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EXCESS ENTHALPIES OF *n*-ALCOHOLS (C_1–C_4) AND *n*-ALKANES (C_6–C_8) WITH 1,2-DICHLOROETHANE AT 303.15 K *

S.K. CHAUDHARI and S.S. KATTI **

Physical Chemistry Division, National Chemical Laboratory, Poona 411008 (India)

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ABSTRACT

Excess molar enthalpies, H_m^E, of binary mixtures of methanol, ethanol, *n*-propanol, *n*-butanol, *n*-hexane, *n*-heptane and *n*-octane with 1,2-dichloroethane were obtained at 303.15 K using a C-80 microcalorimeter (Setaram, France). The H_m^E values are positive (endothermic) over the entire composition range for all the systems. These H_m^E values increase with the increase in the chain length of alcohol or alkane. Curves of H_m^E versus x_1 (mole fraction of alcohol or alkane) are skewed for alcohols, whereas those for the *n*-alkanes are symmetrical. Qualitatively, the results obtained for alcohols are interpreted in terms of positive deviations which result mainly from hydrogen bond breaking, whereas the findings for *n*-alkanes may result from dipole–induced dipole interactions and also from disruption of the orientational order of both components.

INTRODUCTION

Alcohols are strongly associated as a result of hydrogen bonding. It is worthwhile to study the changes in the thermodynamic properties occurring on dilution of an alcohol with any non-polar solvent. The binary systems of *n*-alcohols with *n*-alkanes have been studied extensively [1–3]. However, binary systems containing an alcohol or alkane with a halohydrocarbon, particularly 1,2-dichloroethane, have not been studied thoroughly although a few data are given in refs. 4–6. Therefore, in the present work, excess molar enthalpies, H_m^E, have been obtained for binary mixtures of *n*-alcohols (C_1–C_4) and *n*-alkanes (C_6–C_8) with 1,2-dichloroethane, which was chosen as the common component because of its symmetrical structure.

EXPERIMENTAL

Methanol, *n*-propanol, *n*-butanol (AnalaR grade, S.D. Fine Chemicals, India) and ethanol (Fluka, Pure grade) were purified by fractional distilla-

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** Author to whom correspondence should be addressed.

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TABLE 1

Densities (d) and refractive indices (n_D) of pure components at 298.15 K

Component	d (g cm^{-3})		n_D	
	Obs.	Lit. [7,8]	Obs.	Lit. [7]
Methanol	0.78662	0.78664	1.3265	1.32650
Ethanol	0.78510	0.78504	1.3593	1.35941
n-Propanol	0.79960	0.79969	1.3837	1.38370
n-Butanol	0.80579	0.80586	1.3971	1.39730
n-Hexane	0.65491	0.65481	1.3723	1.37226
n-Heptane	0.67943	0.67951	1.3852	0.38511
n-Octane	0.69862	0.69849	1.3951	1.39505
1,2-Dichloroethane	1.24580	1.24580	1.4425	1.44210

tion; 1,2-dichloroethane, n-hexane, n-heptane (AnalaR grade, S.D. Fine Chemicals, India) and n-octane (reagent grade, S.D. Fine Chemicals) were fractionated over sodium. All the compounds were stored over 4 Å molecular sieves. The purity of the compounds was better than 99.5 mol%. The purity was also confirmed by measuring densities and refractive indices at 298.15 K. The densities were measured using an Anton Paar vibrating tube densimeter (DMA 602/60) with an accuracy of 20 μg cm^{-3}, and refractive indices using a precision Abbe refractometer (Mark II, Richert) to an accuracy of 1×10^{-4}. The experimental values agree well with the literature values [7,8], as shown in Table 1.

The excess molar enthalpies, H_m^E, were measured with the help of a C-80 microcalorimeter (Setaram, France) at 303.15 K. The data were reproducible within 1.0%.

RESULTS

The excess molar enthalpies obtained at 303.15 K for n-alcohol (1) + 1,2-dichloroethane (2) systems are given in Table 2, and those for n-alkane (1) + 1,2-dichloroethane (2) are given in Table 3. The H_m^E values are plotted against x_1, the mole fraction of component 1, in Figs. 1 and 2, respectively. Excess enthalpies were fitted to the equation

$$H_m^E(\text{J mol}^{-1}) = x_1(1 - x_1) \sum_{n=0}^{5} A_n(2x_1 - 1)^n \qquad (1)$$

The fitting parameters A_0, A_1, A_2, A_3, A_4 and A_5, along with the standard deviation s, are presented in Table 4. Curves of H_m^E/x_1x_2 versus x_1 are shown in Figs. 3 and 4. The excess molar enthalpies at infinite

TABLE 2

Excess molar enthalpies of *n*-alcohol (1) + 1,2-dichloroethane (2) systems at 303.15 K

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
Methanol (1) + 1,2-dichloroethane (2)							
0.0314	376	0.1956	1028	0.4918	957	0.7591	421
0.0772	694	0.2623	1095	0.5556	845	0.8091	320
0.1147	860	0.3208	1105	0.6210	704	0.9052	135
0.1594	963	0.3881	1079	0.6973	542	0.9527	62
Ethanol (1) + 1,2-dichloroethane (2)							
0.0445	554	0.2343	1336	0.5983	1082	0.8636	301
0.0682	767	0.3113	1395	0.6705	898	0.9235	149
0.1183	1036	0.4144	1376	0.7344	696		
0.1716	1224	0.5041	1273	0.8004	482		
n-Propanol (1) + 1,2-dichloroethane (2)							
0.0354	508	0.2471	1638	0.5824	1469	0.8606	475
0.0802	949	0.3304	1730	0.6399	1306	0.9330	224
0.1109	1173	0.4168	1721	0.7068	1066		
0.1798	1478	0.5231	1597	0.7752	808		
n-Butanol (1) + 1,2-dichloroethane (2)							
0.0348	493	0.1748	1563	0.4759	1797	0.7671	991
0.0608	797	0.2444	1765	0.5531	1652	0.8340	697
0.0955	1111	0.3221	1870	0.6378	1437	0.8867	466
0.1310	1350	0.3933	1868	0.6945	1267	0.9342	264

TABLE 3

Excess molar enthalpies of *n*-alkane (1) + 1,2-dichloroethane (2) systems at 303.15 K

x_1	H_m^E (J mol^{-1})	x_1	H_m (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
n-Hexane (1) + 1,2-dichloroethane (2)							
0.0576	441	0.3379	1654	0.6135	1605	0.8713	719
0.1106	781	0.4020	1739	0.6868	1428	0.9417	342
0.1748	1103	0.5100	1747	0.7622	1188		
0.2564	1145	0.5677	1684	0.8290	920		
n-Heptane (1) + 1,2-dichloroethane (2)							
0.0470	401	0.1988	1321	0.4715	1849	0.7828	1180
0.0683	575	0.2505	1510	0.5596	1788	0.8458	889
0.1093	850	0.3213	1703	0.6703	1565	0.8890	669
0.1512	1104	0.3912	1811	0.7302	1380	0.9499	321
n-Octane (1) + 1,2-dichloroethane (2)							
0.0380	371	0.3042	1774	0.6540	1680	0.9189	514
0.0926	812	0.3899	1912	0.7141	1488		
0.1596	1237	0.4828	1938	0.7673	1282		
0.2308	1562	0.5761	1855	0.8185	1048		

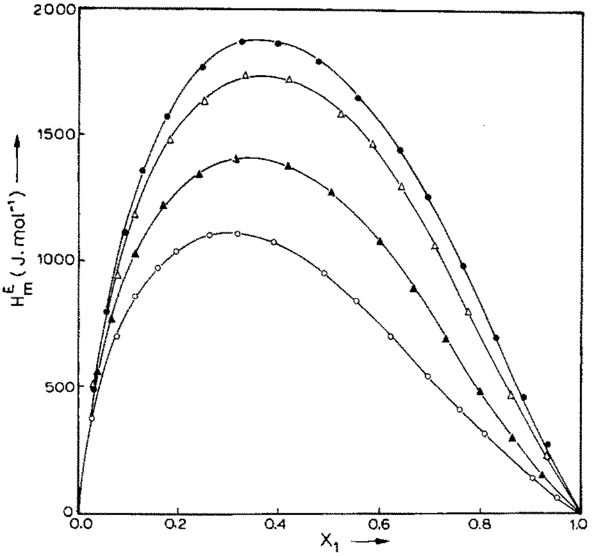

Fig. 1. Excess enthalpy–mole fraction curves for *n*-alcohol (1) + 1,2-dichloroethane (2) systems at 303.15 K: ○, methanol; ▲, ethanol; △, *n*-propanol; ●, *n*-butanol; ———, from eqn. (1).

dilution of alcohols and alkanes in 1,2-dichloroethane were obtained by extrapolating H_m^E/x_1x_2 curves to zero x_1. These values are about 15 ± 1 kJ mol^{-1} and 9 ± 1 kJ mol^{-1} for alcohols and alkanes, respectively.

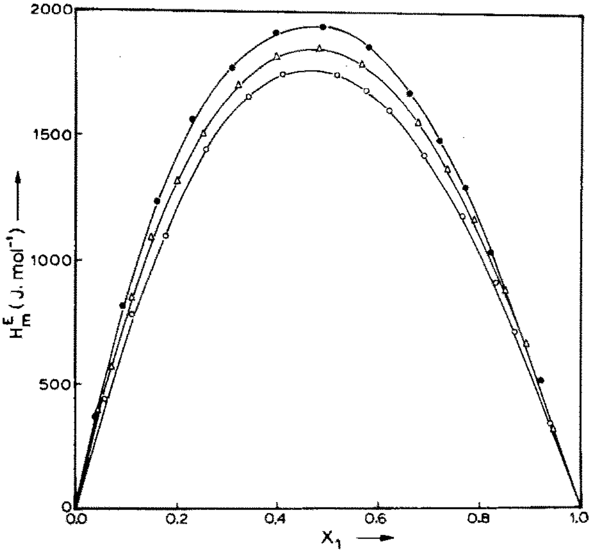

Fig. 2. Excess enthalpy–mole fraction curves for *n*-alkane (1) + 1,2-dichloroethane (2) systems at 303.15 K: ○, *n*-hexane; △, *n*-heptane; ●, *n*-octane; ———, from eqn. (1).

TABLE 4

Parameters of eqn. (1) for $H_m^E - x_1$ data, together with standard deviation s

System	Parameters						s (H_m^E) (J mol^{-1})
	A_0	A_1	A_2	A_3	A_4	A_5	
Methanol (1) + 1,2-dichloroethane (2)	3818.019	−3492.961	−202.1774	1448.307	3999.003	−4811.792	6.4
Ethanol (1) + 1,2-dichloroethane (2)	5149.436	−3087.517	−276.5750	−2232.437	3682.740	−1782.212	6.0
n-Propanol (1) + 1,2-dichloroethane (2)	6567.699	−3135.055	−1.5799	−3099.273	3466.099	−441.2802	3.8
n-Butanol (1) + 1,2-dichloroethane (2)	7032.265	−3092.631	−1857.835	−3222.144	995.8505	155.0645	5.5
n-Hexane (1) + 1,2-dichloroethane (2)	7015.157	−1198.767	172.438	1165.858	52.8383	−1299.521	3.3
n-Heptane (1) − 1,2-dichloroethane (2)	7353.649	−838.2502	738.5248	−1326.708	−106.075	1005.179	4.0
n-Octane (1) + 1,2-dichloroethane (2)	7742.958	−1175.483	723.9576	−1223.779	195.3839	611.9429	3.2

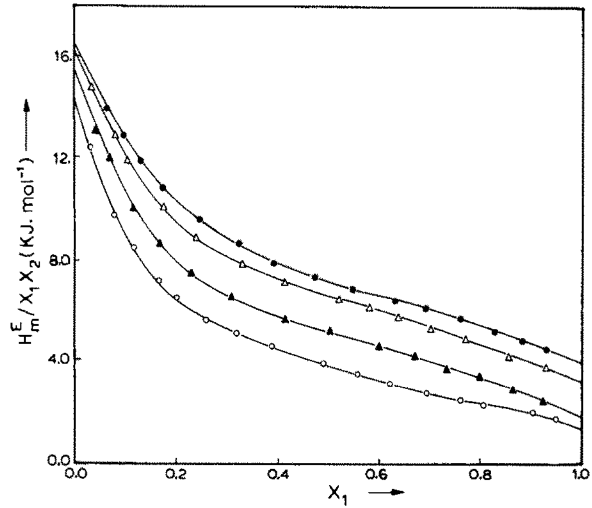

Fig. 3. H^E_m/x_1x_2 vs. x_1 curves for *n*-alcohol (1) + 1,2-dichloroethane (2) systems at 303.15 K (symbols as in Fig. 1).

Rhim and Bae [5] have reported H^E_m data for the *n*-butanol + 1,2-dichloroethane system at 298.15 K and 308.15 K. The present H^E_m values for this system at 303.15 K lie essentially in between these values, as depicted in Fig. 5.

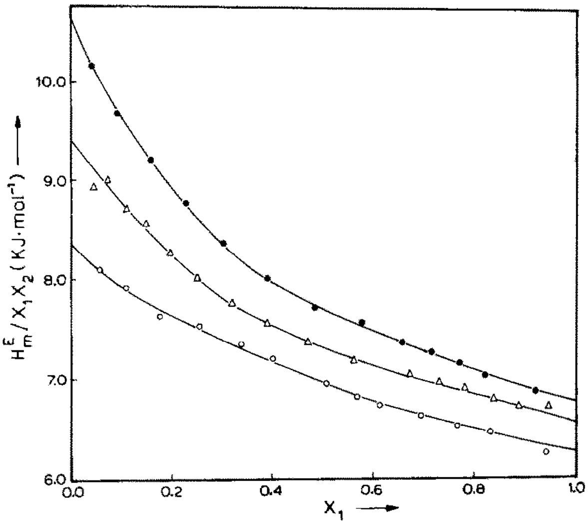

Fig. 4. H^E_m/x_1x_2 vs. x_1 curves for *n*-alkane (1) + 1,2-dichloroethane (2) systems at 303.15 K (symbols as in Fig. 2).

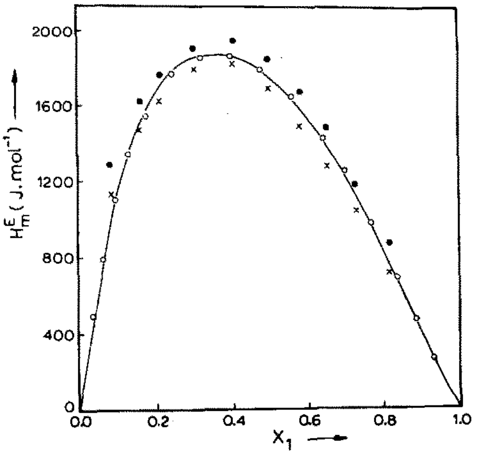

Fig. 5. Comparison of the present H_m^E data with literature data for *n*-butanol (1) + 1,2-dichloroethane (2): ×, data at 298.15 K [5]; ○, data at 303.15 K (this work); ●, data at 308.15 K [5].

DISCUSSION

The results obtained can be interpreted qualitatively in terms of molecular interactions and orientational and structural changes that may take place after mixing. It was observed that the alcohol + 1,2-dichloroethane mixtures exhibit positive deviations. This may result mainly from hydrogen-bond breaking, and to a certain extent from dipole–induced dipole interactions and changes in the orientational order of molecules. Such explanations have been put forward for *n*-alcohol + *n*-alkane systems [1,9,10], and are also applicable to the present systems.

In the case of *n*-alkane + 1,2-dichloroethane systems, the positive deviations observed may be due to dipole–induced dipole interactions and disruption of the orientational order of unlike molecules. Such an explanation has also been given by Delmas and Purves [11] and by Valero et al [12].

Because of Cl–OH specific interactions, which contribute to a negative deviation, the extent of positive deviations observed for *n*-alcohol + 1,2-dichloroethane systems are comparatively less than those observed for *n*-alkane + 1,2-dichloroethane.

The H_m^E versus x_1 curves (Fig. 1) for *n*-alcohols are skewed, and maxima are observed at $x_1 \approx 0.3$–0.4. This may result from specific Cl–OH interactions [13,14]. However, in the case of *n*-alkane + 1,2-dichloroethane systems, H_m^E versus x_1 curves (Fig. 2) are symmetrical and maxima are observed at $x_1 \approx 0.5$.

The magnitude of the maximum values observed in H_m^E versus x_1 curves for the mixtures of ethanol + *n*-hexane at 303.15 K is about 630 J mol^{-1} [15], and for ethanol + 1 chlorobutane is about 810 J mol^{-1} at 298.15 K [14], whereas for the ethanol + 1,2-dichloroethane system (the present case) it is about 1400 J mol^{-1}. This indicates that substitution of an alkane CH_2 group by a Cl atom increases the excess enthalpy substantially. This may result from the greater bulk of the chlorine atoms, which disrupt the orientational order of both the molecules and give more positive contributions to H_m^E.

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