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ENTHALPIES OF MIXING OF BINARY MIXTURES: TRIALKYL PHOSPHATES, DIALKYL KETONES AND DIALKYL ETHERS WITH CHLOROFORM

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ABSTRACT

Partial molar enthalpies of mixing at infinite dilution at 298.15 K and atmospheric pressure are reported for mixtures of four tri-*n*-alkyl phosphates (trimethyl, triethyl, tri-*n*-propyl and tri-*n*-butyl phosphates), four di-*n*-alkyl ketones (dimethyl, diethyl, di-*n*-propyl and di-*n*-butyl ketones) and four di-*n*-alkyl ethers (diethyl, di-*n*-propyl, di-*n*-butyl and di-*n*-amyl ethers) with chloroform. The electron donor ability of a series of phosphates, ketones and ethers in hydrogen bonding formation are studied using the solvent polarity factor, E_T. The accepted model offers a possibility for obtaining the molar enthalpy of complex formation from the partial molar enthalpy of mixing at infinite dilution.

INTRODUCTION

Complex formation in binary liquid systems has been investigated by various spectroscopic methods and also by such classical thermodynamic methods as distribution between immiscible solvents, measurement of colligative properties, and calorimetry. As a result we have a lot of reliable equilibrium constants and enthalpies of complex formation in dilute solution.

In this paper we apply some of the calorimetric methods for investigation of complex formation in binary mixtures of chloroform with tri-*n*-alkyl phosphates, di-*n*-alkyl ketones and di-*n*-alkyl ethers. We have measured the partial molar excess enthalpies at infinite dilution and used thermodynamic equations derived by Matsui et al. [1] for evaluation of enthalpies of complex formation. The excess enthalpies are negative for all the three types of mixtures. These negative excess enthalpies are ascribed to a strong hydrogen bond interaction between triphosphates, diketones and diethers with chloroform.

EXPERIMENTAL

A calorimeter used for measurements of partial molar excess enthalpies at infinite dilution and the experimental procedure have been described elsewhere [2]. The calorimeter is capable of measuring positive and negative molar enthalpies at infinite dilution of liquid mixtures. The partial molar enthalpies at infinite dilution, $H_1^{E,\infty}$, for x_1 between 2×10^{-4} and 8×10^{-4}, for all systems were averaged, over eight determinations, and the standard deviations were calculated using the same form as that already explained.

The working of the calorimeter was checked by measuring the partial molar enthalpies of mixing of benzene + tetrachloromethane at 298.15 K. The enthalpy of mixing of these systems agreed within 2% with the accepted literature values [3]. The solvate samples were introduced into the solvent by a Hamilton syringe.

The densities, necessary for calculating the molar concentration, were measured by a Digitale Dichtemeseinrichtung densitometer (Anton Paar, Graz, Austria) equipped with a Lauda Ultrathermostat and Lauda R52 electronic temperature-regulation system.

The phosphates used: trimethyl (TMP), triethyl (TEP), tri-*n*-propyl (TPP) and tri-*n*-butyl (TBP) were obtained from Merck (reagent grade).

The ketones used: dimethyl (DMK), diethyl (DEK), di-*n*-propyl (DPK) and di-*n*-butyl (DBK) were obtained from Fluka (puriss). All reagents were fractionally distilled under reduced pressure. The middle fractions were kept in a bottle over dried zeolite 4A.

The ethers used: diethyl (DEE), di-*n*-propyl (DPE), di-*n*-butyl (DBE) and di-*n*-amyl (DAmE) were obtained from BDH (reagent grade). All reagents were passed over activated alumina to remove small amounts of peroxide and then distilled under reduced pressure and kept over dried zeolite 4A.

Chloroform (Merck) was washed several times with distilled water and dried over P_2O_5. The purity of the components was checked by gas chromatography and density measurements. The purity was estimated to be 99.8 mole% or better. All measurements were carried out at 298.15 K.

RESULTS AND DISCUSSION

The partial molar enthalpies of mixing at infinite dilution for binary systems: tri-*n*-alkyl phosphates, di-*n*-alkyl ketones, and di-*n*-alkyl ethers with chloroform, all at 298.15 K, together with the reported literature values, are summarized in Table 1. These limiting partial molar enthalpies of mixing may be obtained almost directly from "small increment" solution calorimetry or from "integral" enthalpies of mixing such as those usually represented by ΔH_m.

Since our results are expressed as partial molar enthalpies at infinite dilution, it was necessary to derive the partial derivative of the literature ΔH_m values with respect to the mole fraction of solute x_1 at a constant mole fraction of solvent x_2 in the limit as $x_1 \to 0$. It is readily shown that

$$\lim_{x_1 \to 0} (\partial \Delta H_m / \partial x_1)_{x_2} = \Sigma_i C_i \qquad (1)$$

TABLE 1

Partial molar excess enthalpies of mixing of different solutes at infinite dilution

Solute	$-H_1^{E,\infty}$ (kJ mole^{-1})		Solute	$-H_1^{E,\infty}$ (kJ mole^{-1})		Solute	$-H_1^{E,\infty}$ (kJ mole^{-1})	
	This work	Literature		This work	Literature		This work	Literature[d]
TMP	15.61 ± 0.38		DMK	8.74 ± 0.04	8.33[a] 8.70[b]	DEE	8.91 ± 0.64	8.80
TEP	20.79 ± 0.99		DEK	9.16 ± 0.25		DPE	7.61 ± 0.25	7.87
TPP	23.14 ± 0.79		DPK	9.37 ± 0.37		DBE	5.52 ± 0.17	5.61
TBP	26.15 ± 1.17		DBK	9.96 ± 0.40		DAmE	4.19 ± 0.04	2.91
Solute	$-H_2^{E,\infty}$ (kJ mole^{-1})		Solute	$-H_2^{E,\infty}$ (kJ mole^{-1})		Solute	$-H_2^{E,\infty}$ (kJ mole^{-1})	
	This work	Literature		This work	Literature		This work	Literature
Chloroform (in TBP)	12.22 ± 0.58		Chloroform (in DMK)	4.97 ± 0.17	5.06[a] 4.98[c]	Chloroform (in DEE)	7.82 ± 1.34	7.28[e]

[a] Partial molar enthalpies of mixing at infinite dilution [1].

[b] Based on calorimetric ΔH_m values [4]; extrapolated at infinite dilution from eqn. (1).

[c] Based on calorimetric ΔH_m values [4]; extrapolated at infinite dilution from eqn. (2).

[d] Based on calorimetric ΔH_m values [5]; extrapolated at infinite dilution from eqn. (1).

[e] Based on calorimetric ΔH_m values [5]; extrapolated at infinite dilution from eqn. (2).

If the solute–solvent subscript assignment is reversed, the expression

$$\lim_{x_2 \to 0}\left(\frac{\partial \Delta H_m}{\partial x_2}\right)_{x_1} = \Sigma_i(-1)^i C_i \tag{2}$$

should be used. C_i are the constants tabulated for each pair of liquids reported in literature for the ΔH_m data which were correlated by the Redlich–Kister polynomal. Matsui et al. [1] concluded that the calculation of partial molar enthalpies of mixing from integral molar enthalpies of mixing (ΔH_m) has considerable greater uncertainties than do the values based on measurements with very dilute solutions. In spite of that, Table 1 shows that there is a reasonable agreement between our results and the published data.

For all systems studied in this work it is remarked that $H_1^{E,\infty}$ is negative as a consequence of hydrogen bonding formation in solutions. For the systems TAP + chloroform and DAK + chloroform, the negative enthalpies of mixing increase with increase of the carbon atom number in the alkyl chain of phosphate or ketone; for DAE + chloroform the opposite effect is observed. In these mixtures the donor property of the phosphoryl oxygen is apparently significantly larger than that of the ketone oxygen and etheric oxygen; the partial molar excess enthalpies of mixing have the values −20.79, −9.16 and −8.9 kJ mole^{-1} for triethyl phosphate, diethyl ketone and diethyl ether, respectively.

The donor strengths of the phosphates, ketones or ethers with side chain methyl groups on the α carbon atom will depend on the inductive effect which would tend to strengthen the oxygen as a donor, and steric effect which would tend to weaken it. It appears that in TAP + chloroform and DAK + chloroform the inductive effect predominates whereas in DAE + chloroform, the steric effect predominates.

TABLE 2

Empirical parameters of solvent polarity [13a]

Solvent	E_T (298.15 K) (kJ mole^{-1})
Trimethyl phosphate (TMP)	182.4
Triethyl phosphate (TEP)	174.5
Tri-*n*-propyl phosphate (TPP)	169.4
Tri-*n*-butyl phosphate (TBP)	165.7
Dimethyl ketone (DMK)	176.6
Diethyl ketone (DEK)	166.1
Di-*n*-propyl ketone (DPK)	162.8
Di-*n*-butyl ketone (DBK)	156.9
Diethyl ether (DEE)	144.8 [13b]
Di-*n*-propyl ether (DPE)	142.2 [13b]
Di-*n*-butyl ether (DBE)	139.7 [13b]
Di-*n*-amyl ether (DAmE)	137.2 [13b]
Chloroform	163.6

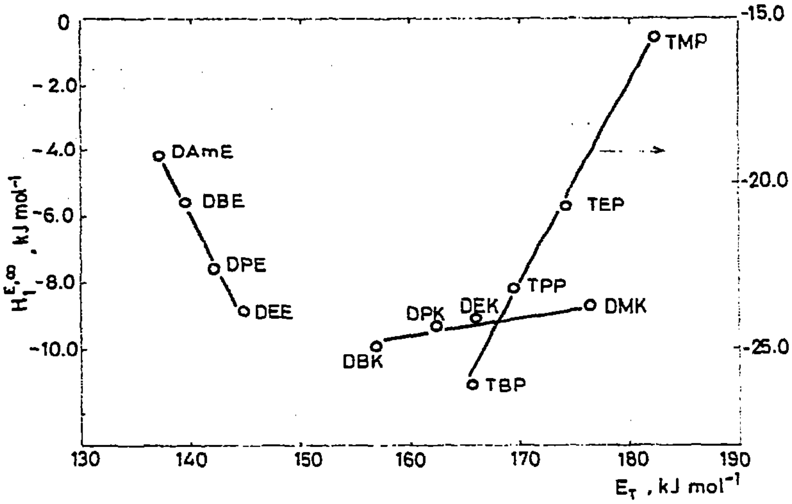

Fig. 1. Dependence of partial molar excess enthalpy at infinite dilution, $H_1^{E,\infty}$, on empirical parameter of solute polarity, E_T (chloroform as solvent).

This effect can be considered in the light of the empirical polarity factor, E_T, of the pure solute [13a] (Table 2). This factor is defined as a solvent polarity parameter based on the solvent dependent electronic $\bar{u} \rightarrow \bar{u}^*$ transition for n-phenolpyridinium betaines. Table 2 shows that E_T values decrease with increasing number of methylene groups in the chain.

Figure 1 illustrates the existence of the linearity between the partial molar excess enthalpy at infinite dilution and the E_T value of solute. The values of the regression coefficients for the linear fit of the plot, for phosphates, ketones and ethers are 0.9967, 0.9668 and 0.9946, respectively.

Matsui et al. [1] have shown that it is possible to analyze the partial molar enthalpies of mixing for binary mixtures in terms of the equilibrium constant (K) and the molar enthalpy of reaction (ΔH^0) for the complex formation represented by

$$\mathrm{A} + \mathrm{B} \overset{K_1}{\rightleftharpoons} \mathrm{AB} \qquad (3)$$

and for the reaction represented by

$$\mathrm{A} + 2\,\mathrm{B} \overset{K_2}{\rightleftharpoons} \mathrm{AB_2} \qquad (4)$$

Taking A + B to be an "ideal associated solution" in which all enthalpy changes are due to the reaction represented by eqn. (3), the following relation is valid

$$\Delta H_1^0 = H_1^{E,\infty}(1 + K_1)/K_1 \qquad (5)$$

and for the system in which reaction may be represented by eqn. (4) it is

$$\Delta H_2^0 = \left[H_1^{E,\infty}(1 + K_1 + K_2)/K_2\right] - \left[H_2^{E,\infty}(K_1 + 1)/K_2\right] \qquad (6)$$

In our recent papers [6,9,11] we reported the determination of equilibrium constants with noncalorimetric methods for the systems TAP + chloroform and DAK + chloroform. These equilibrium constants are presented in Table 3 together

TABLE 3

Equilibrium constants and molar enthalpies of complex formation for different solutes with chloroform

Solute	K (l mole^{-1})	$-\Delta H_1^0$ (kJ mole^{-1})
TMP		
TEP	4.6 [6]	25.3
TPP	5.4 [7]	27.4
	5.2 [6]	27.6
TBP	8.7 [6]	29.1
	5.9 [6]	30.6
	6.1 [8]	30.4
	5.4 [9]	31.0
DMK	$K_1 = 0.967$ [10]	10.1
	$K_2 = 1.117$ [10]	15.4 ($-\Delta H_2^0$)
DEK	0.727 [11] [a]	21.7
DPK	0.765 [11] [a]	21.6
DBK	0.812 [11] [a]	22.2
DEE	1.4 [12]	15.3
DPE	1.0 [12]	15.2
DBE	0.7 [12]	13.4
DAmE	0.6 [12]	11.2

[a] Measured at 293.15 K.

with those reported by other authors for all investigated systems. For the system DMK plus chloroform we take K_1 and K_2 from analysis of vapour pressure by Kearns [10], who shows that, as well as the 1:1 complex AB normally postulated between a DMK molecule A and a chloroform molecule B, 1:2 complexes of the form AB_2 also occur.

Table 3 includes results of our evaluation of ΔH^0 using eqns. (5) and (6), K values (Table 3) and the values of partial molar enthalpies of mixing (Table 1).

REFERENCES

1 T. Matsui, L.G. Hepler and D.V. Fenby, J. Phys. Chem., 77 (1973) 2397.

2 S.K. Milonich, M.M. Kopechni and R.A. Džerki, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 21 (1978) 114.

3 T.J. Findlay and P.J. Kavanach, J. Chem. Thermodyn., 6 (1974) 361.

4 A.N. Campbell and E.M. Kartzmark, Can. J. Chem., 38 (1960) 652.

5 L.A. Beath and A.G. Williamson, J. Chem. Thermodyn., 1 (1969) 51.

6 Dj.M. Petković and Z.B. Maksimović, J. Inorg. Nucl. Chem., 38 (1976) 297.

7 D. Dyrssen and Dj.M. Petković, J. Inorg. Nucl. Chem., 27 (1965) 1381.

8 Dj.M. Petković and B.A. Kezele, Proc. Int. Solv. Extr. Conf., The Hague, The Netherlands, 1971, p. 1137.

9 M.M. Kopečni, Z.E. Ilić and S.K. Milonjić, J. Chromatogr. Sci., 17 (1979) 253.

10 E.R. Kearns, J. Phys. Chem., 65 (1961) 314.

11 Z.B. Maksimović, A. Mikša-Spirić and S.V. Ribnikar, J. Inorg. Nucl. Chem., 35 (1973) 1239.

12 N.F. Pasco, D.V. Fenby and L.G. Hepler, Can. J. Chem., 52 (1974) 2139.

13 a. Z.B. Maksimović, C. Reichard and A. Spirić, Z. Anal. Chem., 270 (1974) 100.
b. A. Mikša-Spirić, M.Sc. Thesis, University of Belgrade, 1974.