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Note

HEATS OF MIXING OF BINARY MIXTURES OF 1,1,2,2-TETRACHLOROETHANE WITH 1-ALCOHOLS

N.V. CHOUDARY and P.R. NAIDU

Department of Chemistry, Sri Venkateswara University, Tirupati 517502 (India)

D.D. DESHPANDE

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076 (India)

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In our systematic investigation of the excess thermodynamic properties of mixtures of the type chloroalkane + 1-alcohol, we have previously reported excess volumes V^E and isentropic compressibilities K_s for 1,2-dichloroethane + 1-alcohol (C_3–C_8) [1,2] and 1,1,2,2-tetrachloroethane + 1-alcohol (C_3–C_8) [3,4]. We observed positive excess volumes and isentropic compressibilities for the binary mixtures containing 1,2-dichloroethane as the common component. Excess volumes and isentropic compressibilities for the mixtures of 1,1,2,2-tetrachloroethane with alcohol showed an inversion in sign. Moreover we found that the mixtures of 1,2-dichloroethane and six alcohols result in more positive excess volumes than the corresponding mixtures with 1,1,2,2-tetrachloroethane as common component. This is explained in terms of two opposing contributions, i.e. (i) expansion in volume due to depolymerization of alcohol aggregates and (ii) contraction in volume due to interstitial accommodation of chloroalkane in the aggregates of alcohols and weak hydrogen bond interactions of the type Cl- - -H–O between unlike molecules. To study this behaviour further, we have measured excess enthalpies of 1,1,2,2-tetrachloroethane + 1-alcohol. The present paper reports H^E for four systems: 1,1,2,2-tetrachloroethane + 1-butanol, + 1-pentanol, + 1-hexanol and + 1-heptanol.

EXPERIMENTAL

All the materials were purified by the methods described in an earlier communication [2]. The purity of the samples was checked by comparing the

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Correspondence should be addressed to Prof. P.R. Naidu, Department of Chemistry, College of Engineering, Sri Venkateswara University, Tirupati 517 502, India.

measured densities of the compounds with those reported in the literature [5]. Densities were determined by using a bicapillary type pycnometer which was accurate of 2 parts in 10^5.

Heats of mixing were determined using a Tian Calvet monocell conduction calorimeter constructed by Deshpande and Prabhu [6]. The details of its working principle are described elsewhere [7]. The calorimeter consists of a pyrex glass cell, cylindrical in shape, which slides into an aluminium cylindrical cavity. The outer surface of the cavity is symmetrically surrounded by 160 thermojunctions made of copper and constantan. A heavy cylindrical block of brass, fixed at the bottom, acts as a sink for the heat flow. The top portion of the sink is provided with a circular opening for the introduction of the experimental cell. The assembly is fitted into an adiabatic flask which can be rotated around a horizontal axle to mix the two components. Heat evolved in the experimental cell is conducted away to a comparatively large surrounding heat sink or, in an endothermic process, heat will flow from the heat sink to the reaction vessel. The arrangement is such that essentially all heat exchange between the reaction vessel and the heat sink takes place through a thermopile, and heat evolved will be proportional to the voltage–time integral curve. The thermopile output can be amplified electrically and recorded.

The experimental pyrex glass cell consists of two unequal compartments separated by a plug with a small quantity of mercury over it. The capacity of the cell is approximately 25 ml. This volume can be varied by introducing mercury or glass rods in the cell. We believe the accuracy to be ± 1.5% for most of the systems.

RESULTS

The experimental excess enthalpies for the four binary mixtures at 303.15 K are given in Table 1 and are also graphically represented in Fig. 1. The dependence of H^E on composition may be expressed by an empirical equation of the form

$$H^E(\text{J mol}^{-1}) = x(1-x)\left[C_0 + C_1(2x-1) + C_2(2x-1)^2\right] \qquad (1)$$

where C_0, C_1 and C_2 are adjustable parameters and x is the mole fraction of 1,1,2,2-tetrachloroethane. The values of the parameters obtained by the least squares method are included in Table 2, along with the standard deviation $\sigma(H^E)$. The values of $\sigma(H^E)$ were obtained using the equation

$$\sigma H^E = \left[\frac{\Sigma\left(H^E_{\text{calc.}} - H^E_{\text{expt.}}\right)^2}{n-P}\right]^{1/2} \qquad (2)$$

TABLE 1

Excess enthalpies H^E (J mol^{-1}) of 1,1,2,2-tetrachloroethane with 1-alcohols at 303.15 K

x_1	H^E	x_1	H^E
1,1,2,2-tetrachloroethane (1)+1-butanol (2)		1,1,2,2-tetrachloroethane (1)+1-pentanol (2)	
0.08727	−148.3	0.05787	−84.2
0.23973	49.8	0.21852	133.0
0.38804	524.5	0.37039	644.1
0.52103	955.2	0.51318	1107.1
0.63221	1188.1	0.62098	1312.3
0.66240	1219.6	0.67396	1347.2
0.82490	1037.4	0.80481	1150.1
1,1,2,2-tetrachloroethane (1)+1-hexanol (2)		1,1,2,2-tetrachloroethane (1)+1-heptanol (2)	
0.05493	−50.5	0.06090	−39.3
0.29960	440.5	0.25683	329.4
0.40129	814.3	0.39940	841.6
0.51371	1210.6	0.51979	1253.2
0.61197	1457.8	0.63601	1501.8
0.66496	1524.7	0.82037	1308.0
0.80478	1371.3		

where n is the number of experimental data and P is the number of parameters.

DISCUSSION

The curves included in Fig. 1 show that mixing is accompanied by an exothermic process in mixtures rich in alcohols and the process becomes

TABLE 2

Values of the parameters C_0, C_1 and C_2 of eqn. (1) and standard deviation $\sigma(H^E)$

System	C_0 (J mol^{-1})	C_1 (J mol^{-1})	C_2 (J mol^{-1})	$\sigma(H^E)$ (J mol^{-1})
1,1,2,2-tetrachloroethane + 1-butanol	3581.3	5998.1	−713.8	1.5
1,1,2,2-tetrachloroethane + 1-pentanol	4302.5	5631.3	−1121.0	3.8
1,1,2,2-tetrachloroethane + 1-hexanol	4670.6	6523.3	209.8	1.2
1,1,2,2-tetrachloroethane + 1-heptanol	4769.2	6321.5	126.1	1.7

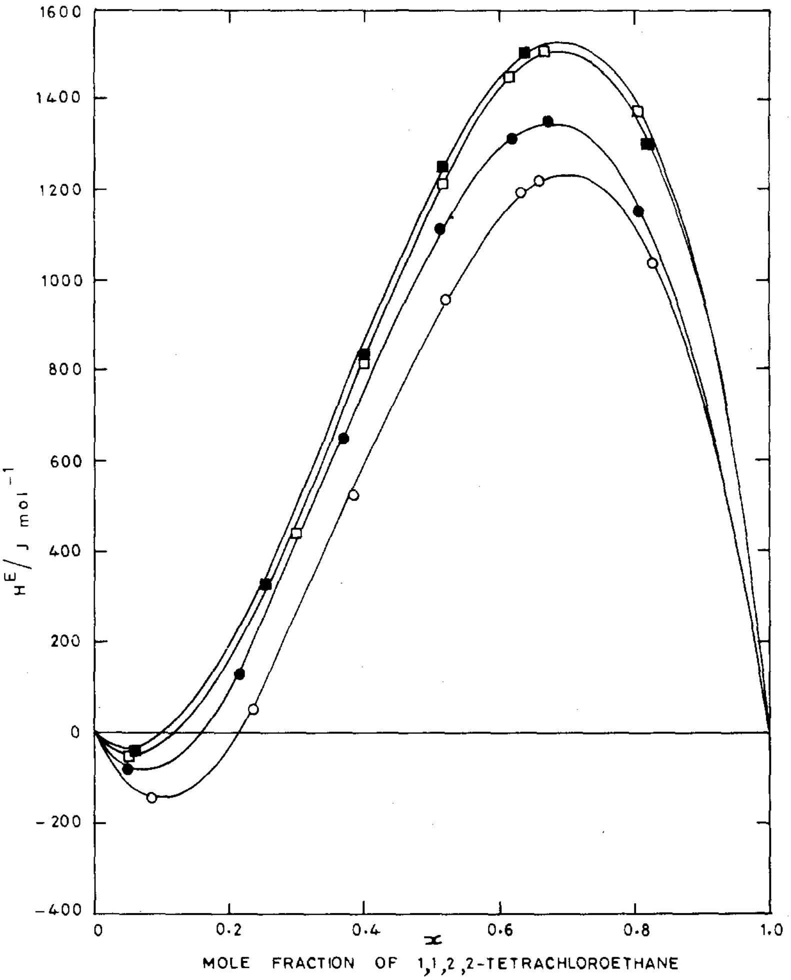

Fig. 1. Excess enthalpies H^E of 1,1,2,2-tetrachloroethane + 1-butanol (○), + 1-pentanol (●), + 1-hexanol (□) and + 1-heptanol (■).

endothermic at approximately 0.2 mole fraction of tetrachloroethane. The trend between excess enthalpy and composition may be explained in terms of two opposing effects (i) deassociation of self associated alcohols and the halogenated hydrocarbon [8] contributing to an endothermic process and (ii) formation of aggregates between unlike molecules through Cl---H–O bonding leading to an exothermic process. The actual value of H^E depends upon the relative strengths of the two opposing effects. The experimental results suggest that the two effects balance each other to different degrees over the composition range studied. This conclusion lends support to the postulates used to interpret the excess volumes of these mixtures [2]. Finally the algebraic values of H^E for the four mixtures fall in the order 1-heptanol > 1-hexanol > 1-pentanol > 1-butanol. This order shows that the deassociation of alcohol aggregates becomes dominant with increase in the chain length of the alcohols.

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