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Excess Molar Enthalpies of an Alkanol + a Cyclic Ether at 298.15 K

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Excess molar enthalpies H_m^E measured at 298.15 K using a flow calorimeter are reported for 12 mixtures of methanol, ethanol, propan-1-ol, or propan-2-ol + tetrahydrofuran (THF), + tetrahydropyran (THP), or + 1,4-dioxane. For all of the systems investigated, H_m^E is strongly positive over the whole mole fraction range and increases in the order methanol < ethanol < propan-1-ol < propan-2-ol. H_m^E(maximum) depends on both the size of the cycloether ring and the number of carbon atoms in the alkanol molecule. The results are explained in terms of the strong self-association exhibited by the alkanol and the cross-association of the O···HO specific interaction.

Introduction

The present work forms part of a program involved in the study of the thermodynamic behavior of some binary systems in which specific interactions between unlike molecules can occur (Letcher et al., 1994a,b; Letcher and Domanska, 1994). We have recently reported the excess molar enthalpies of an alkanol + a branched chain ether at 298.15 K, and the results suggested a relatively strong association between the alkanol and the ether (Letcher and Govender, 1995). We have extended our investigation to include cycloethers.

We have determined H_m^E for methanol, ethanol, propan-1-ol, or propan-2-ol + tetrahydrofuran (THF), + tetrahydropyran (THP), or + 1,4-dioxane}. In interpreting our results we have considered, for the sake of comparison, H_m^E for alkanol + cyclohexane (Nagata and Kazuma, 1977; Battler et al., 1985; Dai and Chao, 1985a), and cycloether + heptane binary mixtures (Inglese et al., 1980).

The degree of interaction between the hydroxyl group in the alkanol and the oxygen atom(s) in the ether depends on the structure and properties of the respective alkanol and ether. The short chain alkanols (methanol, ethanol, propan-1-ol, or propan-2-ol) are strongly self-associated and exhibit intermolecular hydrogen bonding while the cycloethers exert an influence by ring size and shape (Dincer and Van Ness, 1971; Searles and Tamres, 1951).

Experimental Section

The alkanols were dried and distilled as described elsewhere (Riddick et al., 1986) and stored in a glovebox prior to use. THF, THP, and 1,4-dioxane were supplied by Jannsen Chimica with purities exceeding 99.9%. Each of the cyclic ethers was distilled, dried, and degassed before use as previously described (Letcher and Domańska, 1994). The mole fraction of water in each of the liquids was determined by a Karl Fischer titration to be <0.01 mol %. The solvents were kept in a drybox before use. GLC was used to determine the purities of each of the pure liquids. The purity was found to be better than 99.8 mol % for each of the liquids.

A ThermoMetric flow microcalorimeter (2277) was used to determine the molar enthalpies of mixing. All the measurements were made at constant temperature [(298.15 ± 0.01) K]. The calibration and experimental determinations have been described elsewhere (Letcher and Scoones, 1982; Letcher et al., 1994a). A calibrated platinum thermometer and also a calibrated quartz thermometer were used to monitor the temperature which was based on the 1968 temperature scale. The uncertainty in mole fraction is estimated to be ±0.001 and was determined from weighing the pure components and pump reservoirs. These uncertainties were also based on the assumption that the pumps could deliver a steady mixture to at least the same uncertainty as ±0.001 mole fraction. The steadiness of the heat signal confirmed this at least for mixtures in the range $0.1 < x > 0.9$. For very dilute or very concentrated mixtures the estimated uncertainty in mole fraction was probably no better than 0.005. The performance of the calorimeter was checked by measuring H_m^E of the test mixture (benzene + cyclohexane). Agreement with literature results (Elliott and Wormald, 1976) was always within 1%. We estimate that the experimental precision of our results for $0.1 < x > 0.9$ is always better than 1.5% or 10 J·mol^{01}, whichever is the largest. The estimated precision was obtained by comparing 10 results for similar mixtures done at different times but under similar conditions.

Results and Discussion

The H_m^E results are given in Table 1, together with the deviations δH_m^E calculated from the smoothing equation

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

The values of the parameters A_r are given in Table 2.

H_m^E for all mixtures of methanol, ethanol, propan-1-ol, or propan-2-ol + THF, + THP, or + 1,4-dioxane are positive over the whole alkanol mole fraction range with H_m^E (maximum) decreasing in the order: 1,4-dioxane >>> THP ≥ THF. For each of the ethers investigated in this work, H_m^E(maximum) increases with increased chain length of the alkanol.

H_m^E values for six of the twelve mixtures presented here have been reported previously. We have repeated the measurements reported in the literature because some of the results are very different from ours. The $H_m^E(x = 0.5)$ smoothed results reported here for methanol, ethanol, or propan-1-ol + THF are 532, 791, and 933 J·mol^{-1}, respectively, while those of Chao and Dai (1989) are 531, 826, and 946 J·mol^{-1}, respectively. Our $H_m^E(x = 0.5)$ smoothed result for the methanol + THF binary system is 532 J·mol^{-1}

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Table 1. Experimental Excess Molar Enthalpies, H^E_m, for the Binary Mixtures x $C_jH_{2j+1}OH$ + (1 − x) ROR′ and the deviations, δH^E_m, Calculated from Eq 1 and Table 2 at 298.15 K

x	H^E_m/(J·mol^{-1})	δH^E_m/(J·mol^{-1})	x	H^E_m/(J·mol^{-1})	δH^E_m/(J·mol^{-1})	x	H^E_m/(J·mol^{-1})	δH^E_m/(J·mol^{-1})
				Methanol + Tetrahydrofuran				
0.072	200.5	−9	0.309	540.4	4	0.787	265.7	2
0.098	271.0	1	0.329	548.3	4	0.858	183.9	10
0.136	340.6	−3	0.418	544.3	−11	0.909	99.6	−7
0.178	415.8	3	0.586	473.1	−3	0.932	70.7	−7
0.218	463.8	0	0.664	404.6	−1	0.951	50.9	−5
				Methanol + Tetrahydropyran				
0.081	302.5	4	0.295	671.3	−4	0.625	589.1	5
0.123	423.3	7	0.315	685.6	−1	0.699	493.7	−11
0.168	510.8	−4	0.375	703.8	−2	0.778	399.9	−5
0.206	570.9	−8	0.430	706.5	3	0.845	309.8	4
0.247	641.1	7	0.555	649.0	7	0.921	175.6	5
				Methanol + 1,4-Dioxane				
0.081	370.0	−4	0.300	1018.9	−9	0.692	904.0	3
0.129	560.2	−4	0.322	1061.5	0	0.748	799.9	12
0.159	668.6	−4	0.360	1107.7	2	0.848	549.9	12
0.197	795.7	3	0.435	1130.7	−13	0.889	409.1	−2
0.202	816.6	9	0.586	1039.5	−23	0.924	292.8	−5
0.258	948.0	−0	0.671	939.7	−1	0.950	179.6	−20
				Ethanol + Tetrahydrofuran				
0.059	220.0	−5	0.376	809.0	5	0.774	475.5	1
0.101	366.6	5	0.400	808.9	−0	0.822	393.0	3
0.148	490.9	1	0.522	777.0	−0	0.865	317.7	9
0.194	599.8	4	0.629	680.3	−0	0.891	251.8	−3
0.229	646.1	−12	0.665	630.8	−4	0.911	202.7	−9
0.327	780.0	2						
				Ethanol + Tetrahydropyran				
0.077	360.2	−9	0.321	821.9	−1	0.667	706.7	0
0.121	520.8	7	0.373	849.2	1	0.693	659.0	−9
0.165	625.9	4	0.462	853.2	−2	0.749	571.9	−0
0.179	651.2	2	0.481	855.1	2	0.787	494.6	−3
0.218	717.2	−0	0.521	837.0	−0	0.841	360.4	7
0.260	763.4	−7	0.600	791.6	9	0.905	222.9	−1
				Ethanol + 1,4-Dioxane				
0.072	462.8	3	0.336	1407.5	−3	0.758	1130.1	7
0.100	600.0	−11	0.429	1525.2	7	0.783	1045.7	0
0.145	830.7	2	0.502	1530.1	−1	0.831	863.9	−6
0.148	850.8	8	0.581	1471.1	−10	0.867	721.9	1
0.196	1029.9	−7	0.645	1395.8	4	0.898	581.4	1
0.220	1115.8	−4	0.682	1309.9	−8	0.935	383.6	−3
0.230	1160.4	9	0.729	1215.5	9	0.937	376.4	−1
				Propan-1-ol + Tetrahydrofuran				
0.074	309.7	17	0.370	916.2	−2	0.580	874.3	−5
0.112	415.3	−7	0.433	940.7	−1	0.665	784.1	3
0.151	540.6	1	0.450	952.3	9	0.734	665.8	−6
0.216	693.2	−11	0.476	951.4	11	0.789	571.4	2
0.261	791.1	0	0.507	922.7	−6	0.840	456.7	−1
0.329	885.1	0	0.525	920.1	−0	0.939	204.0	5
				Propan-1-ol + Tetrahydropyran				
0.050	200.9	−8	0.269	800.0	−2	0.779	552.4	6
0.080	336.2	14	0.345	902.4	8	0.848	400.0	9
0.096	374.4	−4	0.447	929.1	−5	0.874	324.6	−5
0.157	564.8	−0	0.549	898.7	7	0.906	243.5	−5
0.191	651.5	1	0.615	815.7	−8	0.951	128.6	−1
0.217	701.9	−5	0.711	674.8	−3			
				Propan-1-ol + 1,4-Dioxane				
0.055	405.9	6	0.387	1800.0	0	0.733	1407.8	−6
0.077	555.8	8	0.446	1851.7	0	0.817	1097.4	11
0.140	783.1	−0	0.466	1852.8	−4	0.870	820.9	−9
0.159	1025.0	−13	0.547	1820.2	−1	0.900	675.0	5
0.192	1209.0	4	0.585	1772.1	−1	0.926	518.3	8
0.253	1451.5	−11	0.672	1598.1	2	0.939	415.9	−13
0.321	1690.1	17						
				Propan-2-ol + Tetrahydrofuran				
0.022	150.1	32	0.330	1060.9	−2	0.756	815.6	0
0.087	400.0	−19	0.404	1121.4	3	0.820	676.4	1
0.130	600.1	8	0.494	1120.0	3	0.854	575.4	−8
0.188	790.8	9	0.604	1040.8	3	0.881	499.4	−3
0.223	870.5	−4	0.690	922.6	−4	0.980	140.6	38
0.257	942.0	−8						

Table 1 (Continued)

x	H^E_m/(J·mol^{-1})	δH^E_m/(J·mol^{-1})	x	H^E_m/(J·mol^{-1})	δH^E_m/(J·mol^{-1})	x	H^E_m/(J·mol^{-1})	δH^E_m/(J·mol^{-1})
			Propan-2-ol + Tetrahydropyran					
0.050	265.0	−12	0.300	1040.6	4	0.641	975.9	−4
0.090	451.1	−9	0.400	1120.0	−2	0.680	914.4	−3
0.103	519.4	4	0.447	1124.5	−5	0.756	778.6	13
0.150	700.2	9	0.500	1112.6	−4	0.835	570.9	5
0.207	862.8	7	0.544	1098.9	9	0.862	478.9	−8
0.228	899.3	−6	0.622	1002.9	−3	0.936	236.5	−6
			Propan-2-ol + 1,4-Dioxane					
0.045	375.1	4	0.390	2000.7	31	0.780	1520.3	9
0.071	561.9	−0	0.451	2053.5	9	0.816	1352.2	6
0.110	835.1	2	0.534	2045.7	−14	0.851	1164.2	9
0.153	1092.7	−1	0.579	2020.4	−7	0.900	839.1	−4
0.225	1467.8	3	0.673	1845.3	−19	0.942	515.3	−10
0.252	1565.9	−12	0.741	1676.1	12	0.963	326.0	−17
0.323	1802.2	−14						

Table 2. Coefficients A_r and Standard Deviations σ[a] for an Alkanol + a Cyclic Ether at 298.15 K Calculated Using Eq 1

cyclic ether	A_0	A_1	A_2	A_3	σ/(J·mol^{-1})
		Methanol			
tetrahydrofuran	2126.6	932.9	82.5	208.5	6
tetrahydropyran	2709.4	1051.7	676.8	−93.5	7
1,4-dioxane	4538.0	951.2	112.0	−705.8	11
		Ethanol			
tetrahydrofuran	3163.1	1024.6	207.2	−313.0	6
tetrahydropyran	3386.6	701.9	648.8	1181.5	5
1,4-dioxane	6133.9	387.9	640.7	−209.6	7
		Propan-1-ol			
tetrahydrofuran	3731.5	784.9	166.3	−445.1	8
tetrahydropyran	3686.7	882.4	−68.7	−11.7	7
1,4-dioxane	7416.0	700.4	271.3	−808.3	9
		Propan-2-ol			
tetrahydrofuran	4456.4	813.1	975.0	−934.7	16
tetrahydropyran	4469.7	908.0	590.0	23.2	8
1,4-dioxane	8263.7	−169.3	1060.0	−678.6	14

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

which agrees well with the result of Matous et al. (1972), which is 529 J·mol^{-1}, but not with the result of Arm et al. (1966), which is 462 J·mol^{-1}, and of Keller et al. (1992), which is 479 J·mol^{-1}.

The $H^E_m(x = 0.5)$ smoothed results presented here for methanol, ethanol, or propan-1-ol + 1,4-dioxane) are 1135, 1534, and 1854 J·mol^{-1}, respectively, and are very different from those of Dai and Chao (1985), which are 955, 1201, and 1435 J·mol^{-1}, respectively. Our $H^E_m(x = 0.5)$ smoothed result for the methanol + 1,4-dioxane mixture of 1135 J·mol^{-1} is greater than the result of Singh et al. (1976) (at 30 °C) and Kortum and Valent (1977) (at 25 °C) of 1040 J·mol^{-1}. Our $H^E_m(x = 0.5)$ result for the ethanol + 1,4-dioxane mixture is 1534 J·mol^{-1} while that of Belousov et al. (1970) is 1456 J·mol^{-1}. To confirm our technique and method, we remeasured H^E_m for benzene + cyclohexane and again compared our results to those in the literature (Elliott and Wormald, 1976). In all cases our smoothed results are within 5 J·mol^{-1} of the literature values. We have also repeated the present work a number of times, H^E_m for methanol, ethanol, or propan-1-ol + 1,4 dioxane at $0.4 < x > 0.5$ at least three times. These results which are not included in Table 1 were always within 10 J of the smooth curve obtained from the data in Table 1. The previous results for dioxane systems are lower than the present results. It is possible that the dioxane in the earlier work had reacted with light.

From Table 3, it can be seen that the result of $H^E_m(x = 0.5)$ for an alkanol + a cycloether is less endothermic than the sum of the corresponding $H^E_m(x = 0.5)$ for alkanol + cyclohexane and $H^E_m(x = 0.5)$ for cycloether + heptane mixtures (Nagata and Kazuma, 1977; Battler et al., 1985; Dai and Chao, 1985a; Inglese et al. (1980). This suggests that the H^E_m reported here depends on three effects, i.e., positive contributions from the disruption of alkanol−alkanol hydrogen bonds and ether−ether interactions and a negative contribution from the ether−alkanol interaction. The latter enthalpic contribution, $H_{\text{int}}(x = 0.5)$ can be

Table 3. Excess Molar Enthalpies: $A = H^E_m(0.5C_jH_{2j+1}OH + 0.5ROR')$ and $B = H^E_m(0.5C_jH_{2j+1}OH + 0.5c\text{-}C_6H_{12})$ for j = 1, 2, or 3; $C = H^E_m(0.5ROR' + 0.5C_7H_{16})$; $H_{\text{int}} = A - B - C$

	H^E_m/J·mol^{-1}						
ether	A	ref	B	ref	C	ref	$A - B - C$
				CH_3OH			
C_4H_8O	532	this work	449	Dai and Chao (1985a)	791	Inglese et al. (1980)	−708
$C_5H_{10}O$	677	this work	449	Dai and Chao (1985a)	598	Inglese et al. (1980)	−370
$C_4H_8O_2$	1135	this work	449	Dai and Chao (1985a)	1642	Inglese et al. (1980)	−956
				C_2H_5OH			
C_4H_8O	791	this work	622	Nagata and Kazuma (1977)	791	Inglese et al. (1980)	−622
$C_5H_{10}O$	847	this work	622	Nagata and Kazuma (1977)	598	Inglese et al. (1980)	−373
$C_4H_8O_2$	1534	this work	622	Nagata and Kazuma (1977)	1642	Inglese et al. (1980)	−730
				C_3H_7OH			
C_4H_8O	933	this work	565	Nagata and Kazuma (1977)	791	Inglese et al. (1980)	−423
$C_5H_{10}O$	922	this work	565	Nagata and Kazuma (1977)	598	Inglese et al. (1980)	−241
$C_4H_8O_2$	1854	this work	565	Nagata and Kazuma (1977)	1642	Inglese et al. (1980)	−353
				$CH_3CH(OH)CH_3$			
C_4H_8O	1141	this work	767	Battler et al. (1985)	791	Inglese et al. (1980)	−417
$C_5H_{10}O$	1117	this work	767	Battler et al. (1985)	598	Inglese et al. (1980)	−248
$C_4H_8O_2$	2066	this work	767	Battler et al. (1985)	1642	Inglese et al. (1980)	−343

semiquantitatively obtained by use of the following expression (Diogo et al., 1993):

$$H_{\text{int}} = A - B - C \qquad (2)$$

where $A = H_m^E(0.5C_jH_{2j+1}OH + 0.5ROR')$ and $B = H_m^E(0.5C_jH_{2j+1}OH + 0.5c\text{-}C_6H_{12})$ for $j = 1$, 2, or 3 and $C = H_m^E(0.5ROR' + 0.5C_7H_{16})$.

The values of A, B, C, and H_{int} are shown in Table 3. The negative value of H_{int} indicates an association between the alkanol and the ether. A similar method of analysis was done for an alkanol + a branched ether (Letcher and Govender, 1995). The interaction between an alkanol and a cycloether is generally greater than that between an alkanol and a branched ether. This is no doubt a result of the higher degree of exposure of the oxygen atom in the cycloether molecule as opposed to the branched ether molecule in which the oxygen atom is shielded by hydrocarbon groups.

A detailed analysis into the interactions occurring in the systems reported here will be carried out using the ERAS model of Heintz et al. (1985). The results will be reported when measurements of V_m^E for the same set of mixtures have been determined, together with the α_p (isobaric thermal coefficient) and κ_T (isothermal expansion coefficient) pure component properties which are now being measured at Professor Ahluwalia's laboratory in New Delhi by U.P.G.

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