Interfacial Properties of *tert*-Butyl Alcohol Solutions and Their Relation to Clathrate Formation

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According to a previous report (Glinski, J.; et al. *J. Chem. Phys.* **1996**, *102*, 8816) the surface entropy of the *tert*-butyl alcohol/water system shows a maximum with respect to solute concentration. Such a maximum was formerly related to the formation of clathrate structures at the interfacial region. However, more complex behavior has also been observed in other aqueous systems. It is currently believed that the surface entropy maxima may reflect structural changes similar to a phase transition and specific interactions between solute molecules. To test the clathrate hypothesis, the thermodynamic properties of *tert*-butyl alcohol at water, heptane, and water/heptane interfaces were evaluated. For this purpose, the variation of the surface/interfacial tension as a function of temperature and solute concentration was measured, employing Wilhelmy plate and Du Noüy ring techniques. In aqueous *tert*-butyl alcohol solutions, the maximum of entropy found by Glinski et al. is reproduced. The absence of a large maximum of surface entropy when heptane is used instead of water provides further support to the connection between surface clathrate formation and the anomalous behavior previously observed at *tert*-butyl alcohol/water interfaces. However, some relevant critical points of lower magnitude are observed in the presence of the organic phase. An alternative explanation on its probable origin more related to effective intermolecular interactions rather than to clathrate formation and phase transitions is discussed.

Introduction

Although interfacial properties play a central role in emulsion stability,[1−3] direct measurement of most of these properties at typical drop size scales is not currently possible. As a result, large thermodynamic systems are often used to identify relevant variables and their dependence on surfactant adsorption. Ring and plate evaluations of the interfacial tension for instance, are widely used for this purpose. The usual limitations of these techniques include (among others aspects): (a) deviations from ideal wetting,[2] (b) the need for suitable volume corrections,[4−8] (c) the effect of mutual solubility of the phases on the interfacial measurements,[9,10] and (d) the inability to access very low interfacial tensions at oil/water interfaces.

Further knowledge of interfacial properties can be obtained by measuring the variation of the interfacial tension as a function of temperature. Such a procedure allows determination of the excess entropy (S^σ) and excess enthalpy (H^σ) per surface area of interface, using the following equations:[2]

$$S^\sigma = -(\mathrm{d}\gamma/\mathrm{d}T)_{A,P} \tag{1}$$

$$H^\sigma = \gamma + TS^\sigma \tag{2}$$

where γ, A, and P, are the tension, the interfacial area, and the pressure, respectively.

Entropy and enthalpy determinations are not very common, probably due to the high sensitivity of $\partial\gamma/\partial T$ with respect to the true value of the surface temperature.[11] Despite this limitation, careful determinations had recently shown unexpected variations of the referred thermodynamic variables with respect to solute concentration.[12,13]

In ideal binary systems with one or two liquid phases, the surface tension is expected to decrease linearly with temperature until evaporation or complete mixing. Whenever this behavior is shown by real systems, the enthalpy and entropy come out to be constant.[2] Pure alcohols from hexanol to octadecanol show this behavior.[14,15] This is also the case for aqueous solutions of normal organic acids from pentanoic to tetradecanoic acid.[16] Water/heptylamine and water/octylamine, on the other hand, exhibit a linear increase of the tension with temperature,[7] in a restricted temperature interval toward a maximum tension value. For a further temperature increase, the tension then decreases. Systems with surface-active compounds also show a tension dependence on composition. The interfacial tension between 1-alkanols and water presents a parabolic behavior that is found to depend on their degree of miscibility.[10] In water/alkane systems, the tension changes linearly with the logarithm of the number of carbon atoms (n_C),[17] although comparable accuracy is also obtained with $M^{-2/3}$,[18] where M is the hydrocarbon molecular weight. In two-phase water/long-chain alcohol systems ($n_C = 10-15$), γ increases linearly close to the melting

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2650 *J. Phys. Chem. B, Vol. 106, No. 10, 2002*

Vásquez et al.

point of the alcohol, changing to a parabolic dependence a few degrees above the melting point.[19] This type of first-order phase transition occurs only at the interface, and in some cases, crystallization can be even observed directly with the naked eye.[20] Despite this, the connection between these molecular states and those obtained by compression of spread alcohol monolayers over insoluble substrates[21] is not completely established.

In recent years considerable experimental effort was made in the evaluation of the surface entropy of several aqueous solutions employing ring and plate techniques. These measurements were partially motivated by the very clear maximum of surface entropy found in *tert*-butyl alcohol/water solutions (T/W) at a molar fraction of alcohol equal to $x = 0.0015$.[12] This entropy maximum coincides with a minimum of surface enthalpy and was originally ascribed to the formation of clathrates at an interfacial level. Such an explanation was based on the well-established tendency of *tert*-butyl alcohol molecules to form clathrates in bulk water at higher molar fractions ($x = 0.05$).[22-25] The difference in alcohol concentration between these two systems was justified by the higher surface concentration of *tert*-butyl alcohol relative to bulk.

Similar experiments carried out with *n*-propanol showed two maxima for surface entropy.[13] Since one of the maxima appeared at a similar molar fraction than that of the T/W system; this was attributed to clathrate formation, while the other was cautiously assigned to a phase transition between two superficial structures of different order. From that point on, Glinski et al.[26,27,29,30] had tested several other molecules, obtaining even more involved variations of the surface entropy as a function of solute concentration. These include cyclohexyl and benzyl alcohols,[26] methanol (no maximum),[27] ethanol (one maximum),[28] and *n*-butanol (one maximum)[27] and more complex systems containing 1,2 pentanediol,[29] 1,5 pentanediol,[30] and even L-leucine.[31] In all cases, the speculative nature of the justifications has been emphasized. As pointed out by those authors from the very beginning of their research, several competing process are likely to happen simultaneously in these systems as the surfactant concentration changes: structure-changing effects, aggregate formation, solute−solute repulsion, phase transitions, etc.[12,27] In the light of the rich behavior found, these authors had recently suggested that the unexpected variations of surface entropy could be caused by structural changes similar to those of a phase transition. Such changes are related to the packing of the molecules at the interface and are caused by specific interactions of the hydrophobic parts of the molecules adsorbed.[27] According to this hypothesis, symmetrical molecules will only show one surface entropy maximum while nonsymmetrical ones may show several maxima, due to the different conformations they may adopt as their surface concentration increases.

That interesting conclusion could be related to the high negative values of the entropy found for the adsorption of normal alcohols from the gas phase onto mercury (ref 32 and references therein). As extensively discussed by Posner et al.,[32] these ΔS^σ values are much larger than the corresponding loss of one degree of freedom of translational entropy (9 eu/mol) due to adsorption. Further treatment of the data indicated that (a) short-chain ($n_C < 8$) alcohol monolayers behave as two-dimensional gases over water, (b) the vapor to surface entropy is also very large in aqueous systems, and (c) the entropy of transfer of an alcohol molecule from bulk to surface is close to zero. Posner et al. suggested that the adsorbed alcohol molecules were considerably immersed in the water phase[32,33] and that changes in the internal

degrees of freedom of the hydrocarbon portion of the molecules and cluster formation of water molecules in the immediate neighborhood of the solute molecule might be occurring.

To our knowledge, few theoretical works had addressed this problem. A former statistical mechanical theory[34] was soon discarded by the experimentalists, since it implied severe energetic approximations, unrealistic adsorption values, and anomalous variations of the interfacial areas with chain length and ignored the existence of hydrophilic groups.[19,35] Very recently, molecular dynamics simulations of *tert*-butyl alcohol in water were carried out using dilute (2 mol %) and concentrated (8 mol %) systems.[36] It was observed that *tert*-butyl alcohol has little tendency to aggregate in dilute systems but forms small aggregates spontaneously at higher concentrations. These aggregates persist for several tens of picoseconds, showing preference for tail-to-tail pairwise configurations between the alcohol molecules.

Little attention has been paid to related molecular dynamics simulations of our group[37] regarding the heptane/water/NPE$_3$ (NPE$_3$ = nonyl phenol triethoxylated) system, published back in 1997. In these calculations Guggenheim's formulation[38] was employed to estimate the interfacial entropy of the ternary system using eq 1. For this purpose, sets of 3-D model cells made of heptane/NPE$_3$, water/NPE$_3$, and heptane/water/NPE$_3$ were built, and their energy was subsequently calculated employing NVT-molecular dynamics simulations at different temperatures using an empirical potential. Although the absolute magnitudes of the thermodynamic variables reflected some severe limitations of the calculations,[37] a minimum of surface enthalpy was observed at a given surfactant concentration. That minimum coincided with a maximum of surface entropy, as found in the T/W case. Detailed analysis of the variation of the distinct energy contributions with respect to the surfactant concentration forwarded further microscopic information: While the oil/water interaction energy dropped to zero with increasing surfactant adsorption, a minimum value of the surfactant−solvent energy was found. That minimum was due to the combination of unfavorable cavity energies and favorable surfactant−solvent interactions. Additionally, a surfactant−surfactant interaction energy minimum was also evident. This minimum was caused by the interplay between short-distance (hard core) repulsion and the van der Waals attraction. As a result of these trends, the total energy of the system showed a mimimum value corresponding to an "optimum" interfacial area for the surfactant molecules. That area (97 Å^2) was substantially larger than the expected surface excess (50.4 Å^2), and could not be evaluated with common experimental techniques.

On the basis of the referred calculation,[37] the present authors hypothesized that critical points of interfacial thermodynamic variables might be an indication of the existence of particular surfactant concentrations for which the effective surfactant interaction is favored/disfavored. This agrees in part with the "specific-interaction" presumption between hydrophobic chains enunciated by Glinski et al.[27] If that were the case, this effect could be of general character to binary liquid/surfactant and ternary oil/surfactant/water systems and not exclusively found in the presence of water.

To test this hypothesis, we considered the realization of similar experiments to those reported by Chavepeyer's and Glinki's groups but carried out in nonaqueous *tert*-butyl alcohol/heptane (T/H) solutions and heptane/*tert*-butyl alcohol/water (H/T/W) systems. In the former case, clathrate structures cannot form. At the surface, the hydrophobic tail of the alcohol should be immersed in heptane due to its nonpolar nature, causing the

Interfacial Properties of *t*-BuOH Solutions

J. Phys. Chem. B, Vol. 106, No. 10, 2002 **2651**

hydroxyl groups to be mostly oriented toward the air. In the latter (H/T/W) system, the hydrophobic groups are again supposedly dissolved in the heptane phase, and interfacial clathrate formation is less likely to occur than in purely aqueous solutions, although it is still possible.

In the next section the experimental procedure is described. The results and finally some possible interpretation of the data follows.

Experimental Procedure

Surface tensions were measured in a K10-ST tensiometer from Krüss (±0.1 mN/m) using a Wilhelmy plate. *tert*-Butyl alcohol (Merck, P. A. 99.5%) showed a surface tension of 20.1 mN/m at 25.2 °C, which compares well with the accepted value (20.0 mN/m at 25 °C[39]). Since its surface tension did not lower after distillation, it was used at received. Aqueous *tert*-butyl alcohol solutions were prepared with distilled water by weighing the necessary solute for 11 measurements in an analytic balance. Heptane (Omnisolv, P. A. 99.55%) was eluted twice through zeolite prior to use, attaining a surface tension of 20.6 mN/m at 20 °C ($\gamma = 20.1$ mN/m at 20 °C according to ref 39). In all cases a homemade lid was employed to minimize evaporation effects. With the same purpose, a small 25-mL beaker filled with heptane was placed in one corner of the measurement chamber during T/H measurements (type A evaluations). This beaker was not included in a complementary set of measurements (type B evaluations) in which a different methodology was used to validate the most relevant features of former type A results. For interfacial tensions the Du Noüy ring was used.

Since the adsorption time of surfactants depends on their bulk concentration, the dependence of the surface tension of T/H and T/W systems as a function of time was evaluated using a NIMA 3000 tensiometer with a paper sensor and continuous output. Three *tert*-butyl alcohol molar fractions were chosen for this study. These were located before, in the middle, and after the most significant variations of the entropy in each binary system. In most cases the surface tension changed less than 1.0 mN/m during the first 30 min. Aqueous *tert*-butyl alcohol solutions with $x = 0.0002, 0.0150,$ and 0.2000 [where $x (=x_T)$ is the *tert*-butyl alcohol mole fraction] showed variations of 0.2, 0.4, and 0.4 mN/m the following 15 min after the 30-min equilibration period. T/H systems with $x = 0.00095, 0.029,$ and $0.4500,$ showed variations of 0.4, 0.2, and 0.2 mN/m during the same period of time. Considerably larger tension changes where observed in aqueous and nonaqueous systems after 2 h for the most dilute and the most concentrated samples tested.

In surface tension measurements, 20-mL aliquots of each *tert*-butyl alcohol solution were used. The temperature was varied in 2.5 °C increments starting from 5 °C up to 30 °C. During these experiments the tension was continuously monitored with the plate (measurement type A). After a 30-min equilibration time at each temperature, the tension was evaluated continuously for an additional 15 min. For each *tert*-butyl alcohol concentration, duplicate γ vs T experiments were made. Average values of the tension were computed at each concentration and temperature. The surface entropy was then evaluated from least-squares analysis of all γ vs T data at each *tert*-butyl alcohol concentration.

To check the experimental procedure prior to its application on T/H and H/T/W systems, the maximum of surface entropy found by Glinski et al.[12] for the T/W system was reproduced by employing both plate (Figure 1a) and ring (Figure 1b) sensors. Experimental correction factors for ring measurements in the T/W system were estimated as $F_{p/r} = \gamma_{plate}/\gamma_{ring}$. $F_{p/r}$ values
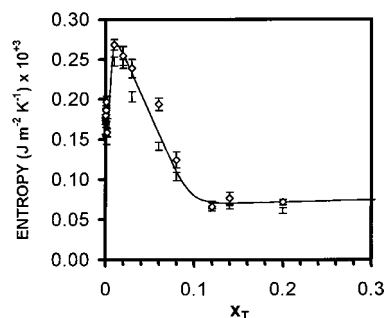
Figure 1. (a) Wilhelmy plate evaluation of the surface entropy of aqueous *tert*-butyl alcohol solutions as a function of the molar fraction of solute, at $T_s = 20$ °C (no markers). (b) Du Noüy ring determinations (◇ markers). The line drawn is only a guide to the eye.

ranged from 0.937 ± 0.002 to 1.003 ± 0.001, depending on the temperature and *tert*-butyl alcohol concentration. The analytical correction factors of Harkins and Jordan[5] and Zuidema and Waters[4] were also computed. The correction factor (Fk) affecting ring measurements in the present tensiometer is equal to Fk = 1.07F, where F is given by Zuidema and Waters' formula. For a ring of radius $R = 9.545 \times 10^{-3}$ m and wire radius $r = 1.85 \times 10^{-4}$ m, $F(R,r)$ is equal to

$$F = 0.725 + \sqrt{0.000436\left(\frac{\gamma_{mes}}{D-d}\right) + 0.0128} \quad (3)$$

here γ_{mes} is the measured tension and $(D - d)$ is the density difference between the immiscible phases. As proved by Chavepeyer and Platten,[6] eq 3—formerly interpolated from Harkins and Jordan's data[4]—is not only reliable but also valid up to vanishing tensions and density differences, in which case it reaches a limit value of $F = 0.8381$.

Since we do not have a densimeter to evaluate the density of *tert*-butyl alcohol solutions as a function of the solvents' temperature (T_s) and solute concentration with a high degree of accuracy, we used published data to estimate it. For this purpose, we studied the data of Franks and Smith,[40] Anderson and Symons,[41] and Visser et al.[42] The data of ref 40 is a linear function of the *tert*-butyl alcohol molar fraction: $D(T_s = 5 °C) = -0.7396x + 1.000$ g/cm³, $D(T_s = 25 °C) = -0.7288x + 0.997$ g/cm³, $D(T_s = 40 °C) = -0.7370x + 0.9922$ g/cm³. The density data of Anderson and Symons corresponds to higher solute concentrations ($x \leq 0.18$) and is also linear on x, but with a completely different proportionality coefficient of -0.4053 ($T_s = 0$ °C). Both sets of data fail to reproduce the density *tert*-butyl alcohol[43] as $x \to 1$. On the other hand, the data of Franks and Smith is quadratic on the temperature at fixed *tert*-butyl alcohol concentration. To calculate the density of the solutions, we used the referred parabolic dependence on the temperature. Additionally, an appropriate correction for the intercept (density of pure water as a function of temperature[43]) and a linear variation on the *tert*-butyl alcohol molar fraction from the pure water density to that of pure *tert*-butyl alcohol were also included. Thus $D(x,T_s)$ in g/cm³ was calculated from $(-5 \times 10^{-6})T_s^2 + (7.3333 \times 10^{-6})T_s + (0.99984 - 0.00014T_s) - 0.22484x$. For the density of air a value of $d \approx 0.001161$ g/cm³ [43] was used.

As can be deduced from Figure 1a,b, there is a reasonable qualitative agreement between ring and plate determinations of the entropy of aqueous solutions, although the correction factors calculated still appear to be too high. Harkins and Jordan's Fk values ranged from 1.0015 to 0.9202,[5] while those of Zuidema and Waters went from 1.0031 to 0.9400.[4] Thus, Fk corrections
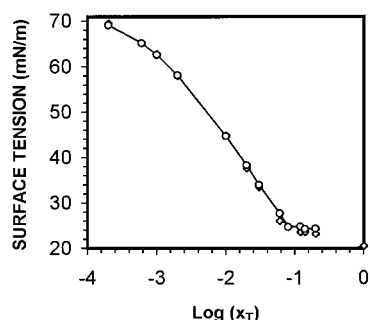
Figure 2. Gibbs adsorption isotherm for the water/*tert*-butyl alcohol system at 20 °C: ○ = plate, ◇ = ring.

predicted by eq 3 are similar in magnitude to those experimentally found ($0.937 < F_{p/r} < 1.003$) but do not show the same dependence with temperature and *tert*-butyl alcohol concentration.

According to the present plate and ring evaluations, the surface entropy of pure *tert*-butyl alcohol is equal to $(0.092 \pm 0.005) \times 10^{-3}$ J m^{-2} K^{-1}, and $(0.083 \pm 0.005) \times 10^{-3}$ J m^{-2} K^{-1}, respectively. These values are in good agreement with those of the literature (0.0900×10^{-3} J m^{-2} K^{-1},[39] 0.105×10^{-3} J m^{-2} K^{-1} [12]). In the case of pure water, values of $(0.162 \pm 0.006) \times 10^{-3}$ J m^{-2} K^{-1} (plate) and $(0.177 \pm 0.004) \times 10^{-3}$ J m^{-2} K^{-1} (ring) were obtained for the surface entropy. These numbers are slightly higher than those previously published: 0.138×10^{-3} J m^{-2} K^{-1},[2] 0.1477×10^{-3} J m^{-2} K^{-1},[39] and 0.150×10^{-3} J m^{-2} K^{-1}.[12]

As shown in Figure 2, ring corrections do not generate appreciable differences in the calculation of Gibbs' adsorption isotherm at fixed temperature ($T_s = 25$ °C in Figure 2). For this figure, the original measured tensions were used without any correction. From this isotherm a surface area of 47 Å^2 per *tert*-butyl alcohol molecule was obtained. Aspee and Lissi[15] reported a value of 43.8 Å^2 for this system.

For A-type measurements on the T/H system with the Wilhelmy plate, heptane solutions from $x = 2 \times 10^{-4}$ to $x = 0.8$ were prepared. To confirm T/H findings, additional evaluations (type B) were made using the same range of *tert*-butyl alcohol concentrations but following an alternative procedure. In this case a set of six samples of a given concentration were measured at each temperature. The beakers were maintained within the thermostatic bath prior to each measurement. At this time, each solution was measured consecutively and subsequently returned to the bath. The plate was submerged within one additional sample vessel between the measurements and the instrument calibrated prior to each evaluation. The surface entropy of heptane evaluated according to techniques A and B with the Wilhelmy plate was $(0.091 \pm 0.006) \times 10^{-3}$ J m^{-2} K^{-1}, and $(0.098 \pm 0.003) \times 10^{-3}$ J m^{-2} K^{-1}, respectively (0.0980×10^{-3} J m^{-2} K^{-1}).[39]

For interfacial measurements (H/T/W systems) the surfactant was formerly dissolved in the heptane phase. The phases in contact were gently stirred altogether during 10 min and left in contact during 24 h prior to the measurements. For ring calibration pure heptane was used. Subsequently, the ring was submerged in the water phase of the interfacial system and a 30-min equilibrium time was allowed before pulling up the ring. *tert*-Butyl alcohol concentrations ranged from $x = 8.4 \times 10^{-5}$ to $x = 3.1 \times 10^{-2}$. Above this maximum concentration the surface tension fell below 1 mN/m and was not accessible with the present instrument.

Although the ring is believed to be more convenient than the plate sensor for interfacial measurement, ring corrections

for the H/T/W system are difficult to estimate. Both the interfacial tension and the density difference between the phases depend on the mutual solubility of water and heptane, the temperature changes, and the *tert*-butyl alcohol concentration. When water and heptane come into contact at room temperature in the absence of *tert*-butyl alcohol, the molar fraction of water in heptane is only $x_{w/h} = 0.00084$, while that of heptane in water is $x_{h/w} = 0.00009$.[9] However, these fractions increase with increasing temperature and *tert*-butyl alcohol concentration.

As discussed, the density of pure water between 0 and 30 °C decreases -0.00014 g/cm^3 for each degree centigrade.[43] In the case of the H/T system (in the absence of water), the density data ($D_H(T)$) from Quayle et al.[44] and Forziati et al.[45] can be fitted to $D_H(T_s) = -0.0009(T_s - 25)$ g/cm^3, where T_s is the temperature in Celsius. Since the surface tension of pure heptane and pure *tert*-butyl alcohol are almost equal at room temperature ($\sim$20.1 mN/m), Fk mostly depends on the difference $D - d$ (see eq 3). According to the data of Kumar et al.,[46] the density of the T/H mixture changes as $D_H(x) = 0.0631x^2 + 0.0341x + 0.6795$ ($R^2 = 0.9994$) as a function of *tert*-butyl alcohol concentration. Thus, for $\gamma = 20.1$ mN/m, Fk = 0.9440. This Fk value only changes 0.0048 units in going from pure heptane to pure *tert*-butyl alcohol at 25 °C. Adding the temperature variation of heptane density to the dependence on *tert*-butyl alcohol concentration, the resulting Fk values ranged from 0.9476 to 0.9409. Thus, if a Krüss ring is used to evaluate the T/H system, the Fk correction is expected to be around 0.1 mN/m only, similar to the limit of detection of the instrument.

For the H/T/W system, the approximate density of each phase can be calculated by employing eq 3 along with the empirical equations previously formulated for each phase:

$$D_W(x_{TW}, T_s) = (-5 \times 10^{-6})T_s^2 + (7.3333 \times 10^{-6})T_s + (0.99984 - 0.00014T_s) - 0.22484x_{TW} \quad (4)$$

$$d_H(x_{TH}, T_s) = -0.0009(T_s - 25) + 0.0631x_{TH}^2 + 0.0341x_{TH} + 0.6795 \quad (5)$$

It has been reported that the H/T/W system is solutropic; i.e., the partition of the alcohol changes from water to oil near the consolute point.[47-49] However, according to Fedoseeva et al.,[48] the hydrophilic/lipophilic balance of *tert*-butyl alcohol is constant at low concentrations and equal to 1.12. If the partition coefficient is known, $x_{TH} = x_T/(1 + K_{H/W})$ and $x_{TW} = x_T(1 - 1/(1 + K_{H/W}))$. To estimate the density difference between the immiscible phases, we used a conservative value of $K_{H/W} = 1.00$. A 20% variation of the coefficient did not change the correction factors appreciably. With $K_{H/W} = 1.00$, $D - d$ values between 0.2976 and 0.3164 were estimated. As will be observed below, ring corrections did not alter the qualitative variation of the surface entropy of the H/T/W system as a function of *tert*-butyl alcohol concentration. It is important to remark at this point that the main purpose of this paper is to study the behavior of the surface thermodynamic variables with respect to *tert*-butyl alcohol concentration. As it is evident from the absolute T/H plate data, the nonmonotonic variation of the surface entropy found for this system is not related to the magnitude of the correction factors but instead is an inherent characteristic of the systems studied.

The interfacial entropy of the H/T system in the absence of *tert*-butyl alcohol was $(0.148 \pm 0.005) \times 10^{-3}$ J m^{-2} K^{-1}.

The error bars were calculated from minimum-square fitting of γ vs T_s data and error propagation formulas.

Interfacial Properties of *t*-BuOH Solutions

J. Phys. Chem. B, Vol. 106, No. 10, 2002 **2653**
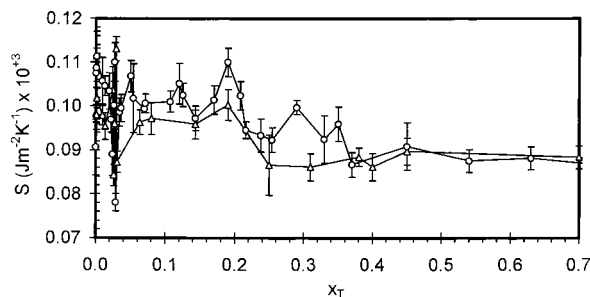
Figure 3. (○) Wilhelmy plate determinations of surface entropy for H/T systems as a function of *tert*-butyl alcohol molar fraction employing technique A. (△) B type measurements.
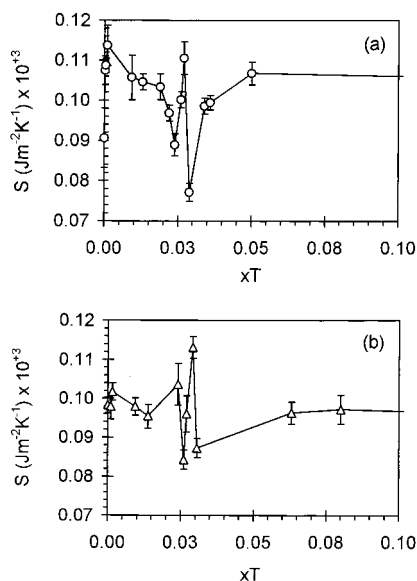

Figure 4. Partial amplification of Figure 3: (a) type A measurement. (b) type B measurement.

Results

In all systems the interfacial tension was found to vary linearly with alcohol concentration. As previously discussed, Figure 1 illustrates the variation of the surface entropy vs *tert*-butyl alcohol molar fraction (x_T) for the T/W system measured with the Wilhelmy plate (part a) and the Du Noüy ring (part b). Both curves reproduce the maximum of surface entropy found by Glinski et al.[12] around $x = 0.015$. Notice that the height of the maximum is around 0.18×10^{-3} J m^{-2} K^{-1}.

Figure 3 shows the surface entropy of nonaqueous T/H solutions. The most relevant feature is the strong variation of the entropy between $0.019 \leq x \leq 0.036$, which can be more clearly appreciated in Figure 4a,b. Since technique type B was used to confirm previous type A results, not all concentrations were reproduced. Still, both results qualitatively agree. According to type A results, there appear to be at least three small maxima located at $x = 0.19$, 0.29, and 0.35. Some other features appear around $x = 0.05$ and 0.12, but the magnitude of the experimental errors in those regions is considerable. Above $x = 0.35$ no other significant variations are observed.

The results of the ring determinations on the H/T/W system are shown in Figure 5. Here, the corrected values (continuous line) are shown along with the uncorrected measurements (broken line). As previously stated, the qualitative aspects of the curve do not change markedly after the corrections. The difference between the measured and corrected values diminishes with tension, as predicted by eq 3, while the density difference does not change considerably. Two maxima ($x =$
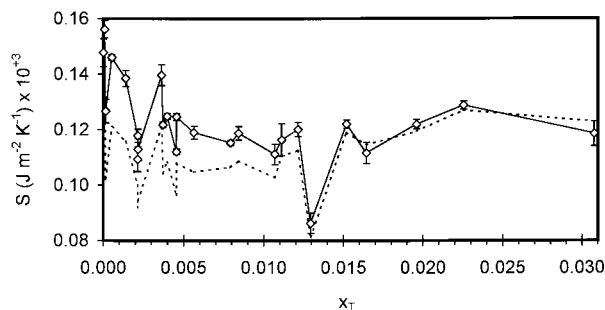
Figure 5. Du Noüy ring evaluation of the interfacial entropy of ternary H/T/W system as a function of the molar fraction of *tert*-butyl alcohol. Entropy values calculated with the corrected interfacial tensions are shown by a continuous curve with circles. Entropy values calculated using measured tensions are shown with a broken line.

5.18×10^{-4}, $x = 3.61 \times 10^{-3}$) and two minima ($x = 2.15 \times 10^{-3}$, $x = 1.29 \times 10^{-2}$) are clearly distinguished. All of them appear to be significant. As in the T/H systems, the size of the critical points ranges from 0.04×10^{-3} to 0.01×10^{-3} J m^{-2} K^{-1}, between $^1/_{10}$ and $^1/_3$ the size of the maximum observed in the T/W system.

Discussion

Figure 1a,b tests the soundness of the experimental methodology. The methodology used is able to reproduce the results of Glinski et al.[12] with a reasonable degree of accuracy. Although small differences between the ring and plate measurements are evident, they can probably be attributed to the approximate density values introduced in eq 3.

Contrary to our initial expectations, the variation of the surface entropy of heptane systems is a complex function of *tert*-butyl alcohol concentration. It should be noticed that the difference between the surface tensions of pure *tert*-butyl alcohol and pure heptane is less 1 mN/m, while the accuracy of the tensiometer is 0.1 mN/m. However, the γ vs T were all linear with high regression coefficients. Thus it is expected that the most distinctive features of the S vs x curve will be reproduced, even if a different instrument/technique with a lower limit of detection is used.

In any event, it is very clear from Figures 3 and 4 that the amplitude of the surface entropy variations with the solute concentration in the H/T system is at most $^1/_5$ of the maximum found in the W/T system. Although there is still some concern regarding the origin of the ordering of water in a W/T system,[50] the entropy variation obtained for the H/T system gives additional support to the effect of clathrate-like structures on the surface properties of W/T systems. As well-recognized by Glinski's and Chavepeyer's groups,[12,27] more than one process may contribute simultaneously to the surface entropy. Some possibilities include (i) structure-changing effects, (ii) repulsion of solute molecules by solvent molecules having higher surface tension, (iii) formation of aggregates of solute molecules at interface by attraction of unscreened parts, and (iv) dimerization of solute. The predominance of each one of these processes will depend on the solute concentration and the temperature. The contrasting behavior found between the surface entropy of W/T and H/T systems is an indication that at room temperature and $x \approx 0.015$, the formation of clathrate-like structures at the surface of the water/*tert*-butyl alcohol system may be the predominant process.

On the other hand, several critical values of surface entropy appear to occur in the case of heptane/*tert*-butyl alcohol, as opposed to those of water/*tert*-butyl alcohol. Since clathrate-

like structures cannot form in heptane, a quite different pattern for the surface entropy was expected from the beginning.

Years ago Efremov[51,52] studied the surface tension of mixtures of C_7–C_{10} alcohols with heptane. At low concentrations of the alcohol, the degree of adsorption was found to increase with the molecular weight of the alcohol. At higher concentrations, the surface tension of the mixture passes through a maximum as a function of composition. The surface entropy curves showed a pronounced minimum, which was interpreted as evidence of complex formation between the alcohols and heptane. A similar conclusion can also be deduced from the behavior of the *n*-butanol/heptane system.[53]

It is clear that the four regions of maximum (minimum) values of surface entropy (enthalpy) found in the H/T systems are difficult to reconcile with the predominance of a phase transitions process, which would be a particular case of "structure changing" effects. Structural changes similar to those occurring in order−disorder transitions had been invoked to account for the two maxima of surface entropy occurring in water/*n*-propanol.[13] In the present (H/T) case, there appear to be four maxima of surface entropy, which seems to be too many to relate to a phase transition process. Since the same symmetrical *tert*-butyl alcohol molecule is sampled in water and heptane, one maximum of surface entropy should be observed in heptane, according to the arguments given in ref 27. It is clear, however, that the heptane molecule has considerably more degrees of freedom than the water molecule. Thus, it could also be argued that the observed entropy behavior of the T/H system is now a demonstration of the structure-changing effects of the heptane molecule as the *tert*-butyl alcohol concentration increases. Further theoretical studies on this subject are required.

Interfacial phase transitions had been reported in parafinic oil/water systems in the presence of normal alcohols ($10 \leq n_C \leq 12$) using the pendant drop technique and pressurized chambers.[54] The transitions are a function of both alcohol concentration and pressure (100−1000 bar). If the interfacial solution is assumed to be regular, the experimental findings can be explained in terms of a two-dimensional phase transition. In the dilute phase the molecules are solvated by the oil, whereas in the most condensed phase there is no solvent interspersed between the aliphatic chains. Similar transitions, such as those reported in ref 53, might occur at constant pressure as a function of temperature and alcohol concentration. However, as it happened in the H/T system, the complex changes of the surface entropy observed for the H/T/W system as a function of alcohol concentration are difficult to justify in terms of phase transitions. On the other hand, it is well-known that the inclusion of hydrocarbon molecules between surfactants lower their interfacial area.[54] This is the case, for instance, for zwitterionic surfactants in the presence of a hydrocarbon (hexadecane, dodecane, heptane, cyclohexane, toluene)/water interface.[54] Whenever this happens, changes between the different conformations of the molecules as a function of surfactant concentrations are likely to occur.

It should be pointed out that in the H/T/W system, the hydrophobic chain of the alcohol should be predominantly oriented toward the heptane phase. Such orientation does not favor clathrate formation at the interfacial level, despite the presence of the water phase. Thus, some patterns of variation of surface entropy are roughly similar to those found in the heptane/*tert*-butyl alcohol system, but in this case, the hydroxyl group is likely to be oriented toward the air. This is another indication that the predominant interfacial process in the T/W system is the formation of surface clathrates. Again, it appears

that the surface probe is capable of sampling the effect of several molecular conformations at the interface. As discussed in the MD simulations reported in ref 37 the effective interactions between surfactant molecules are solvent-mediated, and their effect on the tension is the result of all the contributing interactions.

From the alternatives suggested in the literature,[12,27] these results favor the formation of aggregates of solute molecules as the predominant cause of the entropy variation in nonaqueous T/H and H/T/W systems. Given the molecular complexity of the interface, the effective potential energy surface describing the interaction between solute molecules may have several relative minimum values, each corresponding to a minimum of surface enthalpy and, therefore, to relative maxima of surface entropy. If that where the case, the variation of the interfacial tension with respect to temperature would be probing some relevant features of the effective potential surface between surfactant molecules at the interface.

Conclusions

These experimental results favor the hypothesis of Glinski et al.[12] on the effect of clathrate structures upon the surface entropy of the *tert*-butyl alcohol/water system. The fact that the excess entropy presents different but significant features in H/T and H/T/W systems favors the occurrence of aggregate formation at the interfacial layer as well as structure-changing effects, which might result from "specific interactions" between adsorbed molecules.

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