Thermodynamics of Aggregation of Tri-n-butylamine Hydrochloride in Benzene Solution

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The practical molal osmotic coefficients and molal activity coefficients of tri-n-butylamine hydrochloride in benzene solution were determined by vapour pressure osmometry over the concentration range 0.01—0.20 mol kg^{-1} at 25, 37, 45, and 60 °C. The thermodynamic excess functions were evaluated and the non-ideal behaviour of the investigated system interpreted in terms of an association model which includes an extended series of multimers.

THE non-ideal behaviour of tertiary alkylamine salts in non-polar solvents is well known.[1] The alkylamine salts exist mainly in such systems as undissociated hydrogen-bonded ion pairs or higher oligomers and may be further solvated. Due to the relatively high dipole moments of alkylamine salts and the low permittivity of the solvents, interactions between solute molecules are dominant, while those between solute and solvent molecules are considerably lower. In addition the dipole moments are shielded by the alkyl chains, which prefer coiled rather than extended conformations. The colligative properties of such systems, therefore, may furnish some information about the solute–solute and solute–solvent interactions. In the present paper, the non-ideality of tri-n-butylamine hydrochloride in benzene solution has been studied by vapor pressure osmo-

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[1] Y. Marcus and A. S. Kertes, ' Ion Exchange and Solvent Extraction of Metal Complexes,' Wiley, London, 1969, p. 757.

metry and discussed on the basis of the non-solvating model proposed by Prigogine.[2]

EXPERIMENTAL

Tri-n-butylamine Hydrochloride (*TBAHCl*).—This was prepared and purified as in ref. 3.

Benzene (Riedel de Häen) and biphenyl (Eastman Kodak) were purified as previously.[4] Solutions of tri-n-butylamine hydrochloride in benzene were prepared from the dry amine salt on a molar concentration scale. Their respective molalities were calculated by means of solution densities.[3]

Values of regression coefficients, A_i (kg mol^{-1})^i, of equation (2) and standard error of estimate s for the investigated system at 25, 37, 45, and 60 °C

System	T/°C	$10^{-1}A_1$	$10^{-2}A_2$	$10^{-3}A_3$	$10^{-4}A_4$	$10^{-5}A_5$	$10^{-6}A_6$	10^2s
Tri-n-butylamine hydrochloride–benzene	25	−1.853	4.669	−6.774	5.215	−1.999	0.300	1
	37	−1.440	2.905	−3.743	2.710	−1.007	0.149	1
	45	−1.227	2.210	−2.698	1.895	−0.691	0.101	1
	60	−0.946	1.142	−0.922	0.440	−0.115	0.013	1

Vapour Pressure Osmometry.—The osmometric concentration of tri-n-butylamine hydrochloride in benzene solution at 25, 37, 45, and 60 °C was determined as in ref. 4. In all cases the osmometric concentration was determined with an accuracy of ±1 × 10^{-3} mol kg^{-1}. Biphenyl in benzene was used as a standard.

RESULTS AND DISCUSSION

The isopiestic ratio R was calculated by relation (1) [5] where m and m_R denote the molalities of the investigated

$$R = m_R/m = \phi/\phi_R \qquad (1)$$

and reference solutions, and ϕ and ϕ_R their practical molal osmotic coefficients, respectively. The practical molal osmotic coefficients of the reference system at the molalities used were found to be temperature independent within the range 20—50 °C.[6] At 60 °C the same values were obtained *via* equation (6), using the data for the benzene activity coefficient and the respective biphenyl concentration from ref. 7; therefore, relation (1) [6] was used to calculate ϕ_R values at all the temperatures studied. The values of ϕ_R lie between 0.999 at m_R 0.01 and 0.985 at m_R 0.2 mol kg^{-1}. As a consequence, the behaviour of the biphenyl–benzene system at the temperatures and concentrations studied may be considered to be ideal. The practical molal osmotic coefficients of the investigated systems, calculated from equation (1), were fitted into a polynomial of the form (2) where A_i and i are constants. The coefficients A_i

$$\phi = 1 + \sum_{i=1}^{6} A_i m^i \qquad (2)$$

and standard error of the estimate are given in the Table.

From relation (2) it follows that in extrapolation to infinite dilution the practical molal osmotic coefficient depends linearly on concentration, *i.e.* $d\phi/dm \longrightarrow A_1$ as $m \longrightarrow 0$. Figure 1 presents the concentration dependence of practical molal osmotic coefficients for the system tri-n-butylamine–benzene at 25, 37, 45, and 60 °C; the solid lines are drawn on the basis of equation (2). As can be seen from Figure 1, the deviation from ideal behaviour of the investigated system increases with increasing concentration of the solute and decreasing temperature.

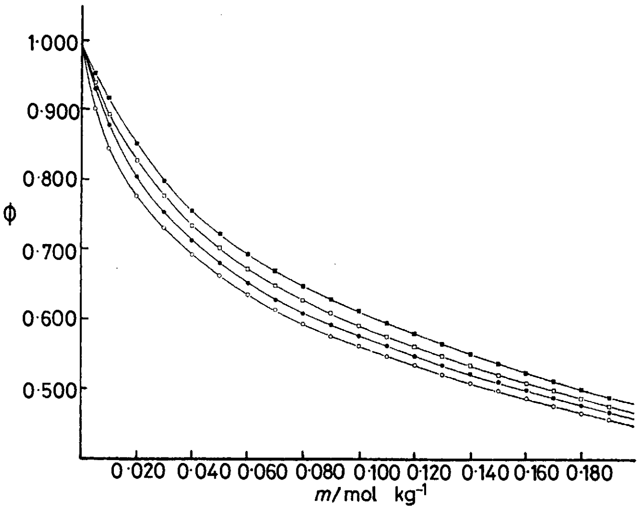

Fig. 1

FIGURE 1 The concentration dependence of the practical molal osmotic coefficients for the TBAHCl–benzene system at 25 (○); 37 (●); 45 (□); and 60 °C (■)

The molal activity coefficients of the solute investigated, $\gamma^*_{2,m}$, defined on the unsymmetric normalization, were calculated using Bjerrum's relation (3) [8] in the

$$d[(1 - \phi)m] + m\,d \ln \gamma^*_{2,m} = 0 \qquad (3)$$

form (4) which was obtained from equation (3) after

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[2] I. Prigogine and R. Defay, 'Chemische Thermodynamik,' VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1962, pp. 401, 428.

[3] Š. Paljk, C. Klofutar, and M. Žumer, *J. Inorg. Nuclear Chem.*, 1976, **38**, 293.

[4] C. Klofutar, Š. Paljk, and D. Kremser, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1729.

[5] G. N. Lewis and M. Randall, 'Thermodynamics,' McGraw-Hill, New York–Toronto–London, 1961, 2nd edn., pp. 320, 392, 398.

[6] K. R. Harris and P. J. Dunlop, *J. Phys. Chem.*, 1967, **71**, 483.

[7] E. A. Guggenheim, 'Mixtures,' Clarendon Press, Oxford, 1952, p. 234.

[8] E. A. Guggenheim and R. H. Stokes, 'Equilibrium Properties of Aqueous Solutions of Single Strong Electrolytes,' in 'The International Encyclopedia of Physical Chemistry and Chemical Physics,' eds. D. D. Eley, J. E. Mayer, and F. C. Tompkins, Pergamon Press, Oxford–London–Edinburgh–New York, 1969, p. 10.

integration between the limits of $m = 0$ and m, taking into account equation (2) for the practical molal osmotic

$$\ln \gamma^*_{2,m} = \sum_{i=1}^{6} \frac{i+1}{i} A_i m^i \qquad (4)$$

coefficients. The molal activity coefficients were determined with the same accuracy as the practical molal osmotic coefficients (see Table).

In extremely dilute solutions equation (4) reduced to (5). From relation (5) it is evident that in extremely

$$\ln \gamma^*_{2,m} = 2\, A_1 m = 2(\phi - 1) \qquad (5)$$

dilute solution the limiting slope of $\ln \gamma^*_{2,m}$ against m is twice of that of ϕ against m. The solvent activity coefficient, $\gamma_{1,X}$, was calculated from the respective practical molal osmotic coefficient *via* relation (6) [5] where X_1 is the

$$\ln X_1\gamma_{1,X} = -mM_1\phi/1\,000 \qquad (6)$$

mole fraction and M_1 the molecular weight of the solvent, respectively.

The values of the benzene activity coefficient for the investigated systems, calculated from equation (6), are close to unity; *e.g.* $\gamma_{1,X} = 1.009$ (25 °C); 1.008 (37 °C); 1.008 (45 °C); and 1.008 (60 °C) at 0.2 mol kg^{-1}.

The change of activity or activity coefficient with temperature at constant composition is given by equation (7) [5] where $\bar{L}_i$ denotes the relative partial molal

$$\mathrm{d} \ln a_i/\mathrm{d}T = \mathrm{d} \ln \gamma_i/\mathrm{d}T = -\bar{L}_i/RT^2 \qquad (7)$$

enthalpy and a_i the activity of constituent i, and R is the gas constant. Since for the system investigated the activity or activity coefficient of the solvent is temperature independent at all concentrations studied, the value of $\bar{L}_1$ may be considered to be zero.

The relative partial molal entropy of the solvent, $\bar{s}_1 - s_1^\circ$, is given by relation (8) [5] in which s_1° is the molal

$$\bar{s}_1 - s_1^\circ = \bar{L}_1/T - R \ln a_1 \qquad (8)$$

entropy of the solvent in its standard state. The relative partial molal entropy of the solvent is close to zero, from equation (8), since for the investigated system $\bar{L}_1$ was found to be zero, and $a_1 = X_1\, \gamma_{1,X}$ is close to unity. Hence it may be assumed that the solute species do not show appreciable effects on the structure of the solvent.

The excess Gibbs free energy per mole of solution g^{E*}, defined on unsymmetric normalization, can be calculated from relation (9).[9]

$$g^{E*} = RT(X_1 \ln \gamma_{1,X} + X_2 \ln \gamma^*_{2,X}) \qquad (9)$$

The excess entropy s^{E*} and excess enthalpy h^{E*} per mole of solution are given by equations (10) and (11).[2] The excess enthalpy h^{E*} is the heat of mixing per mole of solution at constant pressure.[2]

Because $\ln \gamma_{1,X}$ and $\partial \ln \gamma_{1,X}/\partial T$ are close to zero for the investigated system, the excess thermodynamic

$$s^{E*} = -RT\left(X_1 \frac{\partial \ln \gamma_{1,X}}{\partial T} + X_2 \frac{\partial \ln \gamma^*_{2,X}}{\partial T}\right) - R(X_1 \ln \gamma_{1,X} - X_2 \ln \gamma^*_{2,X}) \qquad (10)$$

$$h^{E*} = -RT^2\left(X_1 \frac{\partial \ln \gamma_{1,X}}{\partial T} + X_2 \frac{\partial \ln \gamma^*_{2,X}}{\partial T}\right) \qquad (11)$$

functions, therefore, mainly result from the activity coefficient of the solute and its temperature variation. It can be concluded that the non-ideal behaviour of the investigated system cannot be ascribed to the heat of mixing only but also to the entropy effects.

Considering the non-ideal behaviour of the investigated system as a consequence of a series of association equilibria, due to the dipole–dipole interactions of simple ion-pairs [relation (12)] [10] with the self-association

$$q\mathrm{B}_1 \rightleftharpoons \mathrm{B}_q \qquad (12)$$

constant β_q, the total concentration of solute m related to the monomeric concentration, is given by (13) where

$$m = \sum_1^Q q[\mathrm{B}_q] = \sum_1^Q q\beta_q b^q \qquad (13)$$

b is the free monomer concentration, while the osmometric concentration m_R is given by equation (14).

$$m_\mathrm{R} = \sum_1^Q [\mathrm{B}_q] = \sum_1^Q \beta_q b^q \qquad (14)$$

With this assumption the experimental data (m, m_R) for the TBAHCl–benzene system were interpreted on the basis of an association model, which posited an extended series of multimers. In Figure 2 the values of m/m_R *versus* m_R are presented at 25 °C. From Figure 2 it can be seen that the experimental data fit relation (15) from

$$m/m_R = 1 + Cm_R \qquad (15)$$

which the self-association constant can be calculated from relationship (16) and the stepwise constant K_q for

$$\beta_q = C^{q-1} \qquad (16)$$

equilibrium (17) from (18). From relation (18) it is

$$\mathrm{B}_{q-1} + \mathrm{B}_1 \rightleftharpoons \mathrm{B}_q \qquad (17)$$

$$K_q = C \qquad (18)$$

evident that the stepwise constants for the investigated system are equal, regardless of the value of q. For the TBAHCl–benzene system the values of C, obtained from

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[9] J. M. Prausnitz and P. L. Chuen, 'Computer Calculations for High-pressure Vapour–Liquid Equilibria,' Prentice-Hall, Englewood Cliffs, 1968, p. 80.

[10] F. J. C. Rossotti and H. Rossotti, 'The Determination of Stability Constants,' McGraw-Hill, New York–Toronto–London, 1961, p. 328.

relation (15) by the method of least squares, are: 12.44 ± 0.23 (25 °C); 12.00 ± 0.16 (37 °C); 11.73 ± 0.15 (45 °C); and 11.07 ± 0.16 (60 °C) (kg mol^{-1}).

To describe an associated system, which obeys relation (15), in principle an infinite number of oligomers is required. In practice, however, the free monomer solute concentration b can be obtained by solving the polynomials (13) and (14) with a finite number for Q, neglecting those higher terms in the polynomial which contribute less to the values of m and m_R than the accuracy of the osmometric determination. In our case, the value of Q was 10; the contribution of higher oligomers was $<5 \times 10^{-4}$ mol kg^{-1}. Figure 3 presents the distribution of dominant associated species of the TBAHCl–benzene system in the concentration range studied at 25 °C. The standard enthalpy $\Delta H°$ and entropy $\Delta S°$ for the stepwise reactions (17) can be evaluated from relation (19) from which it is evident that the standard thermodynamic functions are independent of the value of q and that every mole of B–B bonds formed results in the same absorption of heat and entropy effects, provided that no closed ring oligomers

$$\ln C = -\Delta H°/RT + \Delta S°/R \qquad (19)$$

are formed. For the TBAHCl–benzene system the value of $\Delta H°$ is -328 ± 26 cal mol^{-1} and $\Delta S°$ 1.09 ± 0.08 cal mol^{-1} K^{-1} were obtained *via* relation (19), using the method of least squares.

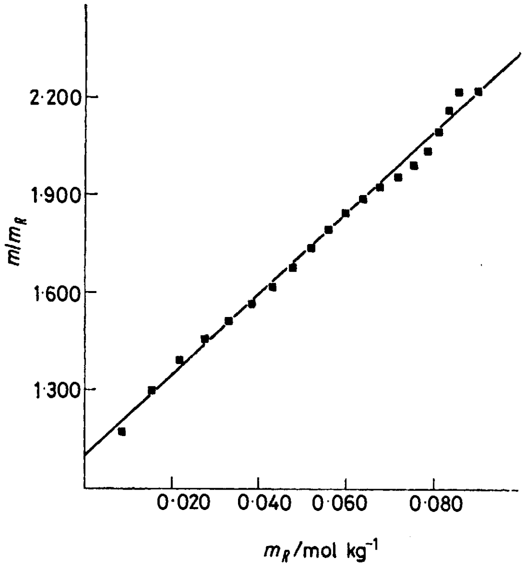

FIGURE 2 m/m_R as a function of m_R for the TBAHCl–benzene system at 25 °C

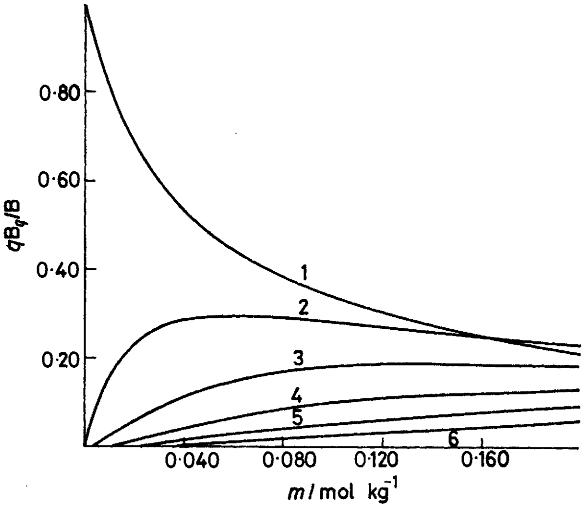

FIGURE 3 The distribution of dominant associated species for the TBAHCl–benzene system at 25 °C

On the other hand, the standard enthalpy $\Delta H°_q$ and entropy $\Delta S°_q$ related to the self-association reaction (12) are dependent on q *via* relations (20) and (21).

$$\Delta H°_q = (q - 1)\Delta H° \qquad (20)$$

$$\Delta S°_q = (q - 1)\Delta S° \qquad (21)$$

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