Excess Molar Enthalpies of 1,1,2,2-Tetrachloroethane with Acetone, Dibutyl Ether, Acetonitrile, and Dimethyl Sulfoxide at 298.15 K

Atri D. Tripathi

Department of Chemistry, Panjab University, Chandigarh-160014, India

Measurements of excess molar enthalpies H^E at 298.15 K have been made for binary liquid mixtures of 1,1,2,2-tetrachloroethane with acetone, dibutyl ether, acetonitrile, and dimethyl sulfoxide. The values of H^E at 298.15 K are negative for all four systems. These results indicate the existence of specific interactions of $CHCl_2CHCl_2$ with all these compounds. The excess molar enthalpies (in absolute values) of these systems decrease in the order dimethyl sulfoxide > acetone > acetonitrile > dibutyl ether.

Introduction

As a part of our continuing efforts to obtain thermodynamic and physicochemical quantities of liquid mixtures of 1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$) (Nath and Tripathi, 1983, 1984, 1986; Tripathi, 1994) with proton acceptor compounds, we have reported the excess molar enthalpies of 1,1,2,2-tetrachloroethane with acetone, dibutyl ether, acetonitrile, and dimethyl sulfoxide at 308.15 K (Pathak et al., 1992). In the present study, we report here the excess molar enthalpies of $CHCl_2CHCl_2$ with the above-mentioned compounds at 298.15 K.

Experimental Section

1,1,2,2-Tetrachloroethane (BDH) and acetone (AR) were purified as described earlier (Nath and Tripathi, 1983). Acetonitrile, dibutyl ether, and dimethyl sulfoxide (99 mol %) were used without further purification. All the compounds were dried by activated molecular sieves. The purities of the chemicals used, as determined by GLC, are given in Table 1.

The purities of the chemicals were checked by measuring densities using a vibrating tube densimeter (model DMA, Anton-Paar 60/602) (Patil et al., 1990). The experimental values of density are compared with the literature values in Table 1. The agreement with the literature values is quite good.

The excess molar enthalpies were determined at 298.15 K using a heat flux microcalorimeter (Setaram c-80) whose temperature was controlled to within ±0.001 K. The reliability of the microcalorimeter was tested by measuring H^E at 298.15 K for cyclohexane + hexane (McLure and Rodriguez, 1982). The experimental values of H^E agreed well with literature values within ±1%. The accuracy in the mole fraction is on the order of 10^{-4} for $CHCl_2CHCl_2$ + acetone, whereas it is 10^{-3} for other systems. The mean deviations of the measured H^E are estimated to be about 1% over most of the mole fraction range.

Results and Discussion

The excess molar enthalpies of 1,1,2,2-tetrachloroethane with dibutyl ether, acetonitrile, acetone, and dimethyl sulfoxide at 298.15 K are given in Table 2. The values of H^E have been fitted by least squares to the equation

$$H^E/(\text{J} \cdot \text{mol}^{-1}) = x_1 x_2 \sum_{i=0}^{3} A_i (x_1 - x_2)^i \qquad (1)$$

where x_1 refers to the mole fraction of $CHCl_2CHCl_2$. The

Table 1. Densities of Pure Components at 298.15 K

component	purity (mol %)	density (g cm^{-3}) exptl	density (g cm^{-3}) lit.[a]
1,1,2,2-tetrachloroethane	99.86	1.586 56	1.586 66
acetone	99.82	0.784 35	0.784 40
dibutyl ether	99.00	0.764 15	0.764 10
acetonitrile	99.00	0.776 28	0.776 49
dimethyl sulfoxide	99.00	1.095 12	1.095 37

[a] Riddick and Bunger (1986).

Table 2. Excess Molar Enthalpies of 1,1,2,2-Tetrachloroethane (1) with Dibutyl Ether (2), Acetonitrile (2), Acetone (2), and Dimethyl Sulfoxide (2) at 298.15 K

x_1	$H^E/$ (J mol^{-1})	x_1	$H^E/$ (J mol^{-1})
1,1,2,2-Tetrachloroethane (1) + Dibutyl ether (2)		1,1,2,2-Tetrachloroethane (1) + Acetonitrile (2)	
0.299	−947	0.045	−157
0.352	−1025	0.105	−443
0.408	−1034	0.189	−769
0.525	−1013	0.298	−1100
0.650	−838	0.451	−1369
0.752	−687	0.502	−1413
0.800	−571	0.652	−1279
0.825	−523	0.725	−1069
0.911	−304	0.791	−857
		0.845	−646
		0.955	−201
1,1,2,2-Tetrachloroethane (1) + Acetone (2)		1,1,2,2-Tetrachloroethane (1) + Dimethyl Sulfoxide (2)	
0.0931	−690	0.101	−1030
0.1510	−1026	0.175	−1748
0.2618	−1570	0.201	−1970
0.4514	−2112	0.351	−3004
0.5968	−2099	0.404	−3201
0.6723	−1993	0.511	−3389
0.7256	−1798	0.600	−3293
0.8144	−1397	0.702	−2885
		0.799	−2231
		0.902	−1225

least squares parameters, along with standard deviations, are reported in Table 3. Graphical presentation of experimental and calculated values at 298.15 K is given in Figure 1.

All four systems show exothermic behavior due to specific interactions. Surendranath et al. (1991) reported H^E for $CHCl_2CHCl_2$ + acetonitrile at 298.15 K. Their values of H^E are negative for this system. The exothermicity showed

Table 3. Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies of 1,1,2,2-Tetrachloroethane + Dibutyl Ether, + Acetonitrile, + Acetone, and + Dimethyl Sulfoxide Systems at 298.15 K

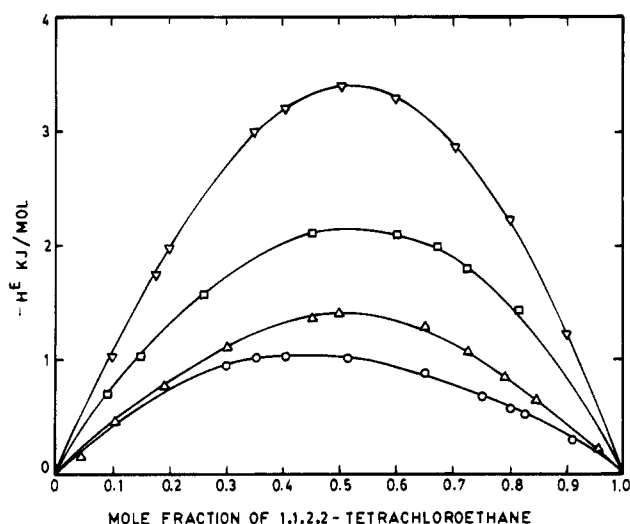| system	A_0	A_1	A_2	A_3	$\sigma/(\text{J mol}^{-1})$
1,1,2,2-tetrachloroethane (1) dibutyl ether (2)	−4090.8	1315.26	−33.38	−1345.21	11.8
1,1,2,2-tetrachloroethane (1) acetonitrile (2)	−5627.8	−264.90	1539.53	294.06	16.6
1,1,2,2-tetrachloroethanee (1) + acetone (2)	−8584.53	−1102.25	−171.50	469.19	16.3
1,1,2,2-tetrachloroethane (1) + dimethyl sulfoxide (2)	−13566.0	−954.06	1404.94	−1020.28	7.0

Figure 1. Experimental H^E values for 1,1,2,2-tetrachloroethane (1) + acetone (2), + dibutyl ether (2), + acetonitrile (2), and + dimethyl sulfoxide (2) at 298.15 K, respectively represented by □, ○, △, and ∇. Solid curves represent the calculated values based upon eq 1.

a marked dependence on the functional group having the order (in absolute values) sulfo > keto > nitrile > ether. The specific interactions are expected to be hydrogen bond formation between the hydrogen of tetrachloroethane and other proton acceptor groups (Pathak et al., 1992).

The values of H^E can be discussed from the viewpoint of the existence of specific interactions leading to the formation of complexes between the components of the various systems. The values of H^E which are low in magnitude for the mixtures of $CHCl_2CHCl_2$ with dibutyl ether (ethers are weakly polar compounds) suggest that $CHCl_2CHCl_2$ forms weak complexes with dibutyl ether whereas acetone is a better proton acceptor than acetonitrile and forms a stronger complex with $CHCl_2CHCl_2$ in the liquid state. The complexation between acetone and 1,1,2,2-tetrachloroethane can be attributed to the formation of strong hydrogen bonds between the hydrogen atom of tetrachloroethane and the lone pair electrons on the oxygen atom of acetone (Nath and Tripathi, 1983, 1984, 1986; Tripathi, 1994).

Excess molar enthalpies for 1,1,2,2-tetrachloroethane + diethyl ether and + diisopropyl ether at 298.15 K have been studied by Becker and Hallauer (1987). The excess molar enthalpy for these systems is negative over the entire composition range. Our value ($H^E = -1023$ J mol^{-1}) for

$CHCl_2CHCl_2$ + dibutyl ether falls in line with the values $H^E = -2346$ J mol^{-1} and $H^E = -1983$ J mol^{-1} reported for $CHCl_2CHCl_2$ + diethyl ether and + diisopropyl ether, respectively, at $x_1 = 0.5$ which further supports the accuracy of our data. Since $CHCl_2CHCl_2$ is self-associated (McClellan and Nicksic, 1965) and dibutyl ether because of its longer chain strongly breaks its self-association, the value of H^E for dibutyl ether is less negative as compared to diethyl ether and diisopropyl ether in the binary mixtures with 1,1,2,2-tetrachloroethane.

Acknowledgment

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