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Excess molar volumes of chloro- or methylcyclohexane + an alkanol at 298.15 K

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Abstract

Excess molar volumes, V_m^E, were measured as a function of mole fraction at 298.15 K and atmospheric pressure for the seven mixtures (chloro- or methylcyclohexane + ethanol or propan-1-ol or propan-2-ol and chlorocyclohexane + methanol). The results are compared with V_m^E values for cyclohexane + alkanol and the effect of the chloro and methyl group is appraised.

Keywords: Excess molar volumes.

1. Introduction

We have previously reported the heat of mixing, H_m^E, for chloro-or methylcyclohexane + methanol or ethanol or propan-1-ol or propan-2-ol [1]. The intention of this work was to investigate the interaction between a chlorinated or methylated cyclohexane and an alkanol, concentrating on the role of the chloro and methyl group in the interactions. The H_m^E results did not reflect a significant interaction between the chlorocyclohexane or the methylcyclohexane and the alkanol [1]. The dominant effect appeared to be dissociation of the alkanol mixing. In this work, we report V_m^E for chloro-or methylcyclohexane + ethanol or propan-1-ol or propan-2-ol and chlorocyclohexane + methanol. The methylcyclohexane + methanol system was not evaluated as the mixture is not miscible over the whole mole fraction range.

2. Experimental

The chlorocyclohexane (Janssen) and methylcyclohexane (Merck) were used without further purification and were quoted to be 98% and > 99% pure respectively. The

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Table 1
Excess molar volumes, V_m^E, for chlorocyclohexane or methylcyclohexane + an alkanol and the deviations, δV_m^E, calculated from Eq. (1) and Table 2 at 298.15 K

x	V_m^E/ cm^3 mol^{-1}	$10^3 \times \delta V_m^E$/ cm^3 mol^{-1}	x	V_m^E/ cm^3 mol^{-1}	$10^3 \times \delta V_m^E$/ cm^3 mol^{-1}	x	V_m^E cm^3 mol^{-1}	$10^3 \times \delta V_m^E$ cm^3 mol^{-1}
$xC_6H_{11}Cl + (1-x)CH_3OH$								
0.023	0.0259	0.3	0.219	0.1338	−1.5	0.644	0.1311	−1.8
0.038	0.0427	2.3	0.262	0.1390	−3.5	0.664	0.1290	−1.7
0.053	0.0562	2.3	0.290	0.1451	−0.3	0.740	0.1185	−1.0
0.079	0.0772	2.9	0.372	0.1486	0.4	0.769	0.1120	−1.5
0.099	0.0882	0.5	0.444	0.1478	1.3	0.796	0.1048	−2.1
0.126	0.1021	−0.8	0.507	0.1471	3.7	0.895	0.0726	2.4
0.158	0.1168	−0.4	0.573	0.1414	2.3	0.933	0.0527	3.5
0.179	0.1239	−0.7						
$xC_6H_{11}Cl + (1-x)CH_3CH_2OH$								
0.028	−0.0042	−0.3	0.280	0.0270	−1.0	0.665	0.1093	−1.7
0.053	−0.0052	0.2	0.325	0.0386	0.1	0.734	0.1170	−0.3
0.071	−0.0045	0.9	0.379	0.0523	0.9	0.817	0.1228	0.1
0.107	−0.0016	1.8	0.426	0.0648	2.2	0.897	0.0887	2.0
0.139	0.0012	0.9	0.480	0.0730	−2.1	0.911	0.0805	1.5
0.176	0.0034	−2.8	0.556	0.0941	2.4	0.939	0.0570	−3.3
0.206	0.0114	−0.5	0.597	0.0991	−0.8			
$xC_6H_{11}CH_3 + (1-x)CH_3CH_2OH$								
0.037	0.0647	−5.8	0.368	0.4147	−1.7	0.701	0.3981	−3.7
0.132	0.2277	3.7	0.423	0.4256	−4.0	0.776	0.3591	−6.2
0.202	0.3132	4.8	0.480	0.4382	3.1	0.835	0.3180	0.4
0.251	0.3439	3.7	0.530	0.4393	4.7	0.931	0.1811	3.6
0.289	0.3827	3.1	0.587	0.4324	3.3	0.938	0.1660	3.0
0.330	0.3955	−6.1	0.641	0.4210	1.8			
$xC_6H_{11}Cl + (1-x)CH_3(CH_2)_2OH$								
0.040	−0.0161	2.5	0.288	−0.0086	−2.4	0.662	0.0935	0.0
0.078	−0.0245	3.4	0.337	0.0060	0.4	0.686	0.0982	−1.3

0.090	−0.0259	3.6	0.385	0.0177	−0.2	0.783	0.1081	−8.0
0.130	−0.0314	−0.3	0.435	0.0298	−1.2	0.842	0.1068	−7.3
0.172	−0.0297	−1.6	0.492	0.0468	0.4	0.918	0.0874	1.9
0.218	−0.0242	−3.1	0.542	0.0643	4.0	0.939	0.0775	7.3
0.248	−0.0159	−0.7	0.595	0.0815	6.3	0.944	0.0755	9.5
$x\mathrm{C_6H_{11}CH_3} + (1-x)\mathrm{CH_3(CH_2)_2OH}$								
0.067	0.0444	5.7	0.327	0.1725	−0.2	0.644	0.2476	−1.6
0.102	0.0638	4.3	0.362	0.1851	−0.5	0.699	0.2490	−1.3
0.134	0.0773	−1.0	0.426	0.2081	1.8	0.772	0.2379	−1.9
0.168	0.0996	2.1	0.465	0.2185	1.4	0.820	0.2168	−4.7
0.197	0.1027	−10.5	0.528	0.2351	3.2	0.905	0.1636	8.6
0.276	0.1518	0.3	0.582	0.2426	0.7	0.988	0.0237	−2.1
$x\mathrm{C_6H_{11}Cl} + (1-x)\mathrm{CH_3CH(OH)CH_3}$								
0.018	−0.0110	−2.3	0.302	0.0635	−2.5	0.678	0.2029	1.0
0.048	−0.0167	0.0	0.347	0.0808	−6.3	0.730	0.2051	−4.4
0.119	−0.0050	6.7	0.389	0.1077	1.9	0.811	0.1973	−7.4
0.139	−0.0010	5.0	0.434	0.1250	0.4	0.860	0.1770	−8.6
0.178	0.0061	−2.1	0.492	0.1508	3.9	0.927	0.1316	4.2
0.218	0.0212	−4.6	0.531	0.1647	4.1	0.940	0.1202	9.8
0.260	0.0444	−1.3	0.601	0.1869	4.1	0.951	0.1047	10.4
$x\mathrm{C_6H_{11}CH_3} + (1-x)\mathrm{CH_3CH(OH)CH_3}$								
0.023	0.0270	−2.5	0.285	0.3119	−2.0	0.573	0.4637	3.3
0.058	0.0739	0.2	0.330	0.3473	−1.6	0.629	0.4680	3.0
0.094	0.1205	2.6	0.357	0.3637	−4.0	0.713	0.4471	−3.4
0.121	0.1532	3.3	0.427	0.4095	0.3	0.768	0.4127	−9.5
0.197	0.2317	−1.1	0.469	0.4313	2.2	0.892	0.2765	1.2
0.249	0.2824	−0.4	0.528	0.4538	3.7	0.916	0.2369	8.0

alkanols were dried and distilled as described before [2] and stored in a glove box. Analysis by the Karl Fisher technique showed that the water contamination of each of the alkanols was less than 0.02 mol%. An Anton Paar DMA 601 vibrating tube densitometer was used to determine the V_m^E values.

3. Results

The measured excess molar volumes V_m^E are given in Table 1. To each set of experimental values, a polynomial of the type

$$\delta V_m^E/(\mathrm{cm^3\,mol^{-1}}) = V_m^E/(\mathrm{cm^3\,mol^{-1}}) - x(1-x)\sum_{r=0}^{r=k} A_r(1-2x)^r \qquad (1)$$

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

Table 2
Coefficients A_r and standard deviations σ^a for $x\{C_6H_{11}Cl$ or $C_6H_{11}CH_3\} + (1-x)ROH$ at 298.15 K by Eq. (1)

Substituted cyclohexane	A_0	A_1	A_2	A_3	$\sigma \times 10^2$/ cm^3 mol
			CH_3OH		
$C_6H_{11}Cl$	0.5752	0.1123	0.4554	0.0487	0.2
			CH_3CH_2OH		
$C_6H_{11}Cl$	0.3184	−0.4476	0.2072	−0.2670	0.2
$C_6H_{11}CH_3$	1.7417	0.0041	0.8454	−0.6201	0.5
			$CH_3(CH_2)_2OH$		
$C_6H_{11}Cl$	0.1945	−0.5510	0.2637	−0.5084	0.5
$C_6H_{11}CH_3$	0.9030	−0.4658	0.4884	−0.3807	0.5
			$CH_3CH(OH)CH_3$		
$C_6H_{11}Cl$	0.5991	−0.7198	0.2853	−0.7404	0.6
$C_6H_{11}CH_3$	1.7646	−0.7081	0.5907	−0.3634	0.4

[a] $\sigma = \left[\sum(V^E_{m(expt)} - V^E_{m(calc)}{}^2/(n-k)\right]^{1/2}$ where n is the number of experimental points.

Table 3
Excess molar volumes $V_m^E\{0.5C_6H_{11}X + 0.5C_jH_{2j+1}OH\}$where X is Cl or CH_3 or H and j = 1,2 or 3

Mixture	$V_m^E(x = 1)/cm^3\ mol^{-1}$	Reference
$C_6H_{12} + CH_3CH_2OH$	0.56	[6]
$C_6H_{12} + CH_3(CH_2)_2OH$	0.41	[6]
$C_6H_{12} + CH_3CH(OH)CH_3$	0.56	[6]
$C_6H_{11}CH_3 + CH_3CH_2OH$	0.44	This work
$C_6H_{11}CH_3 + CH_3(CH_2)_2OH$	0.23	This work
$C_6H_{11}CH_3 + CH_3CH(OH)CH_3$	0.44	This work
$C_6H_{11}Cl + CH_3OH$	0.14	This work
$C_6H_{11}Cl + CH_3CH_2OH$	0.08	This work
$C_6H_{11}Cl + CH_3(CH_2)_2OH$	0.05	This work
$C_6H_{11}Cl + CH_3CH(OH)CH_3$	0.15	This work

4. Discussion

The V_m^E values for (chlorocyclohexane + an alkanol) are sinusoidal for three of the four mixtures reported here. V_m^E is relatively small in all cases at low alkanol concentrations, the dissociation of the alkanol is the dominant feature resulting in a positive V_m^E value for each of the four alkanols. At low chlorocyclohexane concentrations, the situation is more complex and V_m^E is positive for methanol but negative for the other three alkanols. The negative contribution to the V_m^E could be a result of the chlorocyclohexane associating with the alkanol or as a result of the chlorocyclohexane fitting in between the matrix defined by the alkanol self-association.

The V_m^E values for (methylcyclohexane + an alkanol) are positive over the whole composition range for each of the three systems discussed here and V_m^E(max) occurs at $0.55 < x < 0.75$. The skewness of V_m^E again reflects the domination of the dissociation of the alkanol at low alkanol concentrations.

In an attempt to perceive the effect of the chloro and methyl groups on V_m^E for the mixtures addressed here, it is pertinent to compare the results with V_m^E for (cyclohexane + an alkanol). These results have been reported by various workers [3–6] and the values of V_m^E for equimolar mixtures of (cyclohexane + methanol or ethanol or propan-1-ol or propan-2-ol) obtained from the literature together with the V_m^E results for equimolar mixtures of (chloro-or methylcyclohexane + ethanol or propan-1-ol or propan-2-ol and chlorocyclohexane + methanol) reported here are agiven in Table 3.

The addition of a CH_3 group to cyclohexane results in a minor diminution in V_m^E whilst the addition of a Cl group to cyclohexane results in a larger diminution which is always greater than $0.35\ cm^3\ mol^{-1}$ at $x = 0.5$. This again could be a result of the association of Cl---H dissociation but could also be a result of packing.

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