INTERFACIAL ENTROPY OF TERT-BUTYL ALCOHOL

Issarly Rivas, Aly J. Castellanos-Suárez, Máximo García-Sucre and German Urbina-Villalba

SUMMARY

In a previous paper the interfacial entropy of tert-butyl-alcohol (TBA) at a heptane/water interface was evaluated using a du Noüy ring (Vásquez et al., 2002). Here, this problem is revisited using a more accurate instrument for interfacial measurements: the spinning drop tensiometer. The results differ considerably from the previous evaluations. A broad continuous distribution of interfacial entropy with a large maximum at a molar fraction of TBA ($x_{TBA}$) = 0.01 is found. The height of the maximum and the concentration of TBA at which it occurs are similar to the ones exhibited by aqueous solutions of alcohol.

ENTROPÍA INTERFACIAL DEL ALCOHOL TERBUTÍLICO

Issarly Rivas, Aly J. Castellanos-Suárez, Máximo García-Sucre y German Urbina-Villalba

RESUMEN

En un trabajo previo, la entropía interfacial del alcohol terbutílico (TBA) en la interfase heptano/agua fue evaluada utilizando un anillo du Nöüy (Vásquez et al., 2002). En el presente trabajo, el problema es revisado utilizando un instrumento más adecuado para realizar medidas interfaciales: el tensiómetro de gota giratoria. Los resultados difieren considerablemente de las evaluaciones previas. Se encontró una distribución continua de entropía interfacial con un máximo grande a una fracción molar de TBA ($x_{TBA}$) = 0.01. La altura del máximo y la concentración de TBA a la cual es observado, son similares a los exhibidos por soluciones acuosas del alcohol.

Introduction

Still today a systematic study on the surface entropy of pseudo-ternary systems composed of oil, water and surfactant is not available. This is partially due to the high sensitivity of these measurements with respect to the composition of the system and its temperature (Johansson, 1974). However, theoretical calculations suggest that the critical points of interfacial entropy might indicate interfacial compositions at which the effective interaction between surfactant molecules is either favorable or unfavorable (Urbina-Villalba et al., 1997).

Glinski et al. (1998) demonstrated that the surface entropy of aqueous solutions of some co-surfactants show critical points when plotted as a function of the solute concentration (Chavepeyer et al., 1995; Glinski et al., 1995, 1998, 1996, 1999). Ethanol, n-butanol and tert-butanol show one maximum of interfacial entropy (Glinski et al., 1995, 1998), whereas propanol shows two maxima (Glinski et al., 1996) and methanol none (Glinski et al., 1998). Recently, Romero et al. (2009) published new data on the temperature dependence of the surface tension of aqueous solutions of pentanol and hexanol at several alcohol concentrations. It appears from this information that unlike small alkanols, alcohols with ‘long’ hydrophobic chains (5 ≤ N_c ≤ 8, where N_c is the number of carbon atoms in the alcohol molecule) do not show pronounced maxima of surface entropy, while still longer molecules (N_c ≥ 10) are insoluble in water (Glinski et al., 1993).

Graciaa et al. (1993) showed that in a system composed of octane, water and poly-ethoxylated alkyphenols, small chain alcohols adsorb pronouncedly to the interface, acting as spacers between the surfactant molecules. As the molecular weight of the alcohol increases, its interfacial concentration decreases and its solubility in the oil phase increases. As a result, these molecules act as lipophilic linkers between the surfactant and the oil molecules, increasing the solubility of the amphiphile in the non-polar phase (Graciaa et al., 1993).

It is also known that the attainment of three phases in mixtures of oil, water and an ionic surfactant produces low and ultralow values of the interfacial tension between the immiscible phases (Salager et al., 1979; Bourrel et al., 1980). This property is commonly used to manufacture nanoemulsions (Maestro et al., 2008) and it is also employed to improve the efficiency of oil recovery from a reservoir (Healy et al., 1975). In order to produce three phases starting from oil and water, the affinity of the surfactant for these liquids must be balanced. In the case of ionic surfactants, the increase of the salt concentration lowers the solubility of the surfactant in the aqueous phase, favoring its transfer to the oil phase. In general, anionic surfactants with two hydrophobic branches like

KEYWORDS / Butanol / Entropy / Interfacial Tension / Spinning Drop / TBA / Tert-Butyl Alcohol /
2-bis-ethyl-hexyl sulfosuccinate (AOT) produce three phases and ultralow interfacial tensions in the presence of a suitable amount of sodium chloride (Aveyard et al., 1988). However, in the vast majority of the cases, three phases do not occur unless an appropriate alcohol is added to the mixture (Salager et al., 1979). High-molecular-weight alcohols favor the transfer of the surfactant to the oil phase, while small alcohols increase its solubility in the water phase (Bourrel et al., 1980). This change of behavior occurs at \( N_c = 4 \).

Curiously, the most pronounced maximum of surface entropy found in aqueous solutions, corresponds to tert-butyl alcohol \((\sim 0.18 \times 10^{-3} \text{J} \cdot \text{m}^{-2} \cdot \text{K}^{-1}, x_{\text{TBA}} = 0.01)\). The referred maximum is similar to the one exhibited by the aqueous solutions of TBA (Chavepeyer et al., 1993, 1995, Glinski et al., 1995, 1996, 1998) in previous reports was used (K10-ST from Krüss). Unfortunately, the results were inconclusive. The systems with heptane showed several small maxima of considerable lower magnitude than the one of the TBA-water system. In the case of heptane+TBA, the highest maximum did not reach 1/5 of the one exhibited by the aqueous solutions of TBA. In the case of the ternary system, the critical points ranged from 1/10 to 1/3 of its height (Vásquez et al., 2002).

It is well known that the techniques of du Noüy ring and Wilhelmy plate are very reliable for the measurement of the surface tension, but less appropriate for the evaluation of the interfacial tension. The ring method requires volume corrections which depend on its geometry and the density of the phases. The plate determination depends on the wettability of the liquids and requires a special procedure to correct the flotation of the probe in the lighter liquid. Hence, it was decided to confirm the previous findings using a more accurate instrument for interfacial measurements: using the spinning drop tensiometer.

**Experimental Procedure**

**Chemicals**

n-Heptane (H) (Mallinkrodt, 99.6% pure) was elu- ded twice through an aluminum oxide column of 3mm mesh (Sigma-Aldrich) prior to use. Water (W) was distilled and then purified using a Simplicity system (Millipore). Tert-butyl alcohol (TBA; Merck, 99.5% pure) was used as received.

To ensure the absence of contamination, the surfac- tions of all substances were measured prior to use, employing the Wilhelmy plate of a K10-ST tensiometer \((\pm 0.1 \text{mN} \cdot \text{m}^{-1})\). n-Heptane, TBA and water showed surface tensions of 20.5, 20.3 and 72.7mN\cdot m^{-1} at 293.15K, respectively. These tensions are in agreement with values reported by Jasper (1972) of 20.1, 20.0 and 72.9mN\cdot m^{-1}, respectively.

The systems were prepared in vials with equal volumes of water and heptane. All reactants were weighted successively using an AB204 (Mettler Toledo) analytical balance \((\pm 0.0001g)\). Different amounts of TBA were added to each vial in order to prepare thirty three mixtures with molar fractions of alcohol \((x_{\text{TBA}})\) between 0.0 and 0.1. Each flask was initially gently shaken and then left to equilibrate for a month to favor the partition of the alcohol between the organic and aqueous phase. Approximately 1.5ml of the aqueous phase of the vials was used to fill the capillary of the tensiometer. Following, 20\(\mu\)l of the organic phase were added to the capillary using a syringe (SGE Company), and the interfacial tension of the system was measured using the spinning drop (see below). In order to determine the density of the liquid phases, three samples of 1ml were taken from each phase of the vial in order to evaluate their weight using an analytical balance.

**Instrument**

Interfacial tensions were measured using a TGG110-M3 spinning drop tensiometer made at the Universidad de Los Andes, Venezuela. The instrument consists of a glass capillary with an internal diameter 0.6mm, which is placed inside a rotating metal tube with two parallel rectangular windows (one on each side). From the back of the rotating tube, a stroboscopic lamp or a white light bulb is used to illuminate the oil drop. A DS150 OSX+PC camera placed on the opposite side of the capillary, allows taking pictures of the drop at different rotational velocities. These photographs are used later to determine the geometrical characteristics of the drop.

The method of Vonnegut (Vonnegut, 1942) consists in suspending a drop of phase ‘A’ in a capillary filled with an immiscible liquid ‘B’. The capillary is subjected to a centrifugal force along its horizontal axis rotation, until the drop of the phase A adopts a cylindrical shape.
Following the centrifugal force is used to balance the surface tension. If the length of the cylindrical drop is considerably larger than its radius, the equation of Vonnegut can be applied (Vonnegut, 1942; Princen et al., 1967):

$$\gamma = \Delta \rho \omega^2 R^2 / 4$$  \hspace{1cm} (1)

where \(\gamma\): interfacial tension, \(\Delta \rho\): difference in density between the immiscible phases, \(\omega\): angular velocity of the rotating tube, and \(R\): radius of a cylindrical drop. Thus, a measurement of the radius of the drop when it adopts a cylindrical shape, allows determining the interfacial tension of the system.

### Measurements

In order to change the temperature of the capillary, the rotating tube was surrounded by a double-walled metal cylinder whose temperature was regulated using a circulating bath (1160S from VWR). For each composition the variation of surface tension as a function of temperature was determined. At each temperature, the rotational speed of the instrument was increased until the longest axis of the drop (L) was at least 7 times longer than its width (R). A thirty minute period was awaited to attain a stable rotational speed. This was followed by an additional equilibration time of 3h at each temperature.

The tensions were obtained using Eq. 1. The measurement consisted in taking six photographs of the drop. The computer software allows evaluating the diameter of the cylindrical drop (\(\pm 0.01\)mm) from the pictures. If the diameter of the drop is known along with the density difference between the phases, the interfacial tension can be calculated. The error bars of interfacial tension were obtained propagating the errors of \(\Delta \rho\) and \(R\) in the formula.

The density difference between the phases (\(\Delta \rho\)) was calculated using the equilibrium gravimetric densities of the bulk phases of heptane and water in the heptane/water/TBA (H/W/TBA) system at \(T=298\)K (Table I). In the most favorable case, this density difference has to be determined at each temperature for each alcohol concentration. Due to the lack of a density meter, the density of the phases at each composition was only evaluated at \(T=298\)K. In order to estimate the possible influence of this limitation, approximate equations of the density previously employed in Vásquez et al. (2002) were used (see Eqs. 4 and 5 in Vásquez et al., 2002). The partition constant of TBA was assumed to be equal to 1.0 with the sole purpose of this appraisal. Using the referred approximations, the predicted density difference (\(\Delta \rho_{p}\)) comes out to be systematically higher than the gravimetric determination at \(298\)K (\(\Delta \rho_{g}\)). However, as will be shown below, the essential features of the curve of \(S^o\) vs \(x_{TBA}\) do not change significantly due to this temperature dependence of \(\Delta \rho\). This could possibly be due to the partial cancellation of errors when computing \(\Delta \rho\), since the density of each liquid decreases as a function of the temperature.

The excess entropy \(S^o\) was approximated by the variation of the interfacial tension as a function of the absolute temperature (slope of \(\gamma\) vs \(T\)) at each alcohol concentration

\[S^o = \sigma / T\]  \hspace{1cm} (2)

In this case the error bars resulted from a minimum-square fit of the data of \(\gamma\) vs \(T\), taking into account the error in \(\gamma\) resulting from the propagation of errors of the Vonnegut formula.

### Results

Using the present version of the spinning drop tensiometer, the interfacial tension of the clean H/W interface comes out to be \(49.2\pm1.6\) mN·m\(^{-1}\) at \(298\)K. This value is close to the interfacial tension obtained by Zeppieri et al., 2001 using pendant-drop technique \(50.71\pm0.04\) mN·m\(^{-1}\). However, the absolute magnitude of the error is larger.

Table II shows the data of tension and interfacial entropies obtained. The percentage dispersion with respect to the average interfacial tension \(\%D = \sum (\gamma - \bar{\gamma}) / \bar{\gamma}\) is 3.5%. However, the absolute error of the entropy which results from the propagation of errors is significant, although it decreases considerably with the increase of the alcohol concentration.

Figure 1 shows the typical result of a measurement of \(\gamma\) vs \(T\) at a constant alcohol concentration. The tension changes linearly as a function of the temperature, but the slope of the curve varies with the TBA concentration. Notice that the regression coefficients are very good. The worst regression coefficient of the set is 0.9990.

From the behavior of \(\gamma\) vs \(T\) at each concentration it is possible to reconstruct the variation of \(\gamma\) vs \(x_{TBA}\) for each temperature. Figure 2 shows the Gibbs adsorption isotherm for \(T=298\)K.

Despite the excellent linear regressions of \(\gamma\) vs \(T\), the systems corresponding to TBA concentrations in the range \(0.001\leq x_{TBA}\leq 0.01\) show an appreciable dispersion of interfacial tensions with respect to the ideal form of the Gibbs adsorption isotherm. A similar behavior is observed at other temperatures. This might indicate that these concentrations of TBA require equilibration times longer than 3h in the capillary. In this regard it should be noticed that when a drop of oil is added to the capillary for the tension measurement, a fresh oil/water interface is
created, thus, the time required for the equilibration of this new interface is independent of the previous pre-equilibration time required for the appropriate partition of TBA between the immiscible phases of the vials. Despite these limitations, the linear dependence of the Gibbs isotherm is well characterized, and the overall qualitative shape of the curve is correct. Observe that the alternative procedure of building the isotherms at each temperature requires either a large number of capillaries to be equilibrated, or a large number of samples of each composition. Notice also that for the experimental conditions employed, the values of $\Delta p$ do not affect significantly the shape of the adsorption isotherm.

Figure 3 shows the variation of interfacial entropy of the system composed by water (W), heptane (H) and TBA. Three maxima are clearly observed at $x_{TBA}=0.01$, $S^\sigma=(0.037\pm0.005)J\cdot m^{-2}\cdot K^{-1}$ (at 'a'), $x_{TBA}=0.03$, $S^\sigma=(0.08\pm0.02)\times10^{-3}J\cdot m^{-2}\cdot K^{-1}$ (at 'd') and $x_{TBA}=0.10$, $S^\sigma=(0.04\pm0.01)\times10^{-3}J\cdot m^{-2}\cdot K^{-1}$ (at 'g').

The differences between Figures 3 and 4 demonstrate that the spinning drop technique is very sensitive to the density

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<th>$x_{TBA}$</th>
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<th>$313K$</th>
<th>$318K$</th>
<th>$323K$</th>
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<td>44.0</td>
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<td>42.0</td>
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<td>2.9</td>
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<td>2.5</td>
<td>2.3</td>
</tr>
<tr>
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<td>21.4</td>
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<td>19.2</td>
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<tr>
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<td>9.5</td>
<td>8.6</td>
<td>7.7</td>
<td>6.8</td>
<td>5.9</td>
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Table II

**Interfacial Tension ($\gamma$) and Interfacial Entropy ($S^\sigma$) of the Heptane/Water System as a Function of the Molar Fraction of tert-Butyl Alcohol for Several Temperatures.**

$$\gamma (mN \cdot m^{-1})$$

$$S^\sigma \times 10^{-3} (J \cdot m^{-2} \cdot K^{-1})$$

$$r^2$$

<table>
<thead>
<tr>
<th>$x_{TBA}$</th>
<th>$\gamma$</th>
<th>$S^\sigma \times 10^{-3}$</th>
<th>$r^2$</th>
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<td>0</td>
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<td>7.71x10^-7</td>
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<td>0.0066 ±0.067</td>
<td>0.9998</td>
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<td>1.33x10^-6</td>
<td>42.6</td>
<td>0.0064 ±0.065</td>
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<td>1.13x10^-4</td>
<td>39.3</td>
<td>0.0059 ±0.089</td>
<td>0.9999</td>
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<tr>
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<td>3.4</td>
<td>0.101 ±0.058</td>
<td>0.9999</td>
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<tr>
<td>1.92x10^-2</td>
<td>22.5</td>
<td>0.103 ±0.052</td>
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<tr>
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</tr>
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<td>0.9993</td>
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<td>8.79x10^-2</td>
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<td>0.094 ±0.001</td>
<td>0.9994</td>
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<tr>
<td>1.01x10^-1</td>
<td>3.1</td>
<td>0.037 ±0.005</td>
<td>0.9999</td>
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</table>

† The error was calculated using the propagation of errors of Eq. 1 and a linear regression of $\gamma$ vs $T$.  

In-between the maxima of surface entropy, four minima of interfacial entropy can be seen in Figure 3. They correspond to TBA concentrations of $x_{TBA}=0.00029$, $S^\sigma=(0.08\pm0.04)\times10^{-3}J\cdot m^{-2}\cdot K^{-1}$ (at 'b'), $x_{TBA}=0.00813$, $S^\sigma=(0.16\pm0.04)\times10^{-3}J\cdot m^{-2}\cdot K^{-1}$ (at 'd'), $x_{TBA}=0.03$, $S^\sigma=(0.08\pm0.02)\times10^{-3}J\cdot m^{-2}\cdot K^{-1}$ (at 'f') and $x_{TBA}=0.10$, $S^\sigma=(0.04\pm0.01)\times10^{-3}J\cdot m^{-2}\cdot K^{-1}$ (at 'g').

Figure 4 shows the values of the interfacial entropy calculated using the values of $\Delta p$ instead of $\Delta p_{TBA}$. The general form of the curve of $S^\sigma$ vs $x_{TBA}$ is preserved (see also Figure 3). However, quantitative differences appear. These are more pronounced below the principal maximum. In particular, the heights of the secondary peaks formed in the aqueous solutions of TBA $x_{TBA}=0.01$ (see Table II of Glinski et al., 1995), $S^\sigma=0.24\times10^{-3}J\cdot m^{-2}\cdot K^{-1}$, $\Delta \rho_{TBA}$ and $x_{TBA}=0.00559$ decrease considerably. In fact, the smallest secondary peak is now barely distinguishable.
The four observed minima occur at b: $x_{\text{TBA}} = 0.0029$, d: $x_{\text{TBA}} = 0.00052$, c: $x_{\text{TBA}} = 0.00559$, and e: $x_{\text{TBA}} = 0.00992$ are observed. Figure 3. Excess interfacial entropy ($S^\sigma$) as a function of the molar fraction of TBA. The line drawn is only a guide to the eye. Three maxima at a: $x_{\text{TBA}} = 0.00158$, of the molar fraction of TBA. The line drawn is only a guide to the eye. Error bars were not drawn in order to allow a clear observation of the secondary peaks.

In order to check for the consistency of the data, the Gibbs adsorption isotherm was plotted for several temperatures. The one corresponding to $T=298\text{K}$ is shown in Figure 2. A large dispersion of the data is observed in the range 0.0001<$x_{\text{TBA}}$<0.01. Such behavior suggests that despite the period of equilibration of one-month, the 0.5h waited for the stability of the rotational speed, and the 3h of additional equilibration of the liquids in the tensiometer, some of the systems appear to be out of equilibrium.

The magnitude of the error bars in Figure 3 does not allow establishing the existence of secondary critical points of interfacial entropy. Only the principal maximum at $x_\gamma = 0.01$ survives the error analysis: the peak rises well above the base of the curve. Notice that some secondary maxima are defined by several experimental points. However, the absolute value of the excess entropy decreases when the density of the phases is extrapolated using approximate analytical equations (Figure 4).

Since the Wilhelmy plate technique is only appropriate for the evaluation of the surface entropy, the fact that the H+TBA system does not show a pronounced maximum of entropy implies that water is required for this observation. These results strongly suggest that the principal peak of interfacial entropy observed in the systems made of W+TBA and W+H+TBA, have a common origin. Hence, the primary maximum might probably be caused by the presence of clathrate structures at the interface, as formerly proposed by Glinski et al. (1995).

In the previous evaluation of the interfacial entropy of the H/W/TBA system (Figure 6) using a Du Noüy ring (Vásquez et al., 2002), only two maxima ($x_{\text{TBA}} = 0.00052$ and 0.00361) and two minima ($x_{\text{TBA}} = 0.00215$ and 0.0129) were clearly distinguished. Some of these signals could possibly be related to the set of critical points described above, but the highest value of $S^\sigma$ previously found only reached $0.16\times10^{-3}\text{J}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$. This value is considerably lower than the ones reported in the present work. However, the present values are of a similar magnitude of the ones found by Glinski et al. (1995) for the aqueous solution of TBA. Moreover, the number of TBA concentrations studied in this report is considerably higher than before. As a result, the shape of the peaks is defined by more experimental points. Also, the difference between the highest and the minimum interfacial entropies observed in Figure 3 is considerably larger than the span of the critical points previously detected with the Wilhelmy plate (0.08$\times10^{-3}\text{J}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$; Vásquez et al., 2002). It is clear from Figure 6 that the Du Noüy ring produces very different results from the ones of the spinning drop tensiometer for the heptane/water/TBA system.

Discussion

The spinning drop technique is known to be more reliable than the Wilhelmy plate and du Noüy ring methods for measuring interfacial tensions. The instrument employed uses the Vonnegut equation (Eq. 1) to calculate the tension. Consequently, the apparatus does not require the whole profile of the drop, but only its width. It was developed for low interfacial tensions where the deformation of the oil drop can be easily achieved at a moderate rotational speed. In fact, the error of the measurement ($\Delta \gamma$) depends on the value of the tension. The maximum error is 10% the value of the tension. Hence, the accuracy of the instrument increases with the decrease of the interfacial tension. This is well illustrated by the magnitude of the error bars in Figures 1a, b and c.

Moreover, some secondary signals (like point ‘d’ in Figure 4) could only be affirmed that a broad continuous distribution of interfacial entropy exists, with a maximum around $x_\gamma = 0.01$.

Figure 5 shows a comparison of the present measurements with previous Wilhelmy-plate evaluations of the surface entropy corresponding to the water/TBA and heptane/TBA systems (Vásquez et al., 2002). Since the Wilhelmy plate technique is only appropriate for the evaluation of the surface entropy, the fact that the H+TBA system does not show a pronounced maximum of entropy implies that water is required for this observation. These results strongly suggest that the principal peak of interfacial entropy observed in the systems made of W+TBA and W+H+TBA, have a common origin. Hence, the primary maximum might probably be caused by the presence of clathrate structures at the interface, as formerly proposed by Glinski et al. (1995).

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The existence of supramolecular structures of mesoscopic scale was already found in numerical simulations of aqueous solutions of TBA (Finney et al., 2003). Furthermore, the appearance of a meso-heterogeneous phase in the same system has been recently detected by optical methods (Subramanian et al., 2011a). These findings could probably be related to the appearance of secondary maxima of the interfacial entropy in systems with TBA.

Recently, Subramanian and Anisimov (2011) and Subramanian et al. (2011) had convincingly demonstrated that in aqueous solutions TBA aggregation occurs whenever propylene oxide (PPO) is present in the system. PPO is a surface-active by-product of the synthesis of TBA. Following this line of reasoning, it is possible that heptane could decompose during the long pre-equilibration period (one-month) giving rise to surface active peroxides and/or PPO. In this case, a maximum of entropy will be observed when a spinning drop tensiometer is used, but it will not be found with conventional tensiometers (with rings and plates), where the equilibration time only spans a few hours. This possibility can probably be ruled out in the future by repeating the experiments of plate and ring with a month-old sample of heptane, and/or analyzing the heptane phases employed in the experiments after the pre-equilibration period.

Conclusion

The interfacial entropy of a heptane/water interface shows a large maximum at $\gamma_{\text{TBA}}^\text{max}$ = 0.01. Based on the position of the principal maximum, its height ($S^* = 0.23 \pm 0.04 \times 10^{-3} \text{J} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$), the absence of a similar peak in a H/TBA system, and the presence of a large maximum in the W/TBA system at a similar concentration, it is concluded that the presence of water is necessary for the observation of the phenomenon. This fact supports the former hypothesis (Glinski et al., 1995) regarding the existence of clathrates at the interface.

It is clear that despite its apparent simplicity, the process of evaluation of the interfacial entropy is laborious. This thermodynamic variable is very sensitive to changes in composition, temperature, and liquid density. However, the present results suggest that other secondary maxima of entropy could also exist (Vásquez et al., 2002) in the ternary system studied. Accurate density measurements at several compositions and temperatures are necessary in order to confirm the true existence of these signals.

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REFERENCES


Joannson K (1974) On the importance of accurate surface temperature measurements when determining $\gamma$ and $\partial \gamma/\partial T$ for water as functions of T. J. Colloid Interface Sci. 48: 176-177.


Figure 6. Excess interfacial entropy ($S^*$) of the heptane/water/TBA system as a function of the molar fraction of TBA, obtained by means of: ●: spinning drop tensiometer and ○: du Noüy ring tensiometer.