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Received for review December 29, 1986. Accepted June 20, 1987. The authors gratefully acknowledge the Exxon Education Foundation for the financial support of S.W.C.

Practical Osmotic Coefficients and Excess Gibbs Free Energies of Benzene Solutions of Tri-*n*-octylamine and Tri-*n*-octylammonium Bromide at 298.15 K

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The practical osmotic coefficients of benzene solutions of tri-*n*-octylamine up to 6.0 mol kg^{-1}, and tri-*n*-octylammonium bromide up to 1.6 mol kg^{-1}, were measured by the isopiestic technique at 298.15 K. The relations for the concentration dependence of practical osmotic coefficients, solute activity coefficients, and excess Gibbs free energies are given in analytical forms. The nonideality of the systems investigated is discussed on the basis of the structure of the solutions investigated.

Introduction

In connection with a general study of the association of tri-*n*-alkylammonium salts in nonpolar solvents (e.g., ref 1), Klofutar and Paljk (*2*) measured the practical osmotic coefficients of benzene solutions of tri-*n*-octylammonium bromide (TOAHBr) up to 0.3 mol kg^{-1} by the cryoscopic method. Calorimetric measurements (*2*) indicated that the practical osmotic coefficients of benzene solutions of tri-*n*-octylammonium bromide at room temperature should be quite similar to those at the freezing point of benzene.

The aim of the present investigations was to broaden the concentration range of solutions of tri-*n*-octylammonium bromide in benzene to include concentrations where reversal of the association processes of solute molecules may occur (*1*).

Experimental Section

The solvent, reagent grade benzene from the Baker Chemical Co., was stored over molecular sieves (type 4A, Fisher Scientific Co.). Tri-*n*-octylamine (Aldrich Chemical Co.) was distilled and also stored over molecular sieves. The tri-*n*-octylammonium salt was prepared by thoroughly mixing 200 cm^3 of 1 mol dm^{-3} aqueous hydrobromic acid with 200 cm^3 of hexane containing 13 cm^3 of tri-*n*-octylamine. The hexane layer was dried overnight over anhydrous calcium sulfate and the hexane was removed by evaporation. The resulting salt was then recrystallized four times by cooling from a hot saturated hexane solution to the ice point and filtering. The resulting white needles were dried in the dark in a vacuum line until used.

Table I. Molalities of Isopiestic Solutions

m_{DB}/ mol kg^{-1}	m_{TOA}/ mol kg^{-1}	m_{TOA}/ mol kg^{-1}	m_{TOAHBr}/ mol kg^{-1}
0.241	0.250	0.108	0.408
0.523	0.570	0.252	0.680
1.030	1.179	0.395	0.885
1.216	1.401	0.594	1.109
1.751	1.970	0.781	1.273
2.635	2.798	0.875	1.366
2.851	2.994	1.066	1.502
3.586	3.678	1.205	1.595
4.996	4.898		
6.088	5.849		

The isopiestic equilibrations were performed in the same manner as for aqueous solutions (*3*). It was established that equilibrium was reached when the concentration of identical samples were within 0.1% agreement, with one sample losing solvent and the other gaining solvent to attain equilibrium. Dibenzyl (DB) + benzene solutions were used as reference solutions in the case of benzene solutions of tri-*n*-octylamine. To calculate the practical osmotic coefficients of the reference dibenzyl + benzene system at 298.15 K, the relation for the concentration dependence of the practical osmotic coefficient, obtained from the data given in ref *4*, was used in the form

$$\phi_{DB} = 1 + \sum_{i=1}^{2} A_i m_{DB}^{\,i} \qquad (1)$$

where m is the concentration of solute (mol kg^{-1}), and the regression coefficients A_i, calculated by the method of least squares, amount to $A_1 = -0.039$ and $A_2 = 0.0016$, with a standard error of the estimate $s \cong \pm 0.02$.

The practical osmotic coefficents of benzene solutions of tri-*n*-octylamine and tri-*n*-octylammonium bromide, respectively, were calculated from the molality ratio, $R = m_{ref}/m$, and ϕ_{ref} through the relation

$$\phi = \left(\frac{m_{ref}}{m}\right)\phi_{ref} \qquad (2)$$

In calculations of practical osmotic coefficients of benzene solutions of tri-*n*-octylammonium bromide, the values of the

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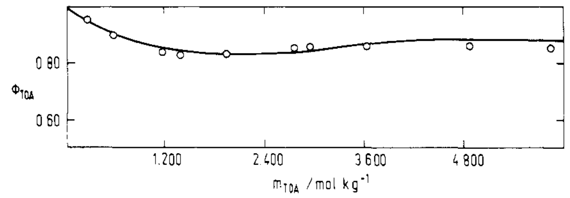

Figure 1. Concentration dependence of osmotic coefficients for benzene solutions of tri-*n*-octylamine at 298.15 K.

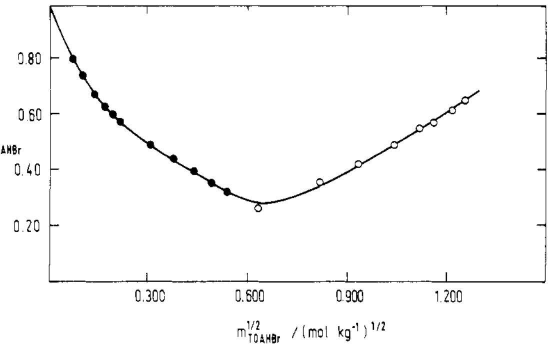

Figure 2. Concentration dependence of osmotic coefficients for benzene solutions of tri-*n*-octylammonium bromide at 298.15 K.

practical osmotic coefficients of the *tri-n*-octylamine + benzene system, obtained from relation 3, were used as reference values.

Results and Discussion

The experimental results of the isopiestic equilibrations for the systems dibenzyl + benzene and tri-*n*-octylamine + benzene, as well as for tri-*n*-octylamine + benzene and tri-*n*-octylammonium bromide + benzene, are presented in Table I.

The relations for the concentration dependence of the practical osmotic coefficients for the systems investigated may be given by polynomials

$$\phi_{\mathrm{TOA}} = 1 + \sum_{i=1}^{3} B_i m_{\mathrm{TOA}}{}^{i} \qquad (3)$$

with values for the regression coefficients of $B_1 = -0.184$, $B_2 = 0.063$, $B_3 = -0.006$, and the standard error of the estimate $s \cong 0.02$, and

$$\phi_{\mathrm{TOAHBr}} = 1 + \sum_{i=1}^{6} C_i m_{\mathrm{TOAHBr}}{}^{i/2} \qquad (4)$$

with values for the regression coefficients of $C_1 = -4.069$, $C_2 = 17.36$, $C_3 = -47{,}10$, $C_4 = 65.58$, $C_5 = -42{,}91$, $C_6 = 10.60$, and $s \cong 0.01$, obtained by the method of least squares.

The practical osmotic coefficients for the systems investigated are given in Figures 1 and 2, respectively. In Figure 2 the practical osmotic coefficients for solute concentrations of $m_{\mathrm{TOAHBr}} < 0.3$ mol kg^{-1} were obtained from reaction 9 in ref *2*. From Figure 2, it can be seen that the isopiestic data merge perfectly with the dilute solution data (*2*).

From Figure 1, it is obvious that the initial deviation from ideal behavior for benzene solutions of tri-*n*-octylamine is negative. The practical osmotic coefficients reach a minimum at $m_{\mathrm{TOA}} \cong 1.4$ mol kg^{-1} and then increase to higher values. This behavior possibly reflects the competition between a weak dipole–dipole association of tri-*n*-octylamine molecules and a solvation process. A more pronounced minimum at $m_{\mathrm{TOAHBr}} \cong 0.4$ mol kg^{-1} can be seen in Figure 2. For such solutions, it was found (1) that the association of simple ion pairs occurs in less concentrated solutions, and (2) that there is a concentration at which the degree of association is a maximum. Toward higher concentrations the association decreases and at the highest concentration such a system may be considered as a fused salt, for which it is known that the ions are unassociated.

The molal activity coefficients, γ, of tri-*n*-octylamine and tri-*n*-octylammonium bromide in the systems investigated were calculated via Bjerrum's equation (*5*)

$$\ln \gamma = (\phi - 1) + \int_0^m \frac{\phi - 1}{m}\,\mathrm{d}m \qquad (5)$$

The concentration dependence of $\ln \gamma_{\mathrm{TOA}}$ can be given by

$$\ln \gamma_{\mathrm{TOA}} = \sum_{i=1}^{3}\left(\frac{i+1}{i}\right) B_i m_{\mathrm{TOA}}{}^{i} \qquad (6)$$

while that of $\ln \gamma_{\mathrm{TOAHBr}}$ as

$$\ln \gamma_{\mathrm{TOAHBr}} = \sum_{i=1}^{6}\left(\frac{i+2}{i}\right) C_i m_{\mathrm{TOAHBr}}{}^{i/2} \qquad (7)$$

using the regression coefficients B_i and C_i, defined by the relations 3 and 4, respectively.

To represent the deviation from ideality of the solution as a whole, the excess Gibbs free energy, G^{ex} (J kg^{-1}) per mole of solute was calculated at 298.15 K from the relation (*6*)

$$\frac{G^{\mathrm{ex}}}{n} = RT(1 - \phi + \ln \gamma) \qquad (8)$$

where n is the number of moles of solute per kilogram of solvent.

For the system tri-*n*-octylamine + benzene the relation

$$\frac{G^{\mathrm{ex}}}{n_{\mathrm{TOA}}} = RT \sum_{i=1}^{3}\left(\frac{1}{i}\right) B_i m_{\mathrm{TOA}}{}^{i} \qquad (9)$$

was obtained from relation 3, 6, and 8, while for the system tri-*n*-octylammonium bromide + benzene the relation

$$\frac{G^{\mathrm{ex}}}{n_{\mathrm{TOAHBr}}} = RT \sum_{i=1}^{6}\left(\frac{2}{i}\right) C_i m_{\mathrm{TOAHBr}}{}^{i/2} \qquad (10)$$

results from relations 4, 7, and 8.

The calculated values of excess Gibbs free energy for the tri-*n*-octylamine + benzene system (relation 9) and for the tri-*n*-octylammonium bromide + benzene system (relation 10) are negative and decrease with increasing solute concentration. However, the deviation from ideal behavior for the investigated systems is in the case of tri-*n*-octylammonium bromide much more evident than in the case of tri-*n*-octylamine. Thus, for example, the value of $G^{\mathrm{ex}}/n_{\mathrm{TOA}}$ at the highest concentration studied, $m_{\mathrm{TOA}} = 6.0$ mol kg^{-1}, amounts to -997 J mol^{-1}, while the value of $G^{\mathrm{ex}}/n_{\mathrm{TOAHBr}}$ amounts to -8009 J mol^{-1} at $m_{\mathrm{TOA}}\mathrm{H}_{\mathrm{Br}} = 1.6$ mol kg^{-1}. The observed nonideality of the systems investigated may be mainly considered to be a consequence of association processes of solute molecules due to dipole–dipole interactions, which are far more intense in the case of tri-*n*-octylammonium bromide than in the case of tri-*n*-octylamine.

Registry No. Tri-*n*-octylamine, 1116-76-3; tri-*n*-octylammonium bromide, 4221-96-9; benzene, 71-43-2.

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Received for review January 14, 1987. Accepted May 8, 1987. We thank the National Science Foundation, Washington, DC, and the Slovene Research Community, Ljubljana, for financial support for this work.