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Excess Molar Enthalpies of Chloroalkanes or Chloroalkenes + Benzyl Alcohol at 298.15 K

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Excess molar enthalpies for benzyl alcohol + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, + trichloroethylene, and + tetrachloroethylene have been measured at 298.15 K with a Parr 1451 solution calorimeter. The excess enthalpies are positive for 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene, and the plot of excess molar enthalpy versus the mole fraction of benzyl alcohol is S shaped for 1,1,2,2-tetrachloroethane.

Introduction

For nonideal solutions the magnitude of their excess enthalpies can be quite significant and give a direct measure of molecular interactions; hence, H_m^E values can provide information needed to test existing theories of solutions.

The thermodynamic properties of binary mixtures containing polar and self-associated components exhibit significant deviation from ideality, arising not only from differences in size and shape but also from possible hydrogen-bonding interactions between unlike molecules. A systematic study of excess molar enthalpies H_m^E of binary mixtures containing chloroalkanes, xylene, toluene, and benzene has been reported by Viswanath et al. *(1−4)*. As a countinuation of these studies, we report enthalpies of chloroalkanes and chloroalkenes with aromatic alcohol. A survey of the literature has shown no excess enthalpy measurements for mixtures of benzyl alcohol with chloroalkanes and chloroalkenes. We report here results for H_m^E for systems of benzyl alcohol + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, + trichloroethylene, and + tetrachloroethylene at 298.15 K.

Experimental Section

The chemicals used were purified by the standard methods described by Riddick, Bunger, and Sakano *(5)*. Benzyl alcohol (Fluka AR grade) was fractionally distilled under reduced pressure, and the middle fraction was collected. 1,2-Dichloroethane (Merck AR grade) was washed with dilute potassium hydroxide solution, dried over anhydrous calcium chloride, and fractionally distilled. 1,1,1-Trichloroethane (Merck AR grade) was washed with concentrated hydrochloric acid and then with 10% sodium chloride solution, dried over solid calcium chloride, and finally fractionally distilled twice, and the middle sample of the second distillation was collected. 1,1,2,2-Tetrachloroethane (Merck AR grade) was shaken with concentrated sulfuric acid for 10 min at 80−90 °C. The operation was repeated until the acid developed no more color. It was then washed with water, steam distilled, dried over potassium carbonate, and finally fractionated. Spectral grade trichloroethylene and tetrachloroethylene (S.D. Fine Chemicals pvt. Ltd., Boisar, India) were fractionally distilled twice, and the middle fraction of the second distillation was collected.

Table 1. Experimental Densities and Refractive Indices at 298.15 K and Comparison with Literature Values

	density/(kg/m^3)		refractive index	
component	lit. *(5)*	exptl	lit. *(5)*	exptl
benzyl alcohol	1.041 27	1.041 53	1.538 37	1.538 47
1,2-dichloroethane	1.246 37	1.246 82	1.442 10	1.442 16
1,1,1-trichloroethane	1.329 90	1.329 50	1.435 90	1.435 88
1,1,2,2-tetrachloroethane	1.586 66	1.586 28	1.491 40	1.491 81
trichloroethylene	1.614 32	1.614 18	1.503 20	1.503 18
tetrachloroethylene	1.662 20	1.661 85	1.413 00	1.413 10

The purities of the samples were checked by comparing the measured densities and refractive indices of the purified samples by means of a pycnometer and Abbe's refractometer, thermostated to the required temperature, with those reported in the literature. The measured values were in agreement with the literature data *(5)* within 0.1% as shown in Table 1.

A Parr 1451 solution calorimeter was used. The calorimeter consists of a glass dewar mixing chamber with a rotating sample cell, a thermistor probe, and a specially designed temperature measuring bridge, all assembled in a compact cabinet. Temperature changes can be plotted directly using a strip chart recorder and can be read to an accuracy of ±0.001 K.

The two-piece cell serves as both the sample holder and agitator. It is closed with a detachable Teflon disk. The liquid sample can be added to the cell from a pipet inserted through the top stem. Excellent thermal insulation is provided by the fully silvered glass dewar which serves as a mixing chamber. It can contain from 90 to 120 cm^3 of solvent. Temperatures are measured with a glass-sheathed thermistor probe, combined with a special bridge designed for a linear response over the range from 293.15 to 303.15 K with the bridge adjusted to that 100 μV represents a

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Table 2. Excess Molar Enthalpies H_m^E for Chloroalkanes or Chloroalkenes + Benzyl Alcohol at 298.15 K

x	$H_m^E/(J\cdot mol^{-1})$	x	$H_m^E/(J\cdot mol^{-1})$	x	$H_m^E/(J\cdot mol^{-1})$	x	$H_m^E/(J\cdot mol^{-1})$	x	$H_m^E/(J\cdot mol^{-1})$
				$(1 - x)\ ClH_2CCH_2Cl + x\ C_6H_5CH_2OH$					
0.0813	649.7	0.2812	920.3	0.4873	862.6	0.6907	548.5	0.9616	50.8
0.1275	776.3	0.3450	904.8	0.5497	776.3	0.7861	389.2		
0.2010	899.5	0.4164	846.1	0.6183	671.3	0.8874	194.5		
				$(1 - x)\ Cl_3CCH_3 + x\ C_6H_5CH_2OH$					
0.0573	468.3	0.2315	676.7	0.4228	601.2	0.6630	416.8	0.9098	112.3
0.1115	589.5	0.3027	661.8	0.4873	574.1	0.7349	337.3	0.9649	36.3
0.1771	660.6	0.3711	630.9	0.5912	485.2	0.8154	237.5		
				$(1 - x)\ Cl_2HCCHCl_2 + x\ C_6H_5CH_2OH$					
0.0521	235.6	0.2658	276.9	0.4906	−72.2	0.6938	−228.8	0.9137	−161.2
0.1265	359.6	0.3412	162.1	0.5643	−111.0	0.7593	−252.3	0.9825	−37.0
0.1928	355.8	0.4188	37.9	0.6005	−154.9	0.8363	−233.5		
				$(1 - x)\ Cl_2C{=}CHCl + x\ C_6H_5CH_2OH$					
0.0698	402.1	0.2791	461.0	0.4735	351.5	0.7073	216.8	0.9240	51.7
0.1490	473.3	0.3491	429.3	0.5598	330.9	0.7719	169.4	0.9799	6.7
0.2138	478.2	0.3991	402.5	0.6350	274.8	0.8521	111.3		
				$(1 - x)\ Cl_2C{=}CCl_2 + x\ C_6H_5CH_2OH$					
0.0679	497.9	0.2875	748.2	0.4810	750.5	0.6881	615.3	0.9094	231.1
0.1506	643.7	0.3532	772.2	0.5571	727.0	0.7685	506.2		
0.2224	728.5	0.4159	772.8	0.6331	672.7	0.8420	379.8		

Table 3. Parameters h_j and Standard Deviation ($\sigma(H_m^E)$) from Eq 1 (T = 298.15 K)

system	h_0	h_1	h_2	h_3	h_4	h_5	$\sigma(H_m^E)^a/\%$
$(1 - x)\ ClH_2CCH_2Cl + x\ C_6H_5CH_2OH$	3287.19	−1989.94	621.83	−861.56	2989.48	−3113.90	2.6
$(1 - x)\ Cl_3CCH_3 + x\ C_6H_5CH_2OH$	2292.78	−16979.50	92.69	760.08	4112.74	−4973.29	3.5
$(1 - x)\ Cl_2HCCHCl_2 + x\ C_6H_5CH_2OH$	−178.93	−2376.00	882.51	−2217.45	1237.09	495.13	2.8
$(1 - x)\ Cl_2C{=}CHCl + x\ C_6H_5CH_2OH$	1441.04	−1231.38	305.97	91.14	32.07.14	−3684.99	3.8
$(1 - x)\ Cl_2C{=}CCl_2 + x\ C_6H_5CH_2OH$	3065.55	−832.12	50.43	199.32	3979.78	−3943.56	2.4

[a] $\sigma(H_m^E)/\% = [[\Sigma((H_m^E{}_{\text{exptl}} - H_m^E{}_{\text{calcd}})/H_m^E{}_{\text{exptl}} \times 100)^2]/(n - p)]^{1/2}$.

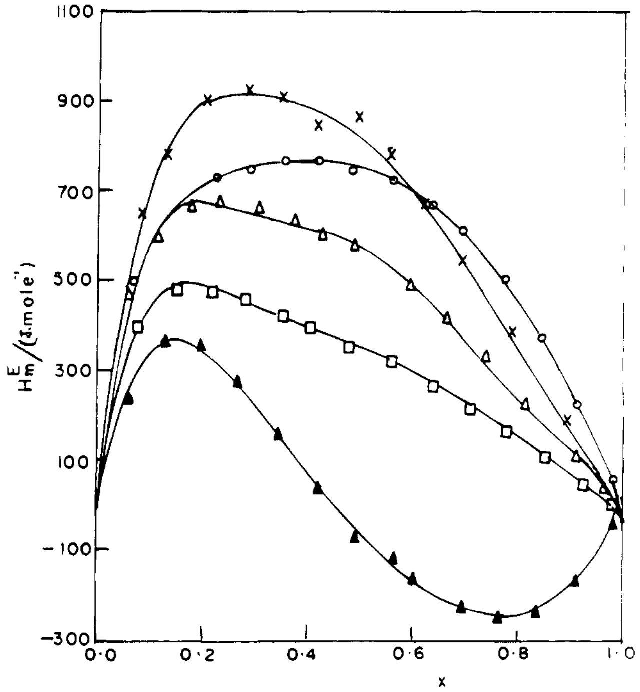

Figure 1. H_m^E versus x for the following systems at 298.15 K: (×) $C_6H_5CH_2OH$ (x) + ClH_2CCH_2Cl (1 − x), (△) $C_6H_5CH_2OH$ (x) + Cl_3CCH_3 (1 − x), (▲) $C_6H_5CH_2OH$ (x) + $Cl_2HCCHCl_2$ (1 − x), (○) $C_6H_5CH_2OH$ (x) + $Cl_2C{=}CHCl$ (1 − x), (□) $C_6H_5CH_2OH$ (x) + $Cl_2C{=}CCl_2$ (1 − x).

temperature change of exactly 0.001 K. The output of the bridge is connected to a strip chart recorder, allowing the temperature change to be measured within an accuracy of 1%. The experimental error of excess molar enthalpies H_m^E is estimated to be less than 1% by comparison of our results on $x\ C_6H_6 + (1 - x)\ CCl_4$ and $x\ C_6H_5CH_3 + (1 - x)\ C_6H_5Cl$ with literature data (*6–9*). The compositions reported are accurate to 0.1%. The components are combined in the dewar mixing chamber, and the resulting temperature change is measured with the thermistor probe. At the start of the experiment, one of the liquids is held in a sealed glass rotating cell in thermal contact with the other component. When the system comes to thermal equilibrium, the contents of the rotating cell are mixed with the surrounding liquid. The temperature changes due to the mixing process are sensed by the thermistor and recorded on the strip chart recorder. The excess molar enthalpy H_m^E is calculated. The reliability of the apparatus and of the method is established by measuring exess enthalpies for the systems $x\ C_6H_6 + (1 - x)\ CCl_4$ and $x\ C_6H_5CH_3 + (1 - x)\ C_6H_5Cl$); throughout the concentration range at 298.15 K our results are in agreement with the literature data (*6–9*) within 1%.

Results and Discussion

The measured molar excess enthalpies H_m^E of benzyl alcohol + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, + trichloroethylene, and + tetrachloroethylene at 298.15 K are given in Table 2 and shown in Figure 1. The results were fitted to

$$H_m^E/(J\cdot mol^{-1}) = (1 - x)x\sum h_j(2x - 1)^j \qquad (1)$$

by the method of least squares. Values of the coefficients h_j and the standard deviation $\sigma(H_m^E)$ (%) representing the fit of each set of results are given in Table 3. For the systems studied, the excess enthalpies at 298.15 K are endothermic except for those of 1,1,2,2-tetrachloroethane. The excess molar enthalpies for benzyl alcohol with chloroalkanes are in the order 1,2-dichloroethane (863 J) > 1,1,1-trichloroethane (574 J) > 1,1,2,2-tetrachloroethane (−72 J). The excess enthalpies for benzyl alcohol with chloroalkenes are in the following order: tetrachloroethylene (750 J) > trichloroethylene (352 J).

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