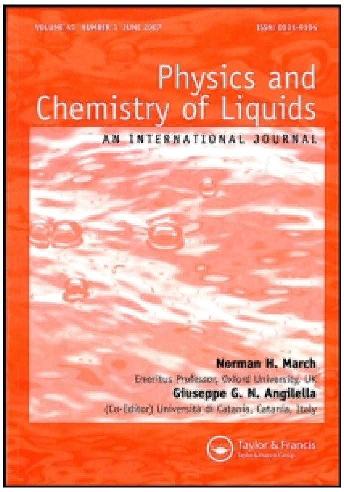

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EXCESS MOLAR ENTHALPIES FOR ISOMERIC CHLOROBUTANES WITH ISOMERIC BUTANOLS

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Excess molar enthalpies for mixtures of each of the isomers of chlorobutane with each of the isomers of butanol were determined at the temperature 298.15 K and atmospheric pressure. Excess molar enthalpies are positive for all the mixtures. The results are discussed in terms of molecular interactions.

Keywords: Excess molar enthalpies; Chlorobutanes; Butanols

INTRODUCTION

Our research program on thermophysical properties of binary mixtures involving isomers of chlorobutane and isomers of butanol includes: excess molar volumes [1-3], excess isentropic compressibilities [4], isobaric vapour-liquid equilibrium [5, 6] and viscosity deviations [2, 3, 7]. In this paper and as extension of our work we report excess molar enthalpies for mixtures of each chlorobutane isomer with each butanol isomer at 298.15 K and atmospheric pressure.

As far as we know only two of the mixtures involving in this study, 1-butanol and 2-methyl-2-propanol with 1-chlorobutane, can be found in the literature [8].

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EXPERIMENTAL

Excess molar enthalpies were obtained with a Thermometric 2277 thermal activity monitor maintained at $\pm 2 \times 10^{-4}$ K operating under constant flow conditions [9]. Two Shimadzu LC-10ADVP HPLC pumps were used to drive the liquids. The pumps were calibrated for each liquid before the start of the calorimetric measurements. The uncertainty in the mole fractions of the mixtures, calculated from the uncertainty in the flow delivered by the pumps, is ±0.001. The calibration of the calorimeter was achieved with reference to the very accurate H^E of the mixture *n*-hexane with cyclohexane [10]. This calibration was checked by determining the excess molar enthalpies of the endothermic system benzene+cyclohexane [11] and of the exothermic system 1,4-dioxane+tetrachloromethane [12] and comparing the results with well-established literature data, in both cases the deviations lie within ±1% over the most composition range. The uncertainty in the determination of excess molar enthalpies could be expected to be ±1%. The technique and calibration were periodically checked.

The liquids used were: 1-butanol (better than 99.8 mol%), 2-methyl-1-propanol and 2-methyl-2-propanol (better than 99.5 mol%), 1-chlorobutane, 2-chlorobutane, 2-methyl-2-chloropropane and 2-butanol (better than 99 mol%) provided by Aldrich and 2-methyl-1-chloropropane (better than 99 mol%) obtained from Fluka. The purity of the materials was checked by GC and by measuring their densities by means of an Anton Paar DMA-58 vibrating tube densimeter. The comparison between measured densities and literature values [13] are shown in Table I.

TABLE I Densities of the pure compounds at 298.15 K and comparison with literature data

	$\rho/g \cdot cm^{-3}$	
Compound	*Exptl.*	*Lit.*
1-Chlorobutane	0.88047	0.8804
2-Chlorobutane	0.86743	0.8671
2-Methyl-1-chloropropane	0.87105	0.8717
2-Methyl-2-chloropropane	0.83678	0.8361
1-Butanol	0.80575	0.80575
2-Butanol	0.80241	0.80241
2-Methyl-1-propanol	0.79784	0.7978
2-Methyl-2-propanol	0.78100	0.7812

RESULTS AND DISCUSSION

Experimental values of excess molar enthalpies are listed in Table II and plotted in Figures 1–4. Each set of results was fitted to the polynomial form:

$$H^E/(\mathrm{J}\cdot\mathrm{mol}^{-1}) = x_1x_2\sum_{j=0}^{k}A_jx_2^{j/2}$$

where A_j are adjustable parameters and x_2 is the mole fraction of butanol. This equation was found to be more suitable for smoothing the results than the usual form involving only integer powers of the mole fraction [8, 14, 15]. The values of the parameters, determined by least-squares optimization, are given in Table III along with the standard deviations.

Our results are in reasonable agreement with those of Pérez *et al.* [8]. Excess molar enthalpies are positive over the whole composition range for all the mixtures and the corresponding plots unsymmetrical. For a given isomer of chlorobutane the maximum H^E values increases in the sequence: 1-butanol < 2-methyl-1-propanol < 2-butanol < 2-methyl-2-propanol and they are shifted to values of butanol mole fraction that are progressively bigger in the same sequence. On the other hand, if we consider a given isomer of butanol, the maximum H^E values are very similar for the four isomeric chlorobutanes. These results indicate that excess molar enthalpies are closely related to the structure of the butanols.

The butanols are self-associated compounds by hydrogen bonding. In the pure state exists an equilibrium between monomers and linear and cyclic polymers. The hydrogen bond energies [16] and the extent of association [17] decrease with chain branching, thus for the isomeric butanols the sequence is 1-butanol > 2-methyl-1-propanol > 2-butanol > 2-methyl-2-propanol. On the other hand, the chlorobutanes are polar liquids but not self-associated. Bearing in mind this information the calorimetric behaviour when these compounds are mixed could be interpreted in terms of the following interactions: (1) The breaking of the self-association by hydrogen-bond existing in butanols; (2) The breaking of the dipole–dipole interactions between chlorobutanes. These two interactions give positive contributions to

TABLE II Excess molar enthalpies for an isomeric chlorobutane(1) with an isomeric butanol(2) at 298.15 K

x_1	$H^E/J \cdot mol^{-1}$	x_1	$H^E/J \cdot mol^{-1}$	x_1	$H^E/J \cdot mol^{-1}$
1-Chlorobutane + 1-Butanol					
0.043	76	0.402	742	0.795	921
0.108	204	0.457	816	0.894	740
0.222	431	0.579	937	0.939	569
0.284	552	0.617	963		
1-Chlorobutane + 2-Butanol					
0.052	213	0.393	1257	0.803	1226
0.105	434	0.491	1383	0.898	912
0.220	779	0.591	1435	0.947	612
0.298	1059	0.691	1391		
1-Chlorobutane + 2-Methyl-1-propanol					
0.039	133	0.381	955	0.790	1087
0.096	292	0.480	1085	0.892	843
0.187	538	0.582	1160	0.945	589
0.284	768	0.684	1179		
1-Chlorobutane + 2-Methyl-2-propanol					
0.041	282	0.390	1351	0.790	1254
0.092	541	0.464	1428	0.895	915
0.196	945	0.589	1474	0.945	609
0.294	1170	0.687	1418		
2-Chlorobutane + 1-Butanol					
0.052	93	0.383	708	0.787	901
0.102	196	0.478	831	0.894	740
0.188	371	0.581	915	0.944	507
0.284	547	0.682	949		
2-Chlorobutane + 2-Butanol					
0.053	231	0.385	1217	0.788	1213
0.097	410	0.486	1348	0.890	902
0.194	748	0.588	1425	0.937	590
0.286	1014	0.688	1356		
2-Chlorobutane + 2-Methyl-1-propanol					
0.074	145	0.392	973	0.791	1067
0.120	289	0.492	1119	0.892	814
0.196	532	0.590	1169	0.945	574
0.303	783	0.689	1170		
2-Chlorobutane + 2-Methyl-2-propanol					
0.038	227	0.383	1360	0.789	1218
0.087	499	0.484	1418	0.893	899
0.187	874	0.585	1425	0.943	602
0.283	1133	0.688	1365		
2-Methyl-1-chloropropane + 1-Butanol					
0.045	72	0.385	686	0.788	906
0.094	159	0.483	815	0.892	722
0.189	348	0.583	913	0.951	460
0.286	528	0.683	946		

TABLE II (Continued)

x_1	$H^E/J \cdot mol^{-1}$	x_1	$H^E/J \cdot mol^{-1}$	x_1	$H^E/J \cdot mol^{-1}$
2-Methyl-1-chloropropane + 2-Butanol					
0.049	167	0.388	1152	0.789	1192
0.095	327	0.486	1316	0.895	893
0.178	664	0.586	1370	0.949	587
0.288	935	0.687	1333		
2-Methyl-1-chloropropane + 2-Methyl-1-propanol					
0.044	120	0.383	912	0.790	1037
0.091	245	0.485	1056	0.893	788
0.188	487	0.584	1121	0.944	535
0.284	733	0.687	1129		
2-Methyl-1-chloropropane + 2-Methyl-2-propanol					
0.045	266	0.387	1318	0.790	1196
0.091	500	0.484	1418	0.891	885
0.190	890	0.586	1440	0.941	608
0.287	1146	0.685	1357		
2-Methyl-2-chloropropane + 1-Butanol					
0.052	96	0.380	714	0.791	928
0.103	187	0.481	848	0.898	749
0.198	391	0.583	935	0.953	533
0.277	554	0.681	969		
2-Methyl-2-chloropropane + 2-Butanol					
0.051	204	0.393	1205	0.790	1233
0.099	387	0.482	1333	0.894	912
0.198	712	0.581	1400	0.950	574
0.288	991	0.685	1371		
2-Methyl-2-chloropropane + 2-Methyl-1-propanol					
0.057	120	0.382	923	0.805	1042
0.105	263	0.489	1066	0.898	788
0.224	525	0.656	1137	0.952	511
0.297	751	0.728	1137		
2-Methyl-2-chloropropane + 2-Methyl-2-propanol					
0.078	483	0.373	1318	0.783	1238
0.120	663	0.472	1414	0.889	909
0.177	871	0.576	1439	0.942	585
0.274	1149	0.677	1390		

H^E; (3) The specific interaction between the Cl atom in chlorobutane and the OH group in butanol. This interaction, by itself, lead to negative H^E values, but it must be taken into account that solvents having specific interactions with OH groups are better hydrogen-bond breakers than inert ones.

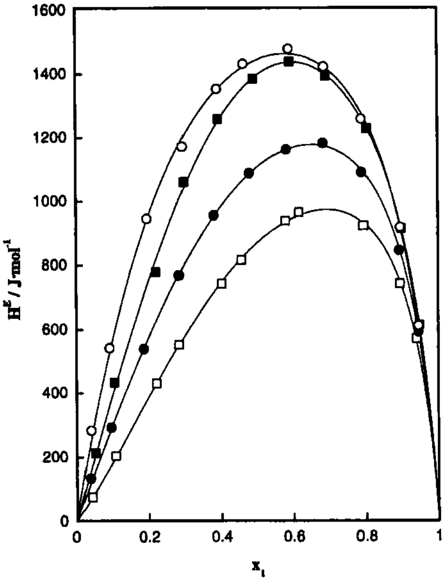

FIGURE 1 Excess molar enthalpies, H^E, of 1-chlorobutane(1)+an isomeric butanol(2) as a function of mole fraction x_1: (□) 1-butanol; (■) 2-butanol; (●) 2-methyl-1-propanol; (○) 2-methyl-2-propanol.

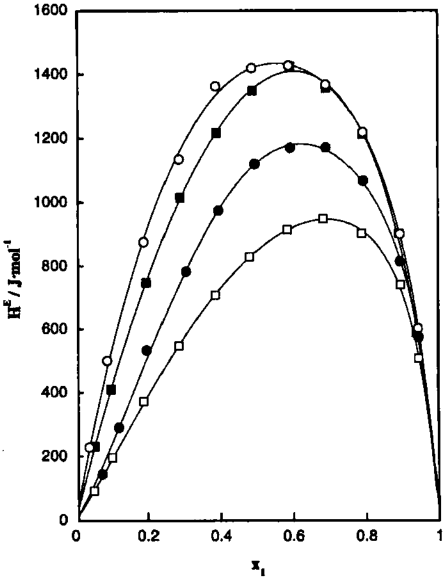

FIGURE 2 Excess molar enthalpies, H^E, of 2-chlorobutane(1)+an isomeric butanol(2) as a function of mole fraction x_1: (□) 1-butanol; (■) 2-butanol; (●) 2-methyl-1-propanol; (○) 2-methyl-2-propanol.

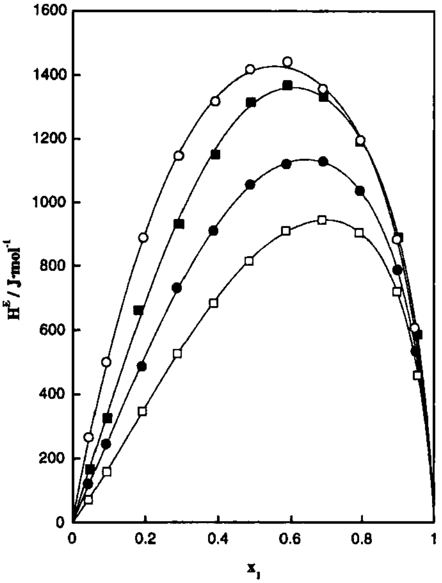

FIGURE 3 Excess molar enthalpies, H^E, of 2-methyl-1-chloropropane(1)+an isomeric butanol(2) as a function of mole fraction x_1: (□) 1-butanol; (■) 2-butanol; (●) 2-methyl-1-propanol; (○) 2-methyl-2-propanol.

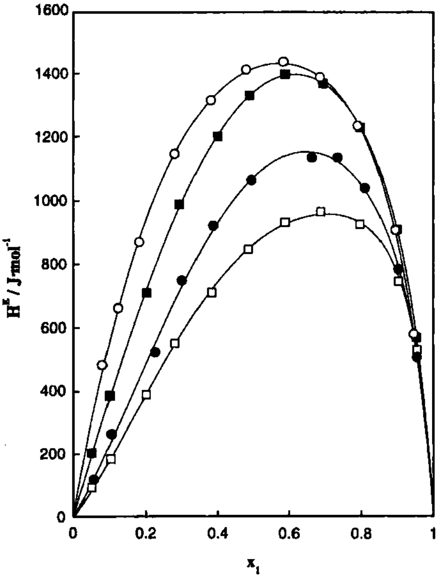

FIGURE 4 Excess molar enthalpies, H^E, of 2-methyl-2-chloropropane(1)+an isomeric butanol(2) as a function of mole fraction x_1: (□) 1-butanol; (■) 2-butanol; (●) 2-methyl-1-propanol; (○) 2-methyl-2-propanol.

TABLE III Parameters, A_i, and standard deviations, $\sigma(H^E)$, for Eq. (3)

System	A_0	A_1	A_2	A_3	$\sigma(H^E)$
1-Chlorobutane +					
1-Butanol	19349	−52137	60273	−25874	3
2-Butanol	21633	−54229	63810	−27217	7
2-Methyl-1-propanol	20245	−50641	55631	−22163	3
2-Methyl-2-propanol	17622	−30664	19303	480	7
2-Chlorobutane +					
1-Butanol	18708	−49980	57123	−24114	3
2-Butanol	16558	−31652	29643	−9995	6
2-Methyl-1-propanol	21540	−61780	80134	−37955	6
2-Methyl-2-propanol	19092	−41834	40704	−11777	6
2-Methyl-1-chloropropane +					
1-Butanol	17630	−45103	50221	−21218	1
2-Butanol	21514	−55672	66835	−29108	7
2-Methyl-1-propanol	18219	−44877	50857	−21615	2
2-Methyl-2-propanol	18073	−37846	35529	−9630	4
2-Methyl-2-chloropropane +					
1-Butanol	22409	−66346	81330	−35875	4
2-Butanol	20549	−49181	55338	−22738	2
2-Methyl-1-propanol	20171	−54081	66239	−30327	7
2-Methyl-2-propanol	16182	−26107	13978	2761	4

In the light of the results the prevailing interaction is the loss of the self-association, because the excess molar enthalpies are strongly dependent of the structure of butanols. For the mixtures containing 2-methyl-2-propanol and 2-butanol the hydrogen bonds are broken to a greater extent on the mixing process leading to a higher excess molar enthalpies than for the mixtures containing 1-butanol and 2-methyl-1-propanol. The breaking of dipolar interactions in chlorobutanes also contributes to the observed endothermic behaviour and is responsible for the greater H^E values in these mixtures when compared with mixtures of isomeric butanols with an aliphatic compound [18]. Finally the exothermic contribution due to the specific Cl−OH interaction is practically outweighed by the increase in the number of broken hydrogen bonds [19].

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