Excess Molar Enthalpies of 1,1,2,2-Tetrachloroethane + 2-Methylfuran, + Tetrahydrofuran, + 1,4-Dioxane, and + Cyclopentanone at 308.15 and 318.15 K

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Excess molar enthalpies at 308.15 and 318.15 K have been determined for 1,1,2,2-tetrachloroethane with 2-methylfuran, tetrahydrofuran, 1,4-dioxane, and cyclopentanone. All four systems are exothermic. The excess enthalpies (in absolute values) decrease in the order tetrahydrofuran > cyclopentanone > 1,4-dioxane > 2-methylfuran.

Introduction

We have previously measured the excess volume, ultrasonic velocities (*1*), dielectric constants (*2*, *3*), and excess enthalpies (*4*) of the binary mixtures of 1,1,2,2-tetrachloroethane with some aromatics and some *n*-donor compounds (acetone, acetonitrile, dibutyl ether and dimethyl sulfoxide). The results obtained are discussed in terms of donor–acceptor interaction between the components. In this paper we report the excess molar enthalpies of binary mixtures of 1,1,2,2-tetrachloroethane with 2-methylfuran, tetrahydrofuran, 1,4-dioxane, and cyclopentanone at 308.15 and 318.15 K. As far as we are aware no data on H_m^E of these systems are available in the literature.

Experimental Details

Materials. 1,1,2,2-Tetrachloroethane (BDH) was dried over anhydrous potassium carbonate and fractionally distilled. Tetrahydrofuran (AR, Thomas Baker & Co.) was dried over potassium hydroxide, refluxed over lithium aluminum hydride, fractionally distilled, and stored over molecular sieves. 1,4-Dioxane (AR, BDH) was mixed with concentrated HCl and water and refluxed under nitrogen atmosphere for 15 h. After this it was dried over potassium hydroxide and distilled over sodium metal. Cyclopentanone (AR, BDH) was purified by distillation over calcium oxide. 2-Methyl furan (AR, BDH) was used without further purification. The densities of tetrachloroethane, 2-methylfuran, tetrahydrofuran, 1,4-dioxane, and cyclopentanone at 20 °C were measured with an Anton Paar vibrating tube densimeter (model DMA 602/60) and found to be 1.594 53, 0.914 81, 0.889 14, 1.033 58, and 0.948 67 g·cm^{-3} which are in good agreement with the literature values of 1.594 49, 0.915, 0.8892, 1.033 61, and 0.948 65 g·cm^{-3}, respectively (*5*, *6*). The enthalpies of mixing were determined using a heat flux microcalorimeter (Setaram c-80). The mixtures were prepared by mass, and the possible error in the mole fraction is estimated to be less than 10^{-4}. For both the densimeter and calorimeter, temperature control by the thermostat was within ±0.003 K. The calorimeter was tested by measurements on benzene + methylbenzene (*7*) and cyclohexane + hexane (*8*) at 298.15 K. The experimental results agreed with literature values within ±1% over the entire mole fraction range. The accuracy of any individual measurement of H_m^E was better than 0.5 J·mol^{-1}.

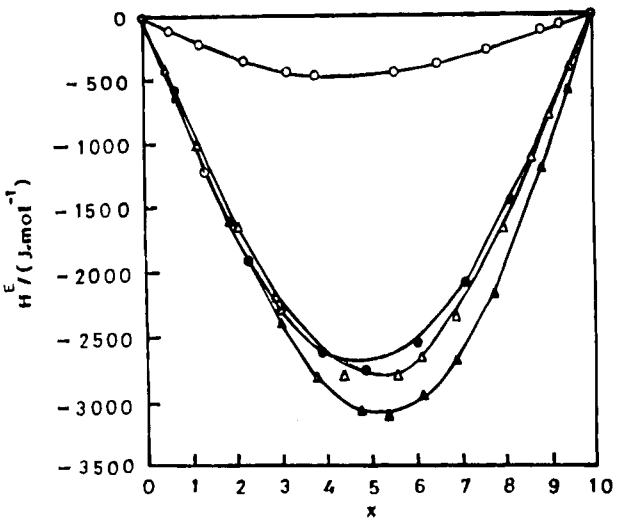

Figure 1. Excess molar enthalpies of binary mixtures $(1 - x)$ tetrachloroethane + x 2-methylfuran (○), + x tetrahydrofuran (▲), + x 1,4-dioxane (●), and + x cyclopentanone (△) at 308.15 K. Lines are calculated from eq 1.

Results

The experimental excess molar enthalpies at 308.15 and 318.15 K for the investigated mixtures are given in Table 1. The results were fitted by the method of least squares to the equation

$$H_m^E = (1 - x)x\sum_{i=0}^{n} h_i(2x - 1)^i \qquad (1)$$

where x is the mole fraction of the second component. The values of the coefficients h_i and the standard deviations S are listed in Table 2. Graphical presentation of experimental and calculated values at 308.15 K is given in Figure 1. It can be seen from Table 1 that all the systems show exothermic behavior and H_M^E (in absolutes values) decrease in the order tetrahydrofuran > cyclopentanone >

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0021-9568/95/1740-0645$09.00/0

Table 1. Excess Molar Enthalpies for (1 − x) 1,1,2,2-Tetrachloroethane + x 2-Methylfuran, + x Tetrahydrofuran, + x 1,4-Dioxane, and + x Cyclopentanone at 308.15 and 318.15 K

T = 308.15 K		T = 318.15 K		T = 308.15 K		T = 318.15 K	
x	H_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})
			(1 − x) 1,1,2,2-Tetrachloroethane + x 2-Methylfuran				
0.0589	−109	0.0881	−141	0.5594	−453	0.5147	−442
0.1241	−218	0.1516	−242	0.6546	−387	0.6137	−378
0.2247	−352	0.2611	−369	0.7655	−274	0.7309	−257
0.3222	−439	0.3992	−453	0.8857	−129	0.8038	−170
0.3837	−469	0.4881	−451	0.9260	−81	0.8737	−91
			(1 − x) 1,1,2,2-Tetrachloroethane + x Tetrahydrofuran				
0.0469	−424	0.0537	−468	0.5335	−3101	0.5874	−2957
0.1097	−988	0.1255	−1082	0.6150	−2966	0.6114	−2902
0.1857	−1630	0.1671	−1424	0.6866	−2687	0.6907	−2601
0.2948	−2401	0.2863	−2274	0.7711	−2174	0.7522	−2250
0.3758	−2809	0.3834	−2756	0.8861	−1198	0.8654	−1361
0.4738	−3047	0.4766	−2994	0.9443	−607	0.9487	−547
			(1 − x) 1,1,2,2-Tetrachloroethane + x 1,4-Dioxane				
0.0674	−660	0.0509	−501	0.7095	−2105	0.5033	−2695
0.1307	−1219	0.1038	−982	0.8121	−1468	0.6158	−2469
0.2269	−1926	0.2040	−1758	0.8604	−1114	0.6609	−2296
0.2962	−2309	0.2756	−2183	0.8957	−843	0.7568	−1794
0.3851	−2628	0.3169	−2372	0.9483	−422	0.8372	−1258
0.4816	−2744	0.4033	−2632	0.9854	−119	0.9544	−362
0.6014	−2559	0.4816	−2703				
			(1 − x) 1,1,2,2-Tetrachloroethane + x Cyclopentanone				
0.0697	−616	0.0682	−607	0.6888	−2341	0.6995	−2275
0.2000	−1675	0.1986	−1654	0.7979	−1666	0.8025	−1641
0.2819	−2205	0.2835	−2189	0.8685	−1121	0.8752	−1082
0.4375	−2785	0.4167	−2705	0.9086	−787	0.9235	−675
0.5566	−2788	0.5045	−2796	0.9518	−416	0.9867	−119
0.6132	−2652	0.6112	−2631				

Table 2. Values of Parameters h_i in Eq 1 along with the Standard Deviations of H_m^E for Various Mixtures at 308.15 and 318.15 K

system	T/K	h_0/(J·mol^{-1})	h_1/(J·mol^{-1})	h_2/(J·mol^{-1})	S/(J·mol^{-1})
(1 − x) 1,1,2,2-tetrachloroethane + x 2-methylfuran	308.15	−1898.8	467.8	440.7	0.32
	318.15	−1789.8	657.3	848.3	0.40
(1 − x) 1,1,2,2-tetrachloroethane + x tetrahydrofuran	308.15	−12394.9	−1110.9	2319.2	0.30
	318.15	−12063.3	−1190.7	2340.5	0.37
(1 − x) 1,1,2,2-tetrachloroethane + x 1,4-dioxane	308.15	−10956.6	1022.0	1793.8	0.28
	318.15	−10787.9	1115.3	1771.0	0.34
(1 − x) 1,1,2,2-tetrachloroethane + x cyclopentanone	308.15	−11343.8	124.1	2642.8	0.38
	318.15	−11186.6	25.9	2233.7	0.50

1,4-dioxane > 2-methylfuran. The high negative values of H_M^E for all the systems indicate the presence of specific interaction due to hydrogen bonding between a hydrogen atom of tetrachloroethane and lone pair electrons on the oxygen atom of the other component as is suggested by Meclellan and Nicksic between tetrachloroethane and dimethyl sulfoxide (*9*).

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Received October 24, 1994. Accepted February 7, 1995.[⊗]

JE940221I

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.