function of temperature for the other five polar compounds studied are illustrated in Figure 5. Except for ethylene glycol, the values of the empty fraction ϵ_e for the seven compounds studied deviate considerably from 0.5, which is a typical value for the NPC compounds[3] (see Table 1). The adjustment of this parameter allows that the van der Waals area of the a polar compound be equal to that of the corresponding homomorphe.
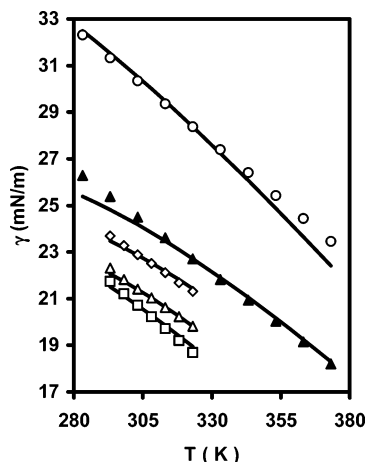
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Figure 5. The patterns of variation for the surface tension as a function of temperature for the other five polar compounds studied: 2-methoxyethanol (○; ref 22), *n*-butanol (▲; ref 22), ethanol(△; ref 23), *n*-propanol (◇; ref 23), and 2-propanol (□; ref 23).

Conclusions

Making use of a quite simple model, we have obtained a general correlation in the framework of the corresponding states scheme that reproduces in a wide range of temperatures with a quite good approximation (~1%) the experimental values of the surface tension for at least seven polar fluids in which different degrees of association occur.

This type of correlation allows not only reproduction of the patterns of variation of the surface tension as a function of temperature for several APC fluids, but also extraction of the corresponding effective van der Waals areas, a parameter whose evaluation is necessary for the thermodynamic treatment of the interface of the multicomponent systems.

According to our results, the degree of association in the APC fluids produces quite similar effects in both the dielectric constant and the surface tension in the region of low reduced temperatures.

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