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THERMODYNAMIC PROPERTIES OF TRILAURYLAMMONIUM BISULPHATE IN BENZENE

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ABSTRACT

We have studied the thermodynamic properties of trilaurylammonium bisulphate ($TLAH_2SO_4$) in benzene at several temperatures by vapour pressure osmometry (VPO). Values of the activity coefficients, γ_i, are given, which allows calculation of the excess thermodynamic functions, G^E, S^E and H^E.

INTRODUCTION

In a preceding paper [1], the aggregation equilibria of trilaurylammonium bisulphate ($TLAH_2SO_4$) in benzene at several temperatures was studied. At the lowest ammonium salt concentrations, great deviation from ideal behaviour was found. On the other hand, the distribution diagrams of the aggregated species, $(TLAH_2SO_4)_n$, at 25.0, 37.0 and 50.0°C showed a high temperature dependence since the trimer is the predominant species at 25.0°C, whilst at 50.0°C the dimer predominates. However, extension of the aggregation process does not depend in practice on temperature, i.e. the monomeric form of the ammonium salt is always the species in lower concentration. These facts can be applied in the back extraction processes using the $TLAH_2SO_4$ as a metal stripping agent [2–5].

In order to find a better understanding of solute–solvent and solute–solute interactions, the excess functions of trilaurylammonium bisulphate in benzene at 25.0, 37.0 and 50.0°C were calculated.

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EXPERIMENTAL

Benzene (Merck p.a.) was purified by standard procedures [6] and freshly distilled before use. Benzil (Merck p.a.) was purified by successive crystallizations in dried methanol. Benzil purity was checked by IR and DTA.

Trilaurylammonium bisulphate was prepared by shaking trilaurylamine (Merck p.a.), previously filtered in order to remove some carbonate impurities [7], with a cold aqueous solution of 2M H_2SO_4. The precipitate formed was dissolved in dry diethylether and placed at 40°C. The resulting white crystalline solid was recrystallized six times. It was then heated at 40°C in order to remove traces of diethylether and stored in vacuum over anhydrous $CaCl_2$.

Solutions of a desired (stoichiometric) molality, B (mole kg^{-1}), were prepared from weighed amounts of the dried substances and freshly boiled redistilled benzene.

Measurements were carried out on a Knauer 1974 model vapour pressure osmometer. Calibration of the probe, containing two thermistors, was made using, as standard, benzene solutions of benzyl. The ΔR values for both the standard and the ammonium salt were recorded on a Houston Recorder as a function of time. In all the samples 2–3 min were enough to attain constant resistance. At least three ΔR values were measured for each solution and the mean value was taken. The drop size was kept as a constant as possible and equal in the two thermistors, so that the precision of the ΔR values ranged between 0.5 and 1.00%.

THEORY

A short theoretical justification of the equations used is given here.

Following the Gibbs–Duhem equation for a binary system at constant T and p

$$\sum n_i \mathrm{d}\mu_i = 0 \tag{1}$$

where Σn_i is the total number of moles in the system and μ_i is the chemical potential. For the solvent

$$\mu_1 = \mu_1^0(T,p) + RT\Phi_1 \ln x_1 \tag{2}$$

where Φ_1 is the osmotic coefficient of the solvent. Differentiating eqn. (2) and using its value in the Gibbs–Duhem equation gives

$$x_1 \ln x_1 \mathrm{d}\Phi_1 + x_1\Phi_1 \mathrm{d} \ln x_1 + x_2 \mathrm{d} \ln x_2 + x_2 \mathrm{d} \ln \gamma_2 = 0 \tag{3}$$

Differentiation of this equation with respect to x_2 and taking into account that $\mathrm{d}x_1 + \mathrm{d}x_2 = 0$ gives

$$x_1 \ln x_1\left(\frac{\mathrm{d}\Phi_1}{\mathrm{d}x_2}\right) + x_2\left(\frac{\mathrm{d} \ln \gamma_2}{\mathrm{d}x_2}\right) - \Phi_1 + 1 = 0 \tag{4}$$

For dilute solutions, we can develop ln x_1 in series, and consequently ln $x_1 = \ln(1 - x_2) \approx -x_2$, and

$$(1 - \Phi_1) - x_2\left(\frac{d\Phi_1}{dx_2}\right) + x_2\left(\frac{d \ln \gamma_2}{dx_2}\right) = 0 \tag{5}$$

Integrating from zero to X_2, we have

$$\ln \gamma_2 = (\Phi_1 - 1) + \int_0^{X_2} (\Phi_1 - 1) d \ln x_2 \tag{6}$$

If we write the Φ_i values in polynomial form

$$\Phi_i = 1 + \sum_{i=1}^{J} a_i m^i$$

where a_i is the coefficient of the polynomial which better adjusts to the previous equation and m is the theoretical molality. Introducing this value of the osmotic coefficient and integrating, we obtain

$$\ln \gamma_2 = \sum_{i=1}^{J} \left(\frac{i+1}{i}\right) a_i m^i \tag{7}$$

It is also possible to calculate the temperature dependence of the activity coefficient of the solute. Differentiating with respect to temperature at constant pressure, and employing the Gibbs–Helmholtz equation

$$\left(\frac{\partial \ln \gamma_2}{\partial T}\right)_{p,B} = \frac{h_2^{\infty} - h_2}{RT^2} = -\frac{\bar{L}_2}{RT^2} \tag{8}$$

where h_2 and h_2^{∞} are the partial molar enthalpy of the solute in the solution and the partial molar enthalpy of the solute at infinite dilution, respectively, and $\bar{L}_2$ is the relative partial molar enthalpy of the solute.

The excess Gibbs function is defined as the difference between the Gibbs function for the solution and the Gibbs function for the solution assumed ideal

$$G^{\mathrm{E}} = G_{\text{real solution}} - G_{\text{ideal solution}} \tag{9}$$

These excess functions measure the deviation of a real from an ideal solution

$$G^{\mathrm{E}} = \sum n_i \mu_i (\text{real}) - \sum n_i \mu_i (\text{ideal}) \tag{10}$$

Employing eqn. (2) for the real and ideal solutions

$$G^{\mathrm{E}} = RT \sum x_i \ln \gamma_i \tag{11}$$

Knowing G^{E} values for different temperatures, it is possible to calculate the entropy and enthalpy excess functions

$$\left(\frac{\partial G^{\mathrm{E}}}{\partial T}\right)_p = -S^E \qquad H^{\mathrm{E}} = -T^2\left(\left\{\frac{\partial (G^{\mathrm{E}}/T)}{\partial T}\right\}\right)_p \tag{12}$$

Finally, we can also determine the interaction solute–solvent parameter, χ, from

$$G^{E} = N\chi RTx_1(1 - x_1) \tag{13}$$

where N is the total number of moles.

DISCUSSION

Table 1 gives the values of the activity coefficient of solvent, γ_1, and solute, γ_2, as a function of molality and temperature. As can be seen, at the three temperatures studied the system shows a strong negative deviation from Raoult's law. This deviation increases with the molality of the system.

It is interesting to compare the behaviour of $TLAH_2SO_4$ in solution with other salts of the same family. Thus, the osmotic coefficient, Φ_2, was calculated at 25°C, for $TLAH_2SO_4$ and for the trilaurylammonium chloride (TLAHCl), trilaurylammonium bromide (TLAHBr), trilaurylammonium iodide (TLAHI), trilaurylammonium nitrate ($TLAHNO_3$) and trilaurylammonium perchlorate ($TLAHClO_4$). As can be seen in Fig. 1, $TLAH_2SO_4$ self-associates at very low concentrations and in a higher proportion than the other trilaurylamines. In these compounds the cation plays an important role in the thermodynamical behaviour in solution. Thus, it can be seen that as we go from TLAHCl to $TLAH_2SO_4$ the deviation from ideality becomes greater.

This behaviour can be explained if we suppose that $TLAH_2SO_4$ can form

TABLE 1

Values of γ_1 and γ_2 and their variation with the molality and temperature

$B_2 \times 10^2$ (mole kg^{-1})	$T = 25$°C		$T = 37$°C		$T = 50$°C	
	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2
2.253	0.99999	0.34751	1.00000	0.39333	1.00000	0.44707
3.072	0.99999	0.26719	0.99999	0.31067	0.99999	0.36338
4.209	0.99998	0.20256	0.99998	0.24138	0.99998	0.29016
4.667	0.99998	0.18581	0.99998	0.22282	0.99998	0.26988
5.904	0.99996	0.15630	0.99997	0.18908	0.99997	0.23193
6.780	0.99995	0.14440	0.99996	0.17478	0.99996	0.21519
8.323	0.99993	0.13325	0.99994	0.15977	0.99994	0.19763
9.741	0.99991	0.12794	0.99991	0.15283	0.99992	0.18844
10.602	0.99989	0.12481	0.99990	0.14867	0.99990	0.18383
11.023			0.99989	0.14638	0.99990	0.18145
12.477	0.99985	0.11317	0.99985	0.13554	0.99987	0.17098
12.951	0.99976	0.08907	0.99978	0.11044	0.99979	0.14707

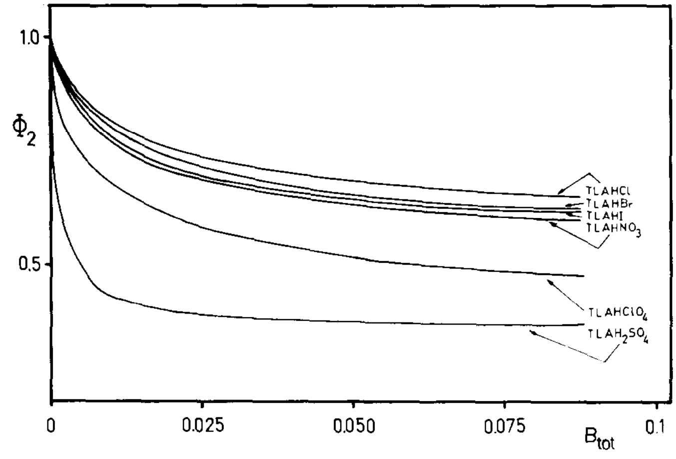
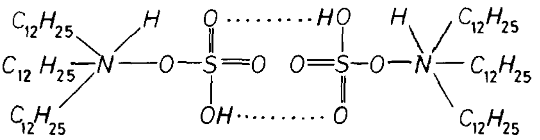
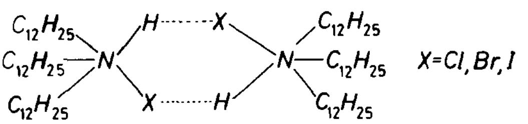


Fig. 1. Osmotic coefficient, Φ_2, as a function of the total concentration, B_{tot}, for different trilaurylammonium salts.

two hydrogen bonds.



These bonds are very strong as shown by the fact that they are stable even at 50°C. For the other salts, however, the self-association probably appears in the form



This interaction is weaker than the hydrogen bond.

On the other hand, as shown by Madariaga et al. [1], the predominant species in the phenomenon of self-association for the $TLAH_2SO_4$, at 25°C, is the trimer, while it is the dimer for the other salts. This fact, evidently, provokes a deviation from ideality. If we suppose that a third $TLAH_2SO_4$ molecule incorporates with the dimer via dipole–dipole interaction, as shown in Fig. 2, it could be explained by considering that the bonds which stabilize the complex are of two different classes, dipole–dipole and hydrogen bonds. The former are more sensitive to temperature. This model could explain the results obtained by Madariaga et al. [1], who calculated the distribution of the different species as a function of temperature.

Another interesting application is to calculate the thermal variation of the activity coefficient of the solute. In Fig. 3 $(d\ln \gamma_2/dT)_p$ is plotted vs. molality, B_2. As the magnitude of B depends on the concentration of the

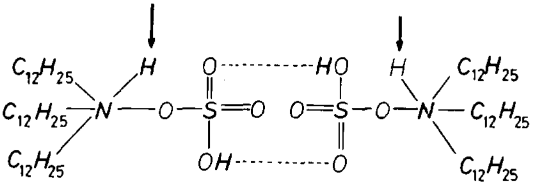


Fig. 2. Formation of a trimer molecule.

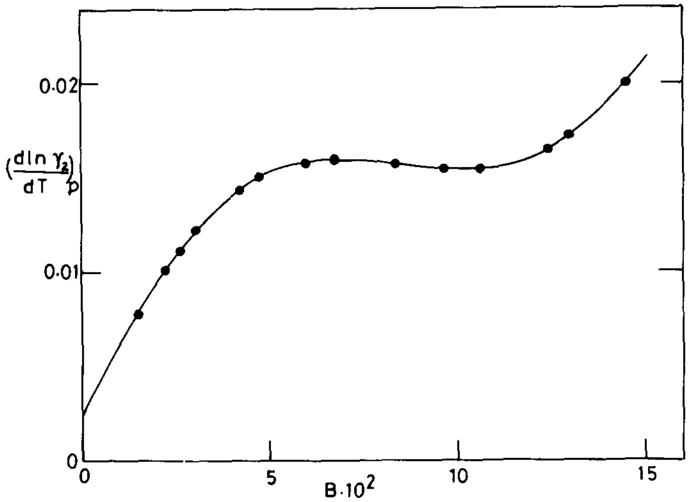


Fig. 3. Plot of $(d \ln \gamma_2/dT)_p$ as a function of the total concentration of $TLAH_2SO_4$.

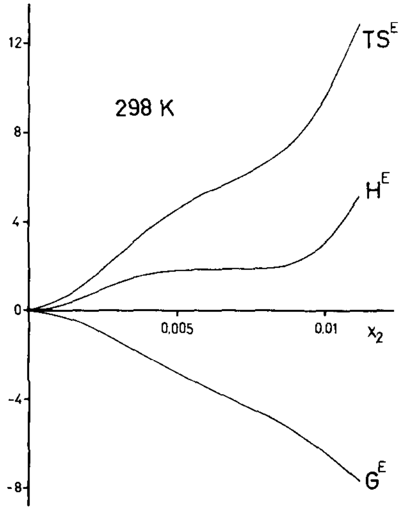


Fig. 4. Excess functions S^E, H^E and G^E as a function of solute molar fraction, x_2, at 298 K.

solution, the extrapolation of B_2 to zero gives the standard partial molar enthalpy, h_2^∞. The value of h_2^∞ was found to be -2.66 kJ mole^{-1}.

It is possible to calculate the excess Gibbs free energy, G^E, from eqn. (11).

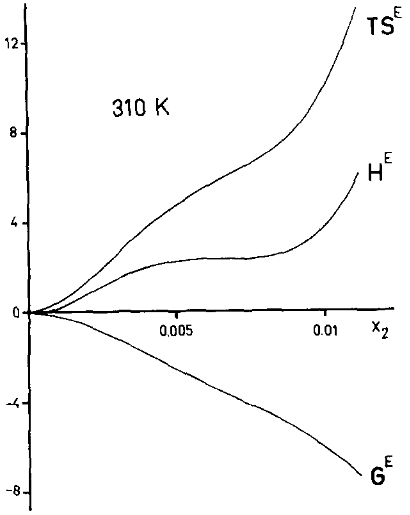


Fig. 5. Excess functions, S^E, H^E and G^E as a function of solute molar fraction, x_2, at 310 K.

If we know G^E values for different temperatures, the entropy and enthalpy excess functions can be obtained. Figures 4–6 give the values of G^E, TS^E and H^E for all temperatures studied. Negative values of G^E indicate that

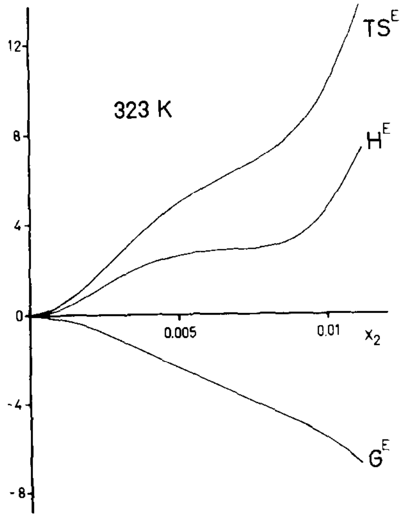


Fig. 6. Excess functions S^E, H^E and G^E as a function of solute molar fraction, x_2, at 323 K.

there is a great compatibility between solute and solvent. This compatibility can be quantitatively calculated from the solute–solvent interaction parameter, χ, which can be obtained from eqn. (13). Figure 7 shows the variation of G^E as a function of x_1x_2, at several temperatures. From the slopes of the three straight lines the values obtained were -0.28 (298 K), -0.26 (310 K) and -0.23 (323 K). This indicates that as the temperature increases, the interaction between $TLAH_2SO_4$ and benzene becomes less favoured. This is logical because as temperature increases the proportion of solvated trimers existing in the system decreases, which confirms the model proposed previously.

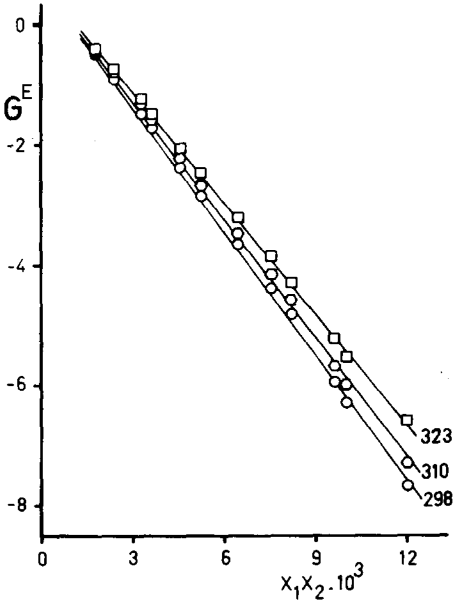


Fig. 7. Variation of the excess Gibbs free energy, G^E, as a function of x_1x_2.

The splitting of χ into the enthalpy and entropy terms is given by

$$\chi = \chi_H + \chi_S$$

where

$$\chi_H = -T\left(\frac{\partial \chi}{\partial T}\right)_B$$

$$= -\frac{\partial (T\chi)}{\partial T}$$

Generally, the entropic term, χ_S, is independent of temperature. However, as can be seen in Fig. 8, the variation of χ_S with temperature is not linear, i.e. χ_S depends on T. These results can be explained if we take into account

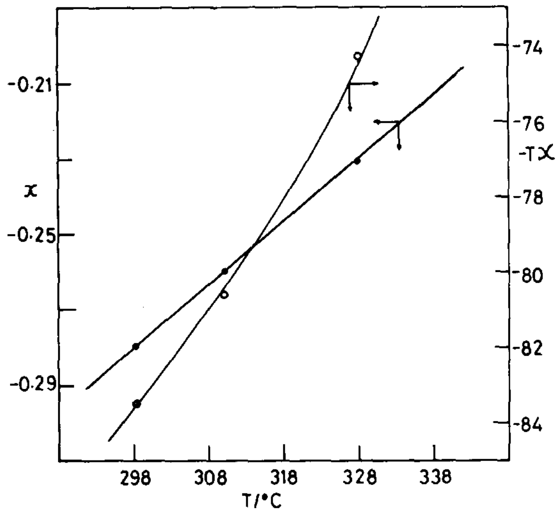


Fig. 8. Variation of χ_S and χ_H with temperature.

that at 323 K, the dimer predominates, and it supposes a decrease in the order of the system, and therefore an increase in the entropic contribution according to experimental observations (Fig. 8).

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