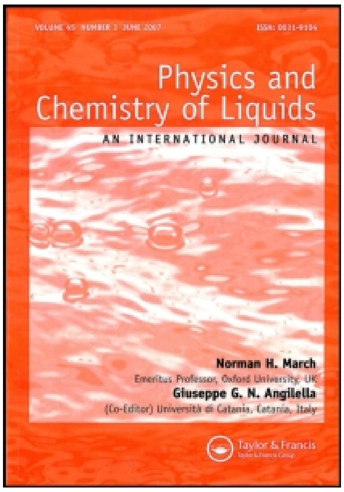

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EXCESS ENTHALPIES FOR MIXTURES OF 1-BROMOBUTANE WITH NORMAL AND ISOALCOHOLS AT 298.15 K

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Excess enthalpies (H^E) for mixtures of 1-Bromobutane with propan-1-ol, Propan-2-ol, butan-1-ol, 2 methyl propan-1-ol. Pentan-1-ol, and 3 methyl butan-1-ol at 298.15 K. have been measured over the entire range of composition with a Parr's 1451 solution calorimeter. All mixed endothermically with the maximum values of H^E occurring at 0.6 to 0.7 molefraction. Comments about the molecular interactions contributing to the excess enthalpies of 1-bromobutane + an alcohol are made on the basis of these results.

KEY WORDS: Calorimeter, binary mixtures, excess enthalpy.

1 INTRODUCTION

The thermodynamic properties of binaries containing polar and self-associated components exhibit significant deviations from ideality, arising not only from differences in size and shape but also from the possible hydrogen bonding interaction between unlike molecules. A survey of the literature showed that chloro or bromo alkane with cyclohexane[1], alkane[2,3], benzene[4], tetra chloromethane[5] and 2,2-dimethyl butane[6] has been made. However, no systematic attempt has been made to study the interactions in mixtures of 1-bromobutane with Normal and Isoalcohols. Recently, Excess Volumes of an alcohol with 1-Bromobutane was reported by Rambabu *et al*[7]. Here, we report new experimental data on H^E for systems of 1-bromobutane with propan-1-ol, Propan-2-ol, butan-1-ol, 2 methyl propan-1-ol, Pentan-1-ol and 3 methyl butan-1-ol at 298.15 K.

2 EXPERIMENTAL

All the chemicals used in this work were purified by the standard methods described by Riddick and Bunger[9]. Alcohols were dried by refluxing with fused calcium oxide and fractionally distilled. 1-Bromobutane (Fluka better than 99 moles per cent pure). The liquid was kept in a molecular sieve to remove any traces of humidity, and was

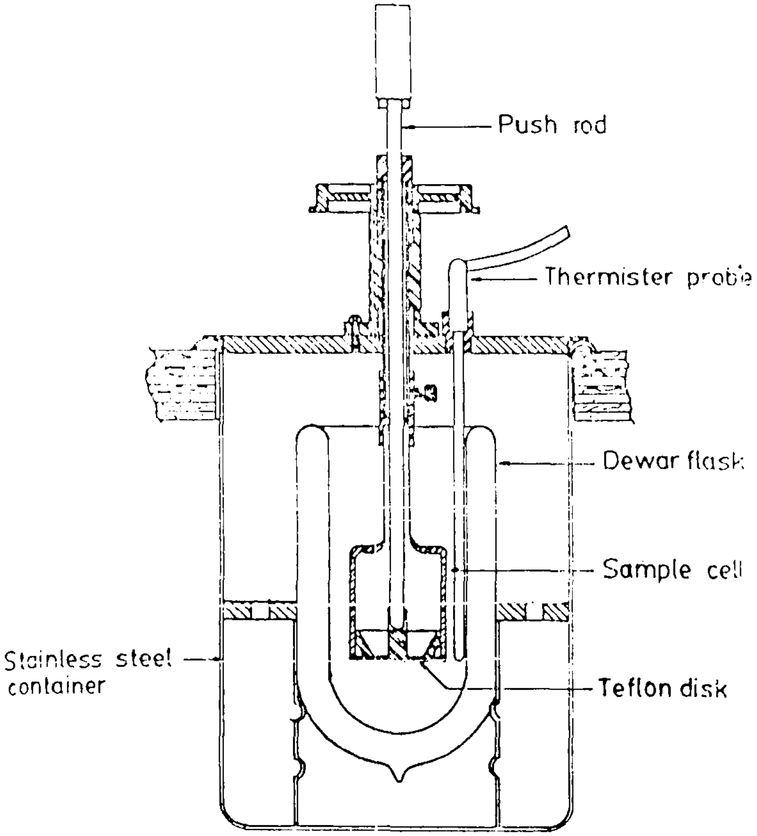

Figure 1

used without further purification. The purity of the samples was checked by comparing the measured densities and boiling points of the purified samples with those reported in the literature (Riddick and Bunger[9] 1970; Timmermans[10] 1965).

A Parr 1451 solution calorimeter was used for the present studies. The calorimeter shown in Figure 1, consists of a glass dewar mixing chamber with a rotating sample cell, a thermister 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 which serves both as a sample holder and agitator consists of a bell which is closed with a detachable teflon disk. Liquid samples can be added to the cell from a pipette inserted through the top stem. Excellent thermal insulation is provided by a fully silvered glass dewar which serves as a mixing chamber. From 90 to 120 ml of solvent can be taken in this vessel. Temperature measurements in this calorimeter are taken with a glass-sheathed thermister probe combined with a special bridge in a system designed for linear response over the range from 293.15 to 303.15 K, within this temperature range each 100 microvolt change in output from the bridge represents a temperature change of exactly 0.001 K. By connecting the output of the bridge to a strip chart recorder, the temperature change can be measured within an accuracy of 1%. Thus the experimental error of excess molar enthalpies H_M^E is estimated to be less than 1% over the molefraction range studied.

The operating principle of this calorimeter is very simple. The components are combined in the dewar mixing chamber and the resulting temperature change is measured with the thermister probe. At start of the experiment one of the liquids is held in a scaled 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 surrounding liquid. The temperature changes due to the mixing process is sensed by the thermister and recorded on the strip chart recorder. The excess molar enthalpy, H_M^E is then calculated knowing the energy equivalent of the system by following equation.

$$H_M^E = (W_1 C_{p1} + W_2 C_{p2} + E)\,\Delta t/n, \tag{1}$$

Where

W_i = Weight of liquid i (gm), C_{pi} = heat capacity of liquid i (Joules/gm-K), E = energy equivalent of calorimeter (Joules/K), (76.65 J. k^{-1}), Δt = temp. change (K), n = number of moles of mixture. The reliability of the apparatus and of the method is established by measuring excess enthalpies of a standard system, cyclohexane + n-hexane, throughout the concentration range at 298.15 K. Our results are in agreement with those obtained by the standard equation Stokes and Marsh[8].

3 RESULTS AND DISCUSSION

The measured excess molar excess enthalpies, H^E are given in Table 1 for 1-Bromobutane with propan-1-ol, Propan-2-ol, butan-1-ol, 2 methyl propan-1-ol, pentan-1-ol, and 3 methyl butan-1-ol at 298.15 K and graphically represented in Figure 2. The results for each mixture were fitted with the smoothening function.

$$H^E/\mathrm{J\ mol}^{-1} = x(1\text{-}x) \sum_{j=0}^{2} h_j (2x - 1)^j \tag{2}$$

by the method of least-squares with each point weighted equally. X represents the molefraction of 1-bromobutane. Values of the coefficients h_j and the percentage of standard deviation, $\%\sigma(H^E)$ representing the fit of each set of results are given in Table 2. For all the mixtures, the excess enthalpies at 298.15 K are positive and the H^Evs. mole fraction curves are symmetrical.

The excess enthalpies are influenced by two opposing effects: (1) absorption of heat due to depolymerization of self-associated alcohols by 1-bromobutane and reduction in dipole-dipole interactions between like molecules; (2) liberation of heat as a result of possible hydrogen bonding interaction between the halogenated group of the alkane and the hydroxyl function of the alcohol. The actual values of H^E would depend upon the relative strength of the two opposing effects. The positive experimen-

Table 1 Excess enthalpies of 1-Bromobutane with alcohols at 298.15 K. X is the molefraction of 1-bromobutane.

X	H^E (J/mol)	x	H^E (J/mol)
1-Bromobutane + Propan-1-ol			
0.0650	163.1	0.4958	815.5
0.1230	276.8	0.5493	880.2
0.1750	365.9	0.6136	942.8
0.2324	451.8	0.6934	979.4
0.2836	522.6	0.7733	939.3
0.3284	588.4	0.8731	718.1
1-Bromobutane + Propan-2-ol			
0.0662	252.8	0.4844	1103.4
0.1252	434.6	0.5377	1155.6
0.1780	575.8	0.6025	1193.8
0.2365	704.2	0.6836	1188.8
0.2877	809.6	0.7663	1094.4
0.3338	888.2	0.8696	800.2
1-Bromobutane-butan-1-ol			
0.0844	253.4	0.5317	1000.3
0.1568	414.5	0.5843	1055.6
0.2195	531.8	0.6473	1101.7
0.2852	638.2	0.7245	1098.8
0.3415	726.9	0.7983	1010.6
0.3900	801.5	0.8886	728.3
1-Bromobutane + 2 methyl propan-1-ol			
0.0829	288.4	0.5379	1137.2
0.1548	476.0	0.5903	1189.8
0.2169	609.7	0.6529	1228.8
0.2830	734.4	0.7279	1214.5
0.3397	873.6	0.8018	1103.4
0.3889	917.3	0.8908	787.6
1-Bromobutane + pentan-1-ol			
0.0966	242.7	0.5755	969.9
0.1773	386.2	0.6264	1026.0
0.2457	489.1	0.6861	1062.4
0.3181	594.6	0.7591	1044.7
0.3778	682.4	0.8245	938.5
0.4294	761.3	0.9050	650.9
1-Bromobutane + 3 methyl butan-1-ol			
0.0977	319.2	0.5805	1072.8
0.1789	495.5	0.6315	1118.4
0.2483	614.5	0.6911	1140.9
0.3186	720.4	0.7601	1112.6
0.3784	804.6	0.8274	989.4
0.4294	877.6	0.9062	682.9

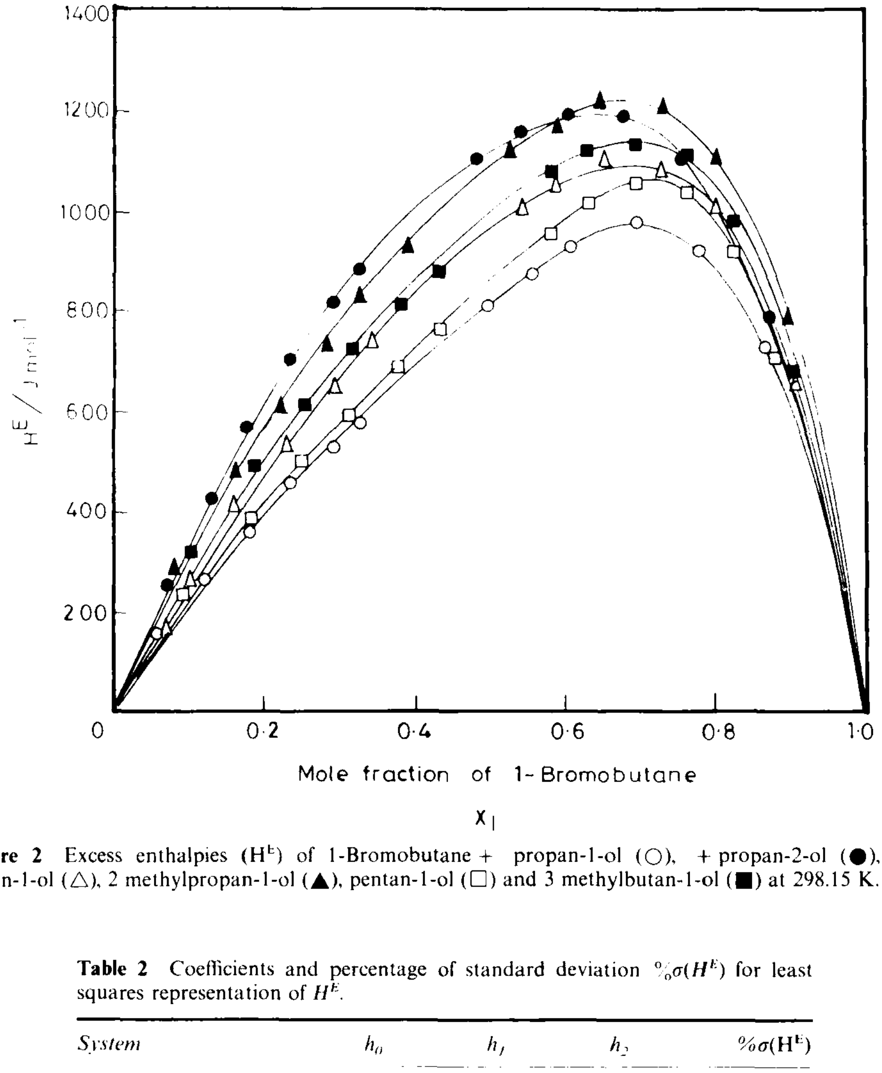

Figure 2 Excess enthalpies (H^E) of 1-Bromobutane + propan-1-ol (○), + propan-2-ol (●), + butan-1-ol (△), 2 methylpropan-1-ol (▲), pentan-1-ol (□) and 3 methylbutan-1-ol (■) at 298.15 K.

Table 2 Coefficients and percentage of standard deviation $\%\sigma(H^E)$ for least squares representation of H^E.

System	h_0	h_1	h_2	$\%\sigma(H^E)$
		J mol^{-1}		
1-Bromobutane + propan-1-ol	3281.553	2605.318	2218.227	0.4
1-Bromobutane + propan-2-ol	4481.368	2080.044	1879.186	0.2
1-Bromobutane + butan-1-ol	3833.925	2661.312	2401.701	0.1
1-Bromobutane + 2 methyl propan-1-ol	4341.428	2782.465	2558.778	0.2
1-Bromobutane + pentan-1-ol	3470.361	2955.304	2603.400	0.1
1-Bromobutane + 3 methyl butan-1-ol	3899.728	2698.124	2935.115	0.2

tal H^E values suggest that the former effect is stronger than the latter. The lower positive values of H^E for the 1-bromobutane with normal alcohols than for that containing Isoalcohols indicates Normal alcohols interacts more strongly than Isoalcohols. This may be attributed to the steric hindrance of the methyl group in Isoalcohols, i.e.,

Propan-1-ol < Propan-2-ol
butan-1-ol < 2 methyl propan-1-ol
pentan-1-ol < 3 methyl butan-1-ol

In case of the systems containing Normal alcohols H^E fall in the order below: i.e.,

butan-1-ol > pentan-1-ol > propan-1-ol.

This trend may be explained on the basis of chain length, steric and electromeric effects.

In case of Isoalcohols,

2 methyl propan-1-ol > propan-2-ol > 3 methyl butan-1-ol

This trend may be explained on the basis of steric and electromeric effects. When the alkyl group of the alcohol becomes more and more branched, the effect of interaction is more and more sterically hindered and the positive H^E values should be in the order.

3 methyl butan-1-ol > 2 methyl propan-1-ol > propan2-ol.

But in contrast the observed H^E values suggest the stronger interaction in the system, 1-bromo butane + 2 methyl butan-1-ol, than that containing 2 methyl propan-1-ol. This may be due to the electromeric effect predominating over the steric effect in the system, 1-bromobutane + 3 methyl butan-1-ol.

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