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The excess enthalpies of mixing of 1,1,2,2-tetrachloroethane with acetone, *n*-dibutylether, acetonitrile and dimethylsulphoxide [a]

Gopal Pathak, Atri Deo Tripathi and Shirish Pradhan
Physical Chemistry Division, National Chemical Laboratory, Pune-411008 (India)

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Abstract

The excess enthalpies of mixing of 1,1,2,2-tetrachloroethane with acetone, *n*-dibutylether, acetonitrile and dimethylsulphoxide were determined at 308.15 K. All four systems showed an exothermic behaviour which was attributed to hydrogen bond formation between the hydrogen of tetrachloroethane and the proton-acceptor groups. The excess enthalpies of these systems decreased in the order dimethylsulphoxide > acetone > acetonitrile > dibutylether. The hydrogen bond energies of these systems were calculated and they also exhibit the same decreasing trend.

INTRODUCTION

Binary systems of 1,1,2,2-tetrachloroethane with polar liquids are of considerable interest due to specific interactions in the liquid state. From an NMR study, McClellan and Nicksie [1] showed that 1,1,2,2-tetrachloroethane is self-associated in the liquid state, while Nath and Tripathi, from the dielectric property, excess volumes and adiabatic compressibilities, showed that it formed a 1 : 1 complex with acetone [2,3]. A literature survey revealed that no calorimetric study has been made of these systems.

In our earlier work, we studied the effect of different proton acceptor and donor groups on the strengths of hydrogen bondings [4–8]. In the present work, we studied the interactions between tetrachloroethane and C=O, C–O–C, C≡N and S=O groups.

EXPERIMENTAL

Acetone, acetonitrile and 1,1,2,2-tetrachloroethane (all AnalaR grade) were further purified by fractional distillation. *n*-Dibutylether and dimeth-

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Correspondence to: S. Pradhan, Physical Chemistry Division, National Chemical Laboratory, Pune-411 008, India.

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ylsulphoxide (DMSO) (> 99% pure) were used without further purification. All the compounds were dried by activated molecular sieves. The enthalpies of mixing were determined at 308.15 K using a heat flux microcalorimeter (Setaram C-80).

RESULTS AND DISCUSSION

The excess enthalpies of mixing of 1,1,2,2-tetrachloroethane(1) with *n*-dibutylether(2), acetonitrile(2), acetone(2) and dimethylsulphoxide(2) are

TABLE 1

Excess enthalpies of mixing of 1,1,2,2-TCE with dibutylether, acetonitrile, acetone and DMSO at 308.15 K

x_1	ΔH^E (J mol^{-1})	x_1	ΔH^E (J mol^{-1})
1,1,2,2-TCE + dibutylether		1,1,2,2-TCE + acetonitrile	
0.0771	-309	0.0537	-230
0.1161	-442	0.0848	-353
0.1804	-653	0.1026	-420
0.2491	-810	0.1104	-453
0.3145	-946	0.1460	-590
0.3486	-970	0.2008	-802
0.3697	-1001	0.2359	-889
0.4434	-1032	0.2714	-1001
0.5590	-997	0.4000	-1322
0.6192	-901	0.4845	-1394
0.6788	-822	0.5152	-1408
0.8392	-449	0.6410	-1284
0.9272	-217	0.7015	-1151
		0.7875	-845
1,1,2,2-TCE + DMSO		0.8332	-699
0.0699	-707	0.9705	-115
0.1148	-1058		
0.1802	-1741	1,1,2,2-TCE + acetone	
0.3061	-2702	0.0547	-387
0.3963	-3077	0.1072	-727
0.4403	-3232	0.2217	-1379
0.5760	-3240	0.2393	-1462
0.6996	-2780	0.3427	-1860
0.8486	-1633	0.4414	-2112
0.9414	-737	0.5722	-2130
		0.6845	-1900
		0.7844	-1512
		0.8829	-932
		0.9053	-765

TABLE 2

The least-squares coefficients of eqn. (1) for the excess enthalpies of mixing of 1,1,2,2-TCE + dibutylether, + acetonitrile, + acetone and + DMSO systems at 308.15 K

System	A_0 (J mol^{-1})	A_1 (J mol^{-1})	A_2 (J mol^{-1})	A_3 (J mol^{-1})	Std. dev. (J mol^{-1})
1,1,2,2-TCE + dibutylether	−5589.3	−459.54	1575.93	755.35	10.1
1,1,2,2-TCE + acetonitrile	−5603.9	−400.63	1639.0	618.88	9.7
1,1,2,2-TCE + acetone	−8600.8	−828.83	481.07	−36.44	6.8
1,1,2,2-TCE + DMSO	−13141.8	−438.24	1826.28	−1528.81	30.7

reported in Table 1. The data were fitted to a least-squares equation of the type

$$H^E = x_1x_2 \sum_{i=0}^{3} A_i(x_1 - x_2)^i \tag{1}$$

The least-squares parameters, along with the standard deviations, are given in Table 2. The ΔH versus x_1 curves for these systems are given in Fig. 1.

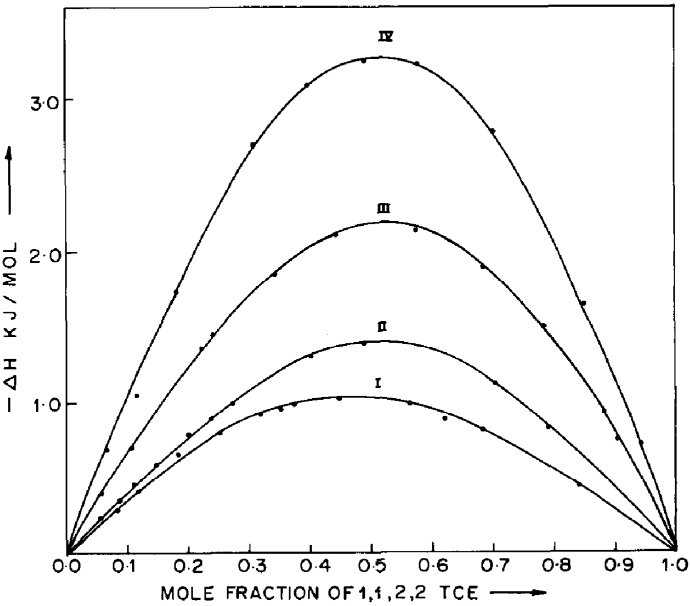

Fig. 1. Molar excess enthalpies of mixing for 1,1,2,2-tetrachloroethane (1) + *n*-dibutylether (2), + acetonitrile (2), + acetone (2) and + dimethylsulphoxide (2) at 308.15 K: I, TCE + *n*-dibutylether; II, TCE + acetonitrile; III, TCE + acetone; IV, TCE + dimethylsulphoxide.

All four systems are exothermic in nature due to specific interactions. The exothermicity showed a marked dependence on the functional group having the order sulpho > keto > nitrile > ether. The specific interactions are expected to be hydrogen bond formation between the hydrogen of TCE and other proton acceptor groups. The excess enthalpies observed are due to the product of the strength of hydrogen bonding and the number of such bonds formed in the mixture.

Nath and Tripathi [2] studied the dielectric properties of acetone and TCE mixtures and concluded that a 1:1 complex forms between the two, while McClellan and Nicksie [1] investigated the DMSO + TCE system by NMR and found a 1:1 type of complex formation. The interactions between acetonitrile and dibutylether with TCE are much weaker than those in the other two systems and, therefore, an AB2 type of complex formation is not expected in acetonitrile–TCE and butylether–TCE mixtures. It is therefore reasonable to assume that all four systems form essentially 1:1 complexes in the mixtures. The partial molar enthalpies of DMSO, acetone, acetonitrile and dibutylether in TCE are approximately the hydrogen bond energies of the complexes [9]. However, TCE is slightly self-associated and dimethylsulphoxide, acetone, dibutylether and acetonitrile have strong specific interactions in the pure liquid state. The mixing of any of these compounds with TCE leads to three interactions: (1) Dissociation of self-associated TCE molecules by other interacting molecules. (2) Breaking of specific interactions of the second compound by TCE molecules. (3) Specific interactions, dominantly H-bond formation, between TCE and the other compound.

The first two interactions are endothermic while the last is an exothermic reaction. The observed enthalpy of mixing is therefore the net effect of two endothermic and one exothermic reactions. The enthalpies of H-bonded complexes (ΔH_c) are therefore obtained as $\Delta H_c = \Delta H_1 - \Delta H_2 - \Delta H_3$, where ΔH_1, ΔH_2 and ΔH_3 are the partial molar enthalpy of the proton acceptor in TCE, the partial molar enthalpy of the proton acceptor in a non-polar solvent and the partial molar enthalpy of TCE in a non-polar solvent, respectively.

The ΔH_1, ΔH_2 and ΔH_3 values were obtained by extrapolating the $\Delta H/x_1x_2$ versus x_1 curve to zero mole fraction. The data on the enthalpies of mixing used to obtain the ΔH_2 and ΔH_3 values were taken from the literature [7,10–12]. The enthalpies of complex formation thus obtained are given in Table 3. The strength of hydrogen bonded complexes between different proton acceptor groups increases as S=O > C=O > C≡N > C–O–C.

The etheral oxygen is a weak proton-acceptor and forms a weak complex with TCE. Acetone is a better proton acceptor than acetonitrile and forms a stronger complex with TCE. This observation is consistent with our earlier work [7,13].

TABLE 3

The enthalpies of complex formation (ΔH_c) of 1,1,2,2-TCE + dibutylether, + acetonitrile, + acetone and + DMSO

System	ΔH_1 (kJ mol^{-1})	ΔH_2 (kJ mol^{-1})	ΔH_3 (kJ mol^{-1})	ΔH_c (kJ mol^{-1})
TCE + dibutylether	−2.8	–		−8.7
TCE + acetonitrile	−3.5	–		−20.8
TCE + acetone	−9.0	–		−23.0
TCE + DMSO	−13.0	–		−25.0
Dibutylether + hexane		0.9	–	
Acetonitrile + hexane		12.3	–	
Acetone + hexane		9.0	–	
DMSO + 1,4-dimethylbenzene		7.0	–	
TCE + hexane			5.0	

The DMSO–TCE complex is stronger than the acetone–TCE complex by about 2.0 kJ mol^{-1}. Structurally, DMSO and acetone are identical but the sulphur atom of DMSO has vacant 3d orbitals which enhance the electron delocalisation on the adjacent carbon atom. The hydrogen atoms on the CH_3 groups of DMSO are therefore expected to be more acidic than those of acetone [14]. The specific interactions between DMSO and TCE are expected to be stronger than those between TCE and acetone which contribute to the stronger complex formation and greater exothermicity of the DMSO–TCE system.

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