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Excess Molar Enthalpies of Chloro- or Methylcyclohexane + an Alkanol at 298.15 K

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Excess molar enthalpies H_m^E were measured as a function of mole fraction at 298.15 K and atmospheric pressure for the eight mixtures chlorocyclohexane or methylcyclohexane + methanol, ethanol, propan-1-ol, or propan-2-ol. The results are compared to H_m^E for cyclohexane + methanol, ethanol, propan-1-ol, or propan-2-ol, and the effect of the chloro and methyl groups is noted.

Introduction

We have previously reported H_m^E values for chlorobenzene or methylbenzene + methanol, ethanol, propan-1-ol, or propan-2-ol (Letcher *et al.*, 1993; Letcher *et al.*, 1991a). The aim of the work was to investigate the interaction between a chlorinated or methylated benzene and an alkanol, focusing on the role of the chloro group or the methyl group on the interactions. The H_m^E results implied that the chloro group did indeed have a small enhancing effect on the interaction between the chlorobenzene and the alkanol (Letcher *et al.*, 1993). The same was not true for the methyl group which had little influence on the magnitude of H_m^E for methylbenzene + methanol, ethanol, propan-1-ol, or propan-2-ol (Letcher *et al.*, 1991a). In this paper we report H_m^E for chlorocyclohexane or methylcyclohexane + methanol, ethanol, propan-1-ol, or propan-2-ol. The only difference between this set of mixtures and the previously reported set (Letcher *et al.*, 1991a, 1993) is that the benzene ring of one of the components has been replaced by a cyclohexane ring.

Experimental Section

The chlorocyclohexane (Janssen) and methylcyclohexane (Merck) were used without further purification and were quoted to be 98 and >99 mol % pure, respectively. The alkanols were dried and distilled as described before (Letcher *et al.*, 1990) and stored in a glovebox before use. Analysis by the Karl Fisher technique showed that the water contamination of each of the alkanols was less than 0.02 mol %.

The estimated error in the excess enthalpy (H_m^E) and mole fraction (x) is less than 3% and 0.1%, respectively, as judged from reproducibility experiments conducted on cyclohexane + heptane mixtures.

A ThermoMetric flow microcalorimeter 2277 was used to determine the H_m^E values. The temperature was accurate to 0.02 K and was monitored by a calibrated quartz thermometer fixed into the cell component.

Results and Discussion

The measured excess molar enthalpies H_m^E are given in Table 1. To each set of experimental values (except the methylcyclohexane + methanol system as it is not miscible over the whole mole fraction range) a polynomial of the type

$$\delta H_m^E/(\mathrm{J{\cdot}mol^{-1}}) = H_m^E/(\mathrm{J{\cdot}mol^{-1}}) - x(1-x)\sum_{r=0}^{r=k} A_r(1-2x)^r \quad (1)$$

was fitted by a method of unweighted least squares. The parameters A_r are given in Table 2.

The ethanol + methylcyclohexane system has been measured previously (Vesely *et al.*, 1975; Nagata and Yamada, 1974). Our results are in excellent agreement with the data reported by Vesely *et al.* and show a maximum variance of less than 2%. When compared with the data reported by Nagata and Yamada, our results show an average lower H_m^E of approximately 5−6% although the discrepancy at the low mole fraction of methylcyclohexane end of the system varies to a greater extent.

Vesely *et al.* (1975) also evaluated the propan-1-ol + methylcyclohexane system. Our results follow a form similar to their reported data and are within 10 J mol^{-1} at each end of the system. The maximum H_m^E from our investigation of this system is approximately 25 J mol^{-1} less than that Vesely *et al.* reported.

The propan-2-ol + methylcyclohexane system was investigated in 1978 by Nagata *et al.* In comparison our results again follow a similar form although our maximum is approximately 5% less than that reported by the earlier researchers.

The H_m^E values for all the mixtures we report are positive, with H_m^E(max) occurring at $0.65 < x < 0.75$ for chlorocyclohexane mixtures and at $0.55 < x < 0.65$ for methylcyclohexane mixtures. The H_m^E values for the related mixtures cyclohexane + methanol, ethanol, propan-1-ol, or propan-2-ol are positive (Letcher *et al.* 1991b) and are most likely a result of the disintegration on mixing of the hydrogen bonds between the alkanol molecules. A comparison of these results with the H_m^E values for the work reported here in Table 1 indicates that a similar process is responsible for the magnitude and sign of the excess enthalpies. This can be inferred from a comparison of H_m^E for equimolar mixtures of chlorocyclohexane or methylcyclohexane + methanol, ethanol, propan-1-ol, or propan-2-ol with the H_m^E values for equimolar mixtures of cyclohexane + ethanol, propan-1-ol, or propan-2-ol (Letcher *et al.*, 1991b) given in Table 3.

There is a significant difference between H_m^E values for chlorocyclohexane + methanol, ethanol, propan-1-ol, or propan-2-ol and the H_m^E values for methylcyclohexane + methanol, ethanol, propan-1-ol, or propan-2-ol. This can be seen at $x = 0.5$ in Table 3. From a comparison of the H_m^E for an equimolar mixture of chlorocyclohexane +

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Table 1. Excess Molar Enthalpies H_m^E for Chlorocyclohexane or Methylcyclohexane + an Alkanol and the Deviations δH_m^E Calculated from Eq 1 and Table 2 at 298.15 K

x	$H_m^E/(J\cdot mol^{-1})$	$\delta H_m^E/(J\cdot mol^{-1})$	x	$H_m^E/(J\cdot mol^{-1})$	$\delta H_m^E/(J\cdot mol^{-1})$	x	$H_m^E/(J\cdot mol^{-1})$	$\delta H_m^E/(J\cdot mol^{-1})$
			$x\ C_6H_{11}Cl + (1-x)\ CH_3OH$					
0.110	296.4	5.8	0.559	778.4	5.2	0.740	761.7	−7.8
0.240	517.5	−8.3	0.624	795.4	5.9	0.775	740.2	−2.1
0.252	544.4	2.2	0.724	774.4	−3.5	0.906	479.6	8.1
0.452	722.2	−1.1						
			$x\ C_6H_{11}CH_3 + (1-x)\ CH_3OH$					
0.018	73.1		0.126	334.9		0.799	404.4	
0.087	280.0		0.129	339.2		0.824	391.6	
0.088	294.1		0.146	354.7		0.845	374.6	
0.100	315.2		0.158	368.6		0.966	218.7	
			$x\ C_6H_{11}Cl + (1-x)\ CH_3CH_2OH$					
0.104	258.1	5.0	0.390	696.8	6.2	0.721	878.0	5.1
0.158	364.4	1.1	0.482	777.6	1.8	0.767	840.2	−5.3
0.210	450.0	−5.6	0.555	828.1	−1.9	0.826	768.2	3.3
0.279	555.2	−4.0	0.660	872.6	−4.0			
			$x\ C_6H_{11}CH_3 + (1-x)\ CH_3CH_2OH$					
0.105	216.5	0.6	0.538	552.3	5.7	0.705	547.5	−5.6
0.152	291.6	2.9	0.627	559.4	−0.6	0.751	536.0	0.8
0.301	435.7	−6.7	0.683	553.9	−3.7	0.809	494.6	4.6
0.457	525.9	3.3						
			$x\ C_6H_{11}Cl + (1-x)\ CH_3(CH_2)_2OH$					
0.103	230.6	−1.2	0.319	645.4	2.0	0.788	888.6	−1.1
0.128	297.6	6.0	0.455	767.0	0.9	0.824	855.5	2.2
0.183	409.3	−6.3	0.564	830.6	−1.6	0.899	664.4	−1.1
0.236	519.2	0.1	0.725	904.5	0.3			
			$x\ C_6H_{11}CH_3 + (1-x)\ CH_3(CH_2)_2OH$					
0.108	137.5	5.1	0.554	504.2	−0.3	0.776	530.0	−10.1
0.176	218.2	−0.8	0.625	539.9	7.5	0.855	470.7	0.9
0.296	338.9	−6.8	0.711	547.3	−3.5	0.912	362.6	8.7
0.460	462.9	4.2						
			$x\ C_6H_{11}Cl + (1-x)\ CH_3CH(OH)CH_3$					
0.097	370.0	6.2	0.319	894.7	7.0	0.569	1087.5	−2.8
0.138	490.4	−3.9	0.326	900.6	3.0	0.727	1085.1	5.2
0.195	646.8	−2.8	0.467	1041.1	3.3	0.816	958.8	−3.0
0.247	760.1	−5.1	0.471	1034.5	−6.3			
			$x\ C_6H_{11}CH_3 + (1-x)\ CH_3CH(OH)CH_3$					
0.093	209.8	2.3	0.315	534.4	1.8	0.572	724.6	−1.6
0.113	243.3	−1.5	0.392	610.0	−2.3	0.646	729.5	0.9
0.179	350.0	−4.1	0.396	613.0	−3.0	0.742	669.8	−2.4
0.233	435.6	4.3	0.491	694.0	3.8	0.756	659.0	1.9

[a] The results for methylcyclohexane + methanol relate only to miscible mixtures.

Table 2. Coefficients A_r and Standard Deviations σ^a for H_m^E {x ($C_6H_{11}Cl$ or $C_6H_{11}CH_3$) + (1 − x) ROH} at 298.15 K Calculated Using Eq 1

substituted cyclohexane	A_0	A_1	A_2	A_3	$\sigma/(J\cdot mol^{-1})$
		CH_3OH			
$C_6H_{11}Cl$	2295.2	−958.1	1913.6	−935.7	6.7
		CH_3CH_2OH			
$C_6H_{11}Cl$	3161.3	−1576.9	2040.0	−957.9	5.3
$C_6H_{11}CH_3$	2146.4	−585.2	1406.2	−535.0	5.2
		$CH_3(CH_2)_2OH$			
$C_6H_{11}Cl$	3178.3	−1211.4	2726.5	−2850.5	3.6
$C_6H_{11}CH_3$	1917.4	−986.1	1397.8	−1305.5	7.5
		$CH_3CH(OH)CH_3$			
$C_6H_{11}Cl$	4235.0	−1138.9	2602.0	−1630.3	5.8
$C_6H_{11}CH_3$	2782.4	−1168.5	791.4	194.0	3.3

[a] $\sigma = [\Sigma(H_m^E(\text{exptl}) - H_m^E(\text{calcd}))/(n-k)]^{1/2}$ where n is the number of experimental points.

Table 3. Excess Molar Enthalpies H_m^E{0.5 $C_6H_{11}X$ + 0.5 $C_jH_{2j+1}OH$} Where X = Cl, CH_3, or H and j = 1, 2, or 3

mixture	$H_m^E(x = 0.5)/(J\cdot mol^{-1})$	ref
$C_6H_{11}Cl + CH_3OH$	750	this work
$C_6H_{11}Cl + CH_3CH_2OH$	790	this work
$C_6H_{11}Cl + CH_3(CH_2)_2OH$	795	this work
$C_6H_{11}Cl + CH_3CH(OH)CH_3$	1057	this work
$C_6H_{11}CH_3 + CH_3OH$	480	this work[a]
$C_6H_{11}CH_3 + CH_3CH_2OH$	536	this work
$C_6H_{11}CH_3 + CH_3(CH_2)_2OH$	480	this work
$C_6H_{11}CH_3 + CH_3CH(OH)CH_3$	695	this work
$C_6H_{12} + CH_3CH_2OH$	637	Letcher *et al.* (1991b)
$C_6H_{12} + CH_3(CH_2)_2OH$	587	Letcher *et al.* (1991b)
$C_6H_{12} + CH_3CH(OH)CH_3$	806	Letcher *et al.* (1991b)

[a] Extrapolated value.

hexane (Letcher and Nevines, 1995) and H_m^E for an equimolar mixture of methylcyclohexane + hexane (Veselý *et al.*, 1975) (the values are 493 and 11 J mol^{-1}, respectively) it appears as though the significant difference mentioned above is due to the greater enthalpic effect of dissociation of chlorocyclohexane as compared to the enthalpy of dissociation of methylcyclohexane. The larger positive dissociation enthalpy is due to the polar nature of the chlorobenzene. A comparison of the H_m^E values for chlorocyclohexane + methanol, ethanol, propan-1-ol, or propan-2-ol with H_m^E values for cyclohexane + methanol, ethanol, propan-1-ol, or propan-2-ol at x = 0.5 in Table 3 shows that the effect of a chloro group attached to the cyclohexane ring results in an enhanced H_m^E. If there was a significant association between the chloro group and the hydrogen atom of an alkanol group, one would expect a reduced H_m^E. It appears then that there is little interaction between the chloro group of the chlorocyclohexane and the alkanol. Furthermore, the results indicate that the attachment of a methyl group to the cyclohexane ring contributes a small negative effect to H_m^E and is probably due to the enhanced London dispersive interactions as a result of the increased carbon number of one of the species.

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