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HEATS OF SOLUTION OF CYCLOHEXANOL IN BENZENE SOLUTIONS OF TRI-n-OCTYLAMMONIUM BROMIDE AND DERIVED THERMODYNAMIC FUNCTIONS OF TRANSFER FROM BENZENE

ŠPELA PALJK and CVETO KLOFUTAR

Jožef Stefan Institute, E. Kardelj University, 61000 Ljubljana, Jamova 39 (Yugoslavia)

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ABSTRACT

The integral heats of solution of cyclohexanol (up to 0.10 mol kg^{-1}) in benzene solutions of tri-n-octylammonium bromide (up to 0.25 mol kg^{-1}) were measured at 298.15 K. It was found that the partial molar enthalpy of solution of cyclohexanol is concentration independent at a definite concentration of tri-n-octylammonium bromide. The heat of solution was interpreted by the McMillan–Mayer theory and the enthalpic interaction coefficients were calculated. The standard thermodynamic functions of transfer of cyclohexanol from benzene to benzene solutions of tri-n-octylammonium bromide were calculated at 298.15 K. The standard enthalpy of transfer for cyclohexanol is almost compensated by the standard entropy of transfer in calculation of the Gibb's free energy of transfer. The cross pair interaction coefficient was ascribed to complex formation between the hydroxylic proton of cyclohexanol and the bromide ion of tri-n-octylammonium bromide via hydrogen bonding.

INTRODUCTION

In the past we have investigated some physicochemical properties of binary benzene solutions of either tri-n-alkylammonium halides [1–3] or of cyclohexanol [4,5] in order to describe the non-ideal behaviour of these systems by solute–solute and solute–solvent interactions. Furthermore, we have studied the colligative properties of the ternary system benzene + tri-n-octylammonium bromide + cyclohexanol [6] with the aim of elucidating the effects of complex formation between the hydroxylic proton of the alcohol molecule and the bromide ion of the tri-n-octylammonium bromide ion pair on the Gibbs free energy data.

Since great interest in this field has been focussed on the thermodynamic interaction coefficients, mainly in dilute mixtures of highly polar solvents [7] we have found it instructive to apply the McMillan–Mayer theory [8] to the thermochemical data of the above ternary system, where the solvent is non-polar. The enthalpic cross pair interaction coefficient obtained for the complex is discussed relative to the enthalpic pair interaction coefficients for tri-n-octylammonium bromide and cyclohexanol. In addition, the standard thermodynamic functions of transfer of cyclohexanol from benzene to benzene solutions of tri-n-octylammonium bromide have been determined.

EXPERIMENTAL

Benzene (Riedel de Häen) was purified as detailed in ref. 1. Tri-n-octylammonium bromide (TOAHBr) was prepared as in ref. 1, and cyclohexanol (ROH) (Riedel de Häen) was purified as in ref. 4. Calorimetric measurements were performed as described in ref. 5.

RESULTS AND DISCUSSION

The values of the integral heat of solution, $\Delta_{sol}H_{3,int}$ (J), of ROH in benzene solutions of various concentrations of TOAHBr (m_2 up to 0.250 mol kg^{-1}) and at 298.15 K are given in Table 1. In Fig. 1 these values, together with the values of the integral heat of solution of ROH in pure benzene [5], are presented as a function of the number of moles of ROH, n_3.

TABLE 1

Enthalpies of solution of cyclohexanol in 100 ml of benzene solutions of tri-n-octylammonium bromide at 298.15 K

m_2 (mol kg^{-1})	n_3 (mol)	m_3 (mol kg^{-1})	$\Delta_{sol}H_{3,int}$ (J)
0.059	0.0077	0.090	93.0
	0.0058	0.068	69.4
	0.0040	0.046	47.6
	0.0017	0.020	21.8
	0.0010	0.011	12.4
0.120	0.0075	0.090	78.7
	0.0056	0.067	57.7
	0.0038	0.046	40.6
	0.0017	0.020	18.0
	0.0010	0.012	11.4
0.184	0.0076	0.094	71.4
	0.0056	0.068	52.5
	0.0037	0.045	35.1
	0.0018	0.022	17.3
	0.0012	0.015	11.6
0.251	0.0075	0.095	64.0
	0.0047	0.058	39.8
	0.0037	0.047	31.6
	0.0018	0.022	15.1
	0.0009	0.012	8.1

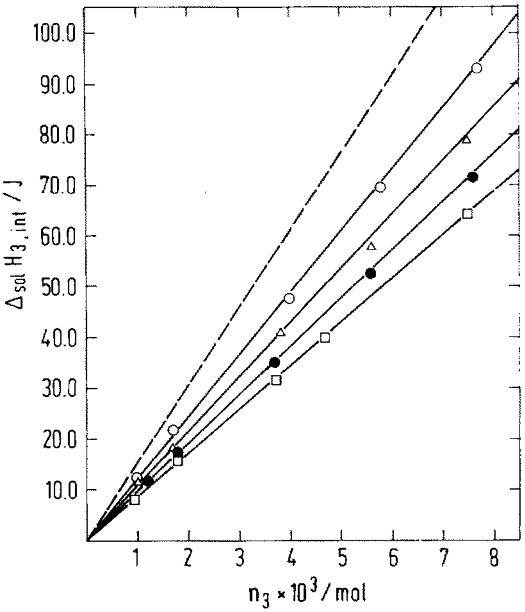

Fig. 1. Enthalpies of solution of cyclohexanol in 100 ml of benzene solutions of tri-n-octylammonium bromide and in pure benzene at 298.15 K; $m_2 = 0.059$ mol kg^{-1} (○), $m_2 = 0.120$ mol kg^{-1} (△), $m_2 = 0.184$ mol kg^{-1} (●), $m_2 = 0.251$ mol kg^{-1} (□), pure benzene (— — —) [5].

From Table 1 and Fig. 1 it can be seen that at a definite quantity of ROH the enthalpy change is smaller the higher the concentration of TOAHBr. The integral heats of solution in the system may be attributed mainly to the dissociation of associated alcohol molecules [4,5], and to the formation of molecular complexes through hydrogen bonding [9] between the hydroxylic proton of ROH and the bromide ion of either a simple TOAHBr ion pair or of the bromide ion of a higher oligomeric species of TOAHBr. From these results it can be concluded that the former process is endothermic while the latter is exothermic. For the ternary system investigated, the dependence of $\Delta_{sol}H_{3,int}$ vs. n_3 is linear and is given by $\Delta_{sol}H_{3,int}$ (J) $= (12234 \pm 171)n_3$ at $m_2 = 0.059$ mol kg^{-1}, $\Delta_{sol}H_{3,int}$ (J) $= (10694 \pm 187)n_3$ at $m_2 = 0.120$ mol kg^{-1}, $\Delta_{sol}H_{3,int}$ (J) $= (9507 \pm 58)n_3$ at $m_2 = 0.184$ mol kg^{-1} and $\Delta_{sol}H_{3,int}$ (J) $= (8586 \pm 107)n_3$ at $m_2 = 0.251$ mol kg^{-1}. From these linear dependencies it follows that the values of partial molar enthalpy of solution, $\Delta_{sol}\overline{H}_{3,int}$ (J mol^{-1}), of ROH at a definite TOAHBr concentration are independent of ROH concentration and equal to the values at infinite dilution, $\Delta_{sol}\overline{H}^{\infty}_{3,int}$ (J mol^{-1}).

To obtain some information about the intermolecular interactions between the two solutes, TOAHBr and ROH, the enthalpic interaction coefficients were determined. According to the McMillan–Mayer theory for the binary benzene + TOAHBr mixture the total enthalpy, $H(m_2)$ (J) per kg of solvent, can be given by [7]

$$H(m_2) = H_B^{\cdot} + \overline{H}_2^{\infty} m_2 + h_{22} m_2^2 + h_{222} m_2^3 + \ldots \tag{1}$$

where $H_B^{\cdot}$ is the enthalpy of 1 kg of pure benzene, $\overline{H}_2^{\infty}$ is the standard partial molar enthalpy of TOAHBr, and h_{22}, h_{222} etc. are the virial coefficients which characterize pair, triplet and higher interactions among ion pairs of TOAHBr. On the other hand, for the ternary benzene + TOAHBr + ROH system, analogously, the total enthalpy, $H(m_2, m_3)$ (J) per kg of benzene can be given by [7]

$$\begin{aligned} H(m_2, m_3) = {} & H_B^{\cdot} + \overline{H}_2^{\infty} m_2 + \overline{H}_3^{\infty} m_3 + h_{22} m_2^2 + 2h_{23} m_2 m_3 + h_{33} m_3^2 \\ & + h_{222} m_2^3 + 3h_{223} m_2^2 m_3 + 3h_{233} m_2 m_3^2 + \ldots \end{aligned} \tag{2}$$

where $\overline{H}_3^{\infty}$ is the standard partial molar enthalpy of ROH, and the virial coefficients characterize the interactions among like and unlike solute molecules. According to this theory, all coefficients may also include possible changes in the interactions between the TOAHBr ion pairs or ROH molecules with benzene molecules. The enthalpy change of solution per mole of ROH, $\Delta_{\text{sol}} \overline{H}_{3,\text{int}}$ (J mol^{-1}), in benzene solution of a definite concentration of TOAHBr, as the concentration of ROH $m_3 \to 0$, can be given by

$$\Delta_{\text{sol}} \overline{H}_{3,\text{int}}^{\infty} = \overline{H}_3^{\infty} - \overline{H}_3^{\cdot} + 2h_{23} m_2 + 3h_{223} m_2^2 + 4h_{2223} m_2^3 + \ldots \tag{3}$$

where $\overline{H}_3^{\infty} - \overline{H}_3^{\cdot} = -L_3^{\cdot}$; $L_3^{\cdot}$ is the relative molar enthalpy of pure ROH [5]. Values of the coefficients $2h_{23} = -82490$, $3h_{223} = 394715$ and $4h_{2223} = -733775$ were obtained through relation (3), by the method of least squares analysis, using a $-L_3^{\cdot}$ value of 16035 J mol^{-1} [5]. The standard error of the estimate amounts to $s = 240$ J mol^{-1}.

In addition, the enthalpic interaction coefficients for binary benzene + tri-n-octylammonium bromide mixtures, as well as for benzene + cyclohexanol mixtures, were calculated from their thermochemical data [1,5] respectively. The values of excess enthalpy, H^{ex} (J kg^{-1}) as a function of concentration were used in the form

$$H^{\text{ex}}(m_i) = h_{ii} m_i^2 + h_{iii} m_i^3 \tag{4}$$

index $i = 2$ for TOAHBr and 3 for ROH.

In the case of TOAHBr, the values of the enthalpic interaction coefficients, obtained via relation (4) by the method of least squares analysis, amount to $h_{22} = -69465$ J mol^{-2} kg and $h_{222} = 157500$ J mol^{-3} kg^2, while in the case of ROH, coefficients h_{33} and h_{333} are related to coefficients B and C of relation (22) [5], respectively, i.e. $h_{33} = -10220$ J mol^{-2} kg and $h_{333} = 3390$ J mol^{-3} kg^2.

The cross-interaction coefficient h_{23} for the system investigated, calculated from the following relation [10]

$$h_{23} = \tfrac{1}{2}(h_{22} + h_{33}) \tag{5}$$

amounts to -39840 J mol^{-2} kg and is close to the value obtained from the solution experiments in the ternary system investigated. It is interesting to note that relation (5) was proposed for the presentation of intermolecular forces among unlike, non-polar, and spherical molecules [11]. However, in the present case, the tri-n-octylammonium bromide ion pair possesses an extremely high dipole moment [3].

It is evident that the values of h_{22}, h_{23} and h_{33} are negative and far lower than the values of the corresponding coefficients for some solutes in aqueous [12] and other polar media [7]. From the values of the enthalpic pair interaction coefficients obtained it may be presumed that the interactions between tri-n-octylammonium bromide ion pairs are stronger than those between the tri-n-octylammonium bromide ion pair and the cyclohexanol molecule, which are stronger than those between cyclohexanol molecules. This may be explained by the following arguments. It is well known that in a non-polar solvent, such as benzene, TOAHBr ion pairs strongly interact with each other with dipole–dipole interactions, producing dimeric and higher oligomeric species and that the solute–solvent interactions in this system are negligible. Thus, the structure of such a solution is rather complex [1]. On the other hand, the molecules of ROH are bonded via hydrogen bonds between hydroxylic groups of alcohol molecules. Thereby, the degree of aggregation of alcohol molecules in benzene solutions is depressed due to the interactions of π-electrons of the aromatic ring of the benzene molecule with the hydroxylic group of the alcohol molecule [4,5]. Furthermore, it may be concluded that the hydrogen bond between the hydroxylic group and a bromide ion, which in non-polar solvents is a strong Lewis base [13], is stronger than the intramolecular hydrogen bond between alcohol molecules. In addition infrared [13] and permittivity data [9] suggest that only one molecule of alcohol is bonded to the halide ion of tertiary or quaternary alkylammonium halides in non-polar solvents. In addition, complex formation between alkylammonium salts and alcohol molecules does not change the degree of association of salt molecules, which may be confirmed from the concentration dependence of the practical osmotic coefficients of the ternary systems investigated [6].

In addition, the enthalpy of isothermal transfer of ROH, $\Delta H_{3,\mathrm{tr}}$ (J), at 298.15 K from benzene at a definite concentration of ROH to a benzene + TOAHBr mixture of the same concentration of ROH

$$\text{ROH (benzene)} = \text{ROH (benzene + TOAHBr)} \tag{6}$$

is related to the excess enthalpies for ternary and corresponding binary systems through the following equation

$$\Delta H_{3,\mathrm{tr}} = H^{\mathrm{ex}}(m_2, m_3) - H^{\mathrm{ex}}(m_2) - H^{\mathrm{ex}}(m_3) \tag{7}$$

where $H^{\mathrm{ex}}(m_2, m_3)$ (J) is the excess enthalpy of the ternary system, which

TABLE 2

The partial thermodynamic functions of transfer of ROH for process (6) at infinite dilution and 298.15 K

m_2 (mol kg^{-1})	$-\Delta\overline{H}^{\infty}_{3,\mathrm{tr}}$ (J mol^{-1})	$\Delta\overline{G}^{\infty}_{3,\mathrm{tr}}$ (J mol^{-1})	$-T\Delta\overline{S}^{\infty}_{3,\mathrm{tr}}$ (J mol^{-1})
0.059	3801	206	4007
0.120	5341	−15	5326
0.184	6528	−321	6207
0.251	7449	−638	6811

for non-electrolyte solutions per kg of solvent can be given by [14]

$$H^{\mathrm{ex}}(m_2, m_3) = \sum_{i=1}^{n}\sum_{j=1}^{n} h_{ij}m_im_j + \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} h_{ijk}m_im_jm_k + \ldots \tag{8}$$

The coefficients h_{ij} and h_{ijk} of relation (8) are the respective enthalpic interaction coefficients. Thus, from relation (7), the standard partial molar enthalpy of transfer of ROH as $m_3 \to 0$, $\Delta\overline{H}^{\infty}_{3,\mathrm{tr}}$ (J mol^{-1}), is given by

$$\Delta\overline{H}^{\infty}_{3,\mathrm{tr}} = 2h_{23}m_2 + 3h_{223}m_2^2 + 4h_{2223}m_2^3 + \ldots \tag{9}$$

The values of $\Delta\overline{H}^{\infty}_{3,\mathrm{tr}}$, given in Table 2, calculated from

$$\Delta\overline{H}^{\infty}_{3,\mathrm{tr}} = \Delta_{\mathrm{sol}}\overline{H}^{\infty}_{3,\mathrm{int}} + L_3^{\bullet} \tag{10}$$

are within experimental error, equal to those obtained via relation (9), in which the determined values of enthalpic interaction coefficients were used.

To determine the standard partial molar free energy of transfer of ROH as $m_3 \to 0$, $\Delta\overline{G}^{\infty}_{3,\mathrm{tr}}$ (J mol^{-1}), for process (6), the relation [15]

$$\Delta\overline{G}^{\infty}_{3,\mathrm{tr}} = RT \ln \gamma_3^{\infty} \tag{11}$$

was used. The values of $\ln \gamma_3^{\infty}$ at 298.15 K were calculated from the corresponding values at the freezing point of benzene [6] via relation

$$\frac{\mathrm{d} \ln \gamma_3^{\infty}}{\mathrm{d}T} = -\frac{\Delta\overline{H}^{\infty}_{3,\mathrm{tr}}}{RT^2} \tag{12}$$

assuming $\Delta\overline{H}^{\infty}_{3,\mathrm{tr}}$ values to be constant in the temperature range studied. The values of $\Delta\overline{G}^{\infty}_{3,\mathrm{tr}}$ obtained, with the values of standard partial molar entropy of transfer of ROH, $\Delta\overline{S}_{3,\mathrm{tr}}$ (J mol^{-1} K^{-1}), calculated through relation

$$\Delta\overline{S}^{\infty}_{3,\mathrm{tr}} = \frac{\Delta\overline{H}^{\infty}_{3,\mathrm{tr}} - \Delta\overline{G}^{\infty}_{3,\mathrm{tr}}}{T} \tag{13}$$

are compiled in Table 2.

The values of the standard partial thermodynamic functions of transfer of ROH for process (6), except the $\Delta\overline{G}^{\infty}_{3,\mathrm{tr}}$ value at the smallest concentration of TOAHBr, are negative and show a tendency to decrease with increasing concentration of TOAHBr. Furthermore, the $\Delta\overline{H}^{\infty}_{3,\mathrm{tr}}$ values are close to the $T\Delta\overline{S}^{\infty}_{3,\mathrm{tr}}$ values.

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