



Miscibility of anhydrous cationic surfactant mixtures

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ARTICLE INFO

Article history:

Received 19 April 2010

Received in revised form 25 June 2010

Accepted 9 July 2010

Available online 22 July 2010

Keywords:

Cationic surfactant mixtures

IGC

DSC

Interaction parameters

Solubility parameters

ABSTRACT

Inverse gas chromatography (IGC) has been used for studying the miscibility of anhydrous cationic surfactant mixtures. Dodecyltrimethylammonium bromide (C_{12} TAB), octadecyltrimethylammonium bromide (C_{18} TAB) and their mixtures have been used as stationary phases. In these types of stationary phases, the working temperature was determined by Differential Scanning Calorimetric (DSC) and Inverse Gas Chromatography (IGC) techniques. Values of the interaction parameters between the cationic surfactants obtained at four different compositions of their mixtures and at five temperatures showed that the miscibility depended on the composition and suggested that the interactions became more unfavorable with the increment of C_{18} TAB concentration in the mixtures. The results have been interpreted by comparing the structure of the anhydrous lamellar liquid crystals with that of the lamellar mesophases formed in aqueous solutions. Deviations of the systems from the parameter solubility model have been discussed in terms of the entropy contribution to the Flory-Huggins interaction parameter.

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1. Introduction

There has been a considerable interest in the studies of surfactant mixtures in aqueous solutions during the past decades, from both theoretical and experimental points of view. The majority of these studies are related to dilute micellar solutions, since they provide the necessary information to enhance their performance in several industrial applications [1–3]. By contrast, studies of cationic surfactant mixtures in concentrated solutions are not very common [4,5], and even less those related to anhydrous surfactant mixtures [6].

In ionic anhydrous surfactant systems, the liquid and liquid crystalline structures are based on the simultaneous occurrence of two kinds of interactions: van der Waals' interactions in the hydrocarbon bilayers, and electrostatic ones in the ionic bilayers. In some cases, steric interactions can appear in the hydrocarbon bilayers, and polar interactions as well as hydrogen bonds can be found in the ionic bilayers. A combination of these interactions can appear in mixed amphiphile systems. Study of their thermodynamic properties can lead to a better understanding of their influence in the formation and stability of the mentioned microstructures. Moreover, this understanding will be useful for theoretical and practical uses in the design of new microstructures.

It has been stated in literature that an increase in the chain lengths reduces the miscibility of fatty acids in the solid state [7,8] and in monolayers [9]. It is also known that the melting point of a

homologous series of surfactants can follow a different law of dependence on the chain length when the number of carbon atoms is even or odd. Lecuyer and Dervichian [10] found that the crystallization behavior of soap mixtures depends on the difference between the length of the hydrocarbon chains.

Studying phases in the decyltrimethylammonium bromide (C_{10} TAB)/cetyltrimethylammonium bromide (C_{16} TAB) system, Varade et al. [4] observed a synergistic effect. According to these authors, this may be due to the difficulty in the packaging of the hydrocarbon chains of different lengths. In the case of aqueous solution mixtures in the homologous series of alkyltrimethylammonium bromides, positive and negative values of the intra-micellar parameter of interaction between surfactants have been informed [11–14]. Similarly, some authors suggested attractive and repulsive interactions depending on the change in the concentration of surfactants [15–17]. Akisada et al. [18] have analyzed the behavior of mixtures of a homologous series of alkyltrimethylammonium bromides and they concluded that in those systems where the difference in chain lengths is equal or less two carbon atoms, the behavior becomes ideal.

We have previously studied the mixed systems of two twin-tailed cationic surfactants, didodecyltrimethylammonium bromide (DC_{12} DAB) and dioctadecyltrimethylammonium bromide (DC_{18} DAB) by IGC [6]. The obtained values of the interaction parameter were positive in all the explored concentration and temperature ranges. Thus, they were indicative of high immiscibility, in agreement with the behavior of the same system in aqueous solution [19].

Taking into account all these previous findings, we assumed that these effects can influence the structures of anhydrous liquid crystals. Understanding steric and energetic factors can also be useful in the

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enrichment of the aggregation structure theory. It is then interesting to analyze the behavior of anhydrous surfactant mixtures of the homologous series of alquiltrimethylammonium bromides, in which the hydrocarbon chain length difference is higher than two carbon atoms.

In this work, we inform the results obtained from the study of miscibility of dodecyltrimethylammonium bromide (C₁₂TAB) and octadecyltrimethylammonium bromide (C₁₈TAB) anhydrous surfactant mixtures by obtaining surfactant–surfactant interaction parameters through IGC. We attempt to analyze the interactions in surfactant mixtures that have a similar polar head to the system previously studied by us [6], but with only one hydrocarbon chain. Our objective was the determination of mutual solubilities of both surfactants and to compare the results with the ones obtained for the same systems in aqueous solutions.

The thermodynamic properties in solutions should be obtained by IGC in temperature zones where the main dissolution process is that of the partition of the probe solute in the stationary phase. In this paper, the working temperature zone has been obtained by DSC and IGC.

IGC is important in analyzing the degree of miscibility in polymers through the different experimentally determined parameters, such as specific retention volume, temperature of glass transition, and parameters of polymer–polymer interaction [20]. An extensive knowledge of the composition–temperature behavior of surfactant-based stationary phases by IGC will be of interest to design new analytical procedures.

2. Materials and methods

2.1. Materials

Dodecyltrimethylammonium bromide (C₁₂TAB) and Octadecyltrimethylammonium bromide (C₁₈TAB) (Sigma, analytical grade) were used as received. All probe solvents (Merck) were 99% or better.

2.2. Differential scanning calorimetry (DSC)

DSC was performed on a Perkin Elmer DSC 6 calorimeter, between 291 and 473 K, with a scanning rate of 10° min⁻¹ and using samples of 5–10 mg for pure surfactants and 10–15 mg for materials collected over chromatography support. The instrument was calibrated with indium.

2.3. Inverse gas chromatography (IGC)

Pure C₁₂TAB and C₁₈TAB and their mixtures were used as stationary phases and deposited on Chromosorb W, AW, 60/80, which was employed as a solid support. The packing and conditioning of the column are described in reference [6]. The data employed in the specific retention volume computation were obtained by using a column 100 cm long, 1/4 in. external diameter, and the packing characteristics are included in Supplementary Material (SM). (Table 1 SM).

The working temperature zone has been obtained by IGC with packing columns. The packing columns prepared to study the

retentive behavior of two probe solutes (n-octane and toluene) between 338.1 and 423.1 K and with 10% of stationary phases on Chromosorb W, AW, 60/80, were columns 180 cm long and 1/8 in. external diameter. The retention time measurement for each solute was performed with a Hewlett Packard, HP 6890 series, GC System, equipped with a flame ionization detector (FID). Column temperature was measured in a range between 388.1 and 403.1 K with an Iron–Constantan thermocouple placed in the direct environment of the column. The temperature stability during experiments was of ±0.2 K. The employed solutes were n-heptane, n-octane, n-nonane, cyclohexane, methylcyclohexane, benzene, toluene, ethyl acetate, dichloromethane, trichloromethane and carbon tetrachloride. The probe solutes were selected trying to cover all possible chemical structures and polarities. Nitrogen was used as carrier gas. Flow rates were measured at the beginning of each experiment with an air-jacketed soap film flowmeter placed at the outlet of the detector. Inlet pressures were measured with a micrometry syringe (through the injector septum) which was connected to an open branch mercury manometer. To ensure that the results were independent of sample size and flow rate and that the measurements were being performed at infinite dilution, the usual checks were made [21].

Solutes were injected with 10 μl Hamilton syringes, as vapor in equilibrium with pure liquid. For all the solutes and for all the range of stationary phase concentrations, the peaks were symmetric. The injector was kept at 423.1 K and the detector at 453.1 K.

Retention times (*t_R*) were measured with a Chem Station system and the retention specific volumes (*V_g⁰*) were calculated with the following relationship [21]:

$$V_g^0 = j \left(\frac{F_f}{w_L} \right) \left(\frac{273.15}{T_f} \right) (t_R - t_0) (p_0 - p_w) / p_0 \quad (1)$$

where *j* is the James–Martin compressibility correction factor, *p₀* represents the outlet column pressure, *F_f* is the flow rate measured at pressure *p₀* and temperature *T_f*, *w_L* is the mass of the stationary phase into the column and *p_w* is the water vapor pressure at *T_f*; *t₀* is the dead time, which was measured by using the methane peak obtained with the FID.

3. Data reductions

The probe solute–surfactant Flory–Huggins interaction parameter, *χ_{1i}*, can be calculated from the specific retention volumes, *V_g⁰*, by the expression [21,22]:

$$\chi_{1i}^\infty = \ln \left(\frac{273.15 R V_i}{V_g^0 p_1^0 V_1} \right) - \left(\frac{p_1^0 (B_{11} - V_1)}{RT} \right) - \left(1 - \frac{V_1}{V_i} \right) \quad (2)$$

where *V_i* stands for the specific volume of the surfactant experimentally measured in the laboratory. *p₁⁰*, *V₁* and *B₁₁* are the vapor pressure, the molar volume and the second virial coefficient of the probe solute, respectively. The vapor pressures were computed using the Antoine equations and the coefficients were taken from Riddick, Bunger and Sakano [23]. The solute densities at different temperatures were estimated from Dreisbach's compilation [24]. The second virial coefficient of the solutes was calculated by Tsonopoulos's correlation using critical constants tabulated in Reid et al. [25]. The interaction parameter obtained for probe solutes in C₁₂TAB and C₁₈TAB are included in Table 2 of SM. (Table 2 SM).

When the stationary phase is a surfactant mixture, Eq. (2) allows the determination of the ternary probe solute (1)–surfactant (2)–surfactant (3) interaction parameter, *χ₁₍₂₃₎*, assuming an additive specific volume

Table 1
B (cal.cm⁻³) interaction parameter in the C₁₂TAB/C₁₈TAB mixtures.

388.1K		393.1K		398.1		403.1K	
φ ₂	B	φ ₂	B	φ ₂	B	φ ₂	B
0.1543	-8.2 ± 2.7	0.1527	-6.0 ± 2.5	0.1510	-3.7 ± 2.4	0.1492	-1.9 ± 2.3
0.3814	-4.4 ± 1.3	0.3786	-3.8 ± 1.4	0.3755	-2.7 ± 1.3	0.3721	-1.8 ± 1.2
0.6128	-4.4 ± 1.4	0.6100	-3.2 ± 1.3	0.6069	-1.9 ± 1.2	0.6035	-1.1 ± 1.2
0.8803	-4.6 ± 3.2	0.8790	-0.9 ± 2.9	0.8777	1.8 ± 2.7	0.8761	4.3 ± 2.5

Table 2

Interaction parameters (χ_{1i}) of probe solutes in the C₁₂TAB/C₁₈TAB and in the DC₁₂DAB/DC₁₈DAB systems at 373.1 K.

Probe solutes	C ₁₂ TAB ^a	C ₁₈ TAB ^a	DC ₁₂ DAB	DC ₁₈ DAB
n-hexane	–	–	1.45	1.43
n-heptane	2.30	2.22	1.48	1.43
n-octane	2.26	2.12	1.53	1.44
n-nonane	2.16	2.16	–	–
Cyclohexane	1.97	1.95	0.72	0.91
Methylcyclohexane	1.96	1.92	0.80	0.97
Benzene	0.89	1.14	1.22	1.24
Toluene	0.96	1.21	1.23	1.21
Dichloromethane	0.75	0.99	0.39	0.73
Trichloromethane	–0.56	–0.20	–0.53	–0.16
Carbon tetrachloride	0.72	0.94	0.57	0.78
Ethyl acetate	2.04	2.29	1.51	1.79

^a Extrapolate values.

for the surfactant mixture, $v_m = w_2v_2 + w_3v_3$ (where w_i is the weight fraction of surfactant i in the mixture) [22]:

$$\chi_{1(23)}^{\infty} = \ln\left(\frac{273.15R(w_2v_2 + w_3v_3)}{V_g^0 p_1^0 V_1}\right) - \left(\frac{p_1^0(B_{11}-V_1)}{RT}\right) - \left(\phi_2\left(1-\frac{V_1}{V_2}\right) + \phi_3\left(1-\frac{V_1}{V_3}\right)\right) \quad (3)$$

where ϕ_i stands for the volume fraction for component i in the stationary phase, and V_i the molar volume of component i in the mixture.

On the contrary, assuming the Scott–Tompa approximation [26], which describes a ternary system as a simple balance of the corresponding binary systems, it is possible to calculate the surfactant–surfactant interaction parameter, χ_{23} , by using the equation:

$$\chi_{1(23)}^{\infty} = \phi_2\chi_{12}^{\infty} + \phi_3\chi_{13}^{\infty} - \phi_2\phi_3\chi_{23}\left(\frac{V_1}{V_2}\right). \quad (4)$$

The dependence of χ_{23} on the solute probe nature has been considered from a different point of view [27–33]. We used the Farooque and Deshpande [32] methodology by rearranging the above expression as follows:

$$\frac{(\chi_{1(23)}^{\infty} - \chi_{13}^{\infty})}{V_1} = \left(\frac{\phi_2(\chi_{12}^{\infty} - \chi_{13}^{\infty})}{V_1}\right) - \phi_2\phi_3\left(\frac{\chi_{23}}{V_2}\right). \quad (5)$$

A plot of the left-hand side of this expression vs the first term of the right-hand side yields a lineal function; ϕ_2 can be calculated from its slope while χ_{23} can be obtained from the intercept. The physical meaning of the slope was interpreted in terms of an effective average column composition that the solutes are probing.

The values of the surfactant–surfactant interaction parameters can be analyzed as $B = RT(\chi_{23}/V_2)$ (in cal.cm^{–3}) called energy density.

4. Results and discussion

4.1. Surfactant mixtures

The studied system consists of C₁₂TAB and C₁₈TAB either pure or mixed, deposited on Chromosorb W which produced lamellar mesophases at work temperature [34]. Their phase transition temperatures were determined by DSC and IGC. DSC experiments showed the phase changes from crystal to liquid crystal occurring at 372.5 K for C₁₂TAB and at 378.1 K for C₁₈TAB. Fig. 1 shows the thermogram of the lower percentage of C₁₂TAB/C₁₈TAB mixture (0.1669% of C₁₂TAB) with one peak at 371.4 K.

IGC measurements of the retentive behavior of n-octane and toluene between 338.1 and 423.1 K indicate (in the $\ln V_g$ vs $1/T$ plot) retention changes at 368.1 K for C₁₂TAB and at 373.1 K for C₁₈TAB. The

Filename:	C:\Program Files\Pyr...\BOT+BDOT02.d6d
Operator ID:	Susana Bardavid
Sample ID:	BOT+BDOT02
Sample Weight:	10.870 mg
Comment:	BOT+BDOT02

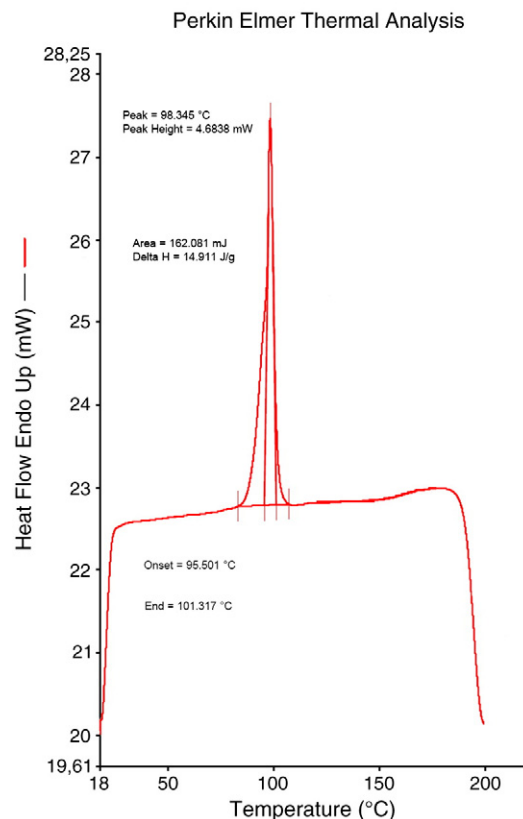


Fig. 1. DSC heating curve of 0.2 C₁₂TAB in the C₁₂TAB/C₁₈TAB mixture on solid support.

anhydrous crystal to lamellar phase transition in pure dodecyltrimethylammonium chloride (C₁₂TAC) occurs at about 356.1 K [35]. Taking into account the effect of changing the counterion, the agreement is good.

The DSC technique is very accurate in determining the pure component properties and the IGC results can be used as supplement to the DSC results in the case of surfactant deposited on solid support. The values of transition temperatures obtained by IGC are always lower than those obtained by DSC, and even more when the very start detection method is used to obtain the transition temperature by means of gas chromatography [20,36,37]. According to these results, it is possible to point out that both pure surfactants and their mixtures appear as lamellar mesophase at the working temperature range (388–403 K). Thus, we can infer that the probe solutes dissolve in a stationary phase formed by an ordered structure of lamellar mesophase. The $\ln V_g$ vs $1/T$ plot for two probe solutes in both surfactants are included in Fig. 2 and 3.

4.2. Interaction parameter surfactant–surfactant

The variation of B (cal cm^{–3}) with the composition in terms of fraction volume of C₁₈TAB (ϕ_2) is shown in Fig. 4 and their values are included in Table 1, with the respective error values at a level of confidence of 95%. All B values are negative, except for two points at the higher volume fractions employed.

Negative B values indicate attractive interactions and hence high miscibility. On the contrary, positive values of B indicate repulsive interactions between the two components and are related to immiscibility [20,22,30,38–40]. Theoretically, this parameter is

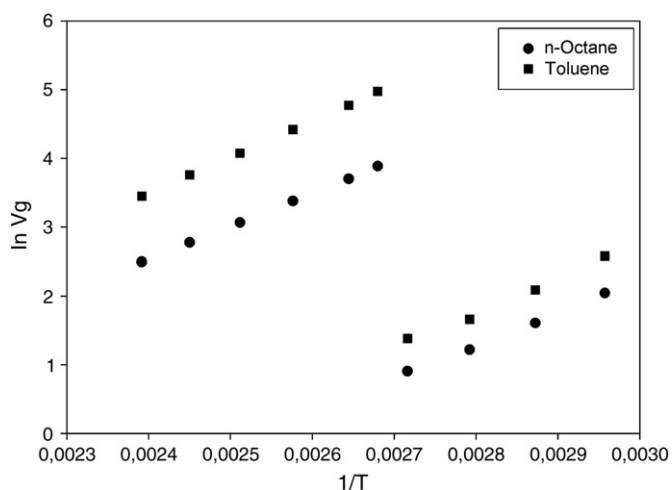


Fig. 2. Van't Hoff retention diagram for probe solutes in $C_{12}TAB$: (●), n-octane; (■), toluene.

independent of concentration. Nevertheless, it has frequently been found that it depends on concentration [29].

For each studied temperature, Fig. 4 shows lower B negative values at lower volume fractions of component 2 ($C_{18}TAB$). Negative B values suggest that the interaction between the two surfactants is more favorable with increasing $C_{12}TAB$ concentration. In general, B parameter values increase as ϕ_2 increases. This shows a somewhat linear tendency in all values except B parameter value at the higher volume fraction at 388.1 K.

The errors in parameters B obtained in this system are almost ten times higher than in our previous study [6]. This is a consequence of the lower solubility of the hydrocarbon probe solutes in the $C_{12}TAB/C_{18}TAB$ systems, as it can be observed in Table 2. In Table 2 we have included the ($\chi_{1,i}$) interaction parameter values extrapolated to 373.1 K to the $C_{12}TAB/C_{18}TAB$ system together with the interaction parameter values obtained at same temperature for the $DC_{12}DAB/DC_{18}DAB$ system.

Studies of anhydrous mixtures of pure $C_{18}TAB$ and $C_{12}TAB$ have not been carried out previously. However, there are some previous studies in aqueous solutions in which these surfactants form mixed micelles [11,18]. Schulz et al. [11,41,42] have studied a series of surfactant mixtures of different homologous series, and found a non-ideality, which depends greatly on the length difference between the hydrocarbon chains of the components, as a consequence of the

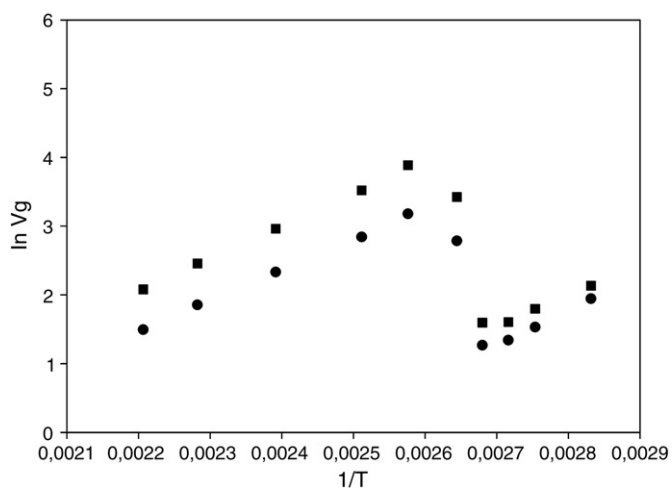


Fig. 3. Van't Hoff retention diagram for probe solutes in $C_{18}TAB$: (●), n-octane; (■), toluene.

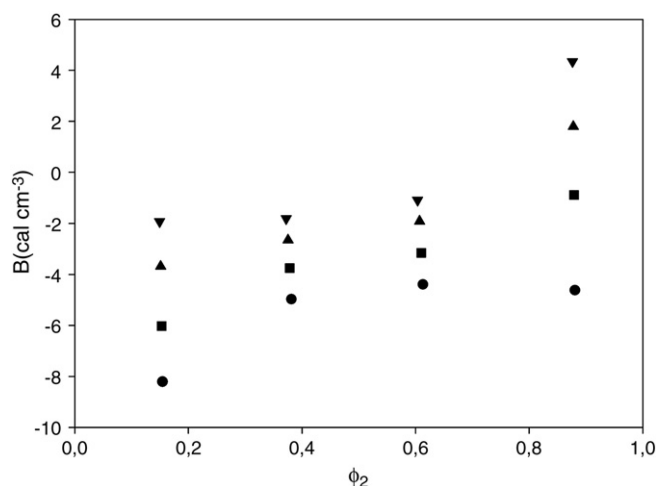


Fig. 4. Interaction parameters between $C_{12}TAB$ and $C_{18}TAB$ as a function of volume fraction (ϕ_2) of $C_{18}TAB$. Temperature: (●), 388.15 K; (■), 393.15 K; (▲), 398.15 K; (▼), 403.15 K.

reduction in the contact between the surface of micellar hydrocarbon core and water. Schulz et al. have obtained [11] negative interaction parameter values for aqueous micellar solutions for the systems $C_{10}TAB/C_{16}TAB$ and $C_{10}TAB/C_{18}TAB$.

Neutron reflectivity measurements of alkyltrimethylammonium bromides ($C_{10}TAB-C_{18}TAB$) monolayers at the water–air interface have shown that their thickness do not differ significantly, while their roughness differ significantly [43,44]. Varade et al. [4] explained it in terms of packing of the adsorbed molecules: $C_{10}TAB$ forms a loosely packed surfactant monolayer, while $C_{16}TAB$ produces a densely packed one. When mixed, the packing of $C_{10}TAB$ dominates the compactness by destroying the dense packing of the pure $C_{16}TAB$ layer. The lower tendency to form an ordered liquid crystalline phase can be accounted for by considering the different chain lengths of the surfactants in the mixture.

In the mixture of surfactants deposited on a solid support, higher ordering can be expected due to the fact that the polar head would be directed to the solid surface. Thus, we can infer that the probe molecules would find an environment similar to what happens when a hydrocarbon of higher molecular weight is used as a stationary phase.

The molecules of pure lineal aliphatic hydrocarbons and their mixtures are ordered according to their longitudinal axis, parallel to each other and are free to move [45], like the orientation in nematic liquid crystals [46]. This ordering is greater in the liquid crystals of pure anhydrous surfactants and their mixtures, like the S_A smectic liquid crystals [47–49], because the first polar layer is anchored to the solid support surface, while there is an alternance of hydrocarbon and polar bilayers, both in the liquid-like state [50]. In other systems, the adsorbed layer molecular organization has been found similar to the lamellar mesophase [51,52]. Due to the different interactions in the hydrocarbon bilayer (van der Waals) and in the headgroups bilayer (polar, electrostatic, and hydrogen bonds) the headgroups cannot be submerged in the hydrocarbon bilayer. Moreover, no voids exist in the non-polar bilayer. When $C_{12}TAB$ is the main component, the inclusion of $C_{18}TAB$ in the $C_{12}TAB$ bilayer may be possible by folding the $C_{18}TAB$ chain, giving a limited solubility. The inclusion of $C_{12}TAB$ molecules into the $C_{18}TAB$ bilayer at high ϕ_2 values is difficult because the C_{18} chains must be folded to avoid voids, but in the lamellar liquid crystals they are almost stretched. This causes a reduction in the mutual solubility, like the behavior in the solid state [10].

A possible effect of the reduction in miscibility is the formation of domains of pure $C_{12}TAB$ liquid crystal and of pure $C_{18}TAB$ mesophase intercalated between each other, as detected in other systems [53].

It must be pointed out that the coating of the support was formed by a superposition of several bilayers. An increase in the temperature will increase the disorder inside the superposed bilayers and the undulations in the regions far from the solid surface, as in other lamellar mesophases [54]. Eventually, the disorder results in the transformation of the lamellar mesophase to an isotropic liquid [55–57]. The increase in disorder leads the lamellar structure to a structure similar to that of a mixture of linear hydrocarbons [58] (except in the monolayer immediately bond to the solid support surface). Since mixtures of liquid linear hydrocarbons with different chain length have positive deviations to Raoult's law, whose magnitude depends on the difference in carbon atoms number [45], this leads to a reduction in miscibility, which is the observed behavior in the studied systems when the temperature is raised.

4.3. Solubility parameter of surfactant mixture

Another treatment of the solubility parameters (δ_i) may give some new information about the interactions in the mixture of surfactants. According to Huang, et al. [59] the solution properties of probe solutes in mesophases can be obtained by IGC and can be analyzed using Flory's theory pattern of liquid crystal [60,61]. The differences in interaction parameters may be attributed to the variation in the solute access to functional groups within the mesophase structure to be studied.

From the regular solution theory [21,30] the interaction parameter is given by:

$$\chi_{1,i} = \frac{V_1}{RT}(\delta_1 - \delta_i)^2 + \chi_s \quad (6)$$

where δ_1 and δ_i are the solubility parameters. The first term in the right-hand side of Eq. (6) represents the enthalpic contribution to the interaction parameter $\chi_{1,i}$, while the term χ_s is the entropic contribution, which has a value around 0.3 for isotropic solutions of solutes in polymers. In our case, it is expected to find that the value χ_s is higher due to contributions from a disorder parameter according to Flory's model [59] and it would represent the deviation from the solubility parameter model.

The solubility parameter of the stationary phase, pure surfactants and their mixtures, δ_i , can be calculated by fitting $\chi_{1,i}$ and δ_1 by using to the following equation [62,63]:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{1,i}}{V_1}\right) = \left(\frac{2\delta_i}{RT}\right)\delta_1 - \left(\frac{\delta_i^2}{RT} + \eta\right) \quad (7)$$

where η is the average value of χ_s/V_1 .

When a mixture is used as stationary phase, the solubility parameter of the mixture (δ_m) can be compared to that predicted by the regular solution theory (RST), in which δ_m is the volume average of the two components.

$$\delta_m = \phi_i\delta_i + \phi_j\delta_j \quad (8)$$

If there was a specific interaction, the value of δ_m should be higher than that obtained by Eq. (8). A measure of the solubility parameter of the surfactant mixtures would then be a good indicator to predict miscibility.

The entropic term χ_s may be considered as a specific interaction term which represents the deviations of the system from the model, represented by the first term in the right-hand side of Eq. (6). It may be positive or negative. Fig. 5 shows the solubility parameter of the surfactant mixture as a function of ϕ_2 ($C_{18}TAB$) and temperature together with those values predicted by the model. It may be seen that the values of $\delta_{2,3}$ are higher than those predicted by the theory. This indicates that additional specific interactions contribute to the

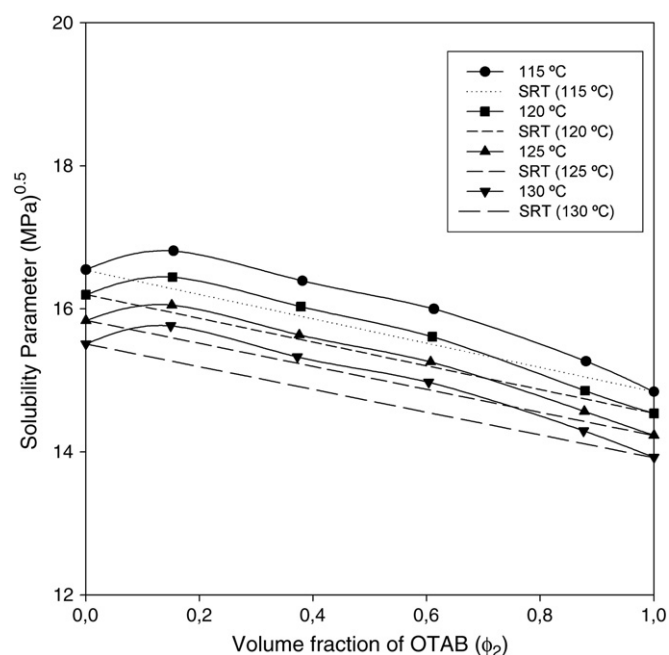


Fig. 5. Solubility parameter of the surfactant mixture as a function of ϕ_2 ($C_{18}TAB$). Temperature: (●), 388.15 K; (■), 393.15 K; (▲), 398.15 K; (▼), 403.15 K.

vaporization process which is not considered in the regular solution theory, and this is characteristic of a certain degree of miscibility in the surfactant mixture. The positive value of χ_s suggests an increase in disorder in the surfactant mixture at a molecular level. A glance in Fig. 5 shows that χ_s decreases when ϕ_2 increases, in agreement with the previous conclusion that the miscibility decreases with increasing $C_{18}TAB$ proportion in the mixed surfactants. Moreover, increasing the temperature also reduces χ_s , as established previously (see Fig. 4).

5. Conclusions

The studied thermodynamic properties are important in relation to the design of new analytic procedures using these liquid crystals. Studies of mixtures of pure $C_{18}TAB$ and $C_{12}TAB$ have not been carried out previously. The IGC experiments with a mixture of $C_{12}TAB$ (component 3) and $C_{18}TAB$ (component 2) have shown that the miscibility of one component in the other depends on the overall composition. The solubility in $C_{12}TAB$ decreases when the volume fraction of $C_{18}TAB$ (ϕ_2) increases. This indicates that the miscibility is not complete in any proportion, as was observed in mixed crystalline soaps having very different chain lengths [11], in anhydrous mixtures of twin-tailed surfactants (didodecyldimethylammonium bromide and dioctadecyldimethylammonium bromide [6]) and in aqueous vesicles of mixed twin-tailed surfactants [19]. This can be explained by considering that the structure of anhydrous lamellar liquid crystals formed by melting the crystals must fulfill the same conditions that solid crystals and lamellar mesophases formed in aqueous solutions, i.e., polar headgroups must be in polar layers and chains in apolar bilayers, so that no voids must appear in the apolar bilayers.

Increasing temperature also reduces the miscibility: this is probably due to the gradual transformation of the lamellar structure from a smectic A to a nematic-like arrangement, which afterwards becomes an isotropic liquid. Nematic liquid crystals have a similar structure (although more ordered) to the long-chain liquid aliphatic hydrocarbons. Mixtures of linear aliphatic hydrocarbons having different chain lengths show positive deviations from the Raoult's law, i.e., they undergo a mutual repulsion (although it is small) [45]. The values of the entropic terms that represent deviations of the system from the solubility parameter model suggest an increasing

disorder at minor values of ϕ_2 , in agreement with higher miscibility found in this concentration zone.

In conclusion, the mutual miscibility of homologous in anhydrous liquid crystalline state seems to be governed by the proportion of components and temperature, and by the difference in chain length. This is an interesting result, since it suggests the possibility of using these liquid crystals in analytical procedures. We are planning to explore this phenomenon more deeply by changing the difference in chain lengths between components.

Acknowledgments

This work was sponsored by CIUNT (Consejo de Investigaciones de la Universidad Nacional de Tucumán) and partially by PICT 10-14560 of ANPCyT (Agencia Nacional de Promoción Científica y Tecnológica). E.L.A. is a member of CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas de la Republica Argentina).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molliq.2010.07.005.

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