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THERMOCHEMICAL BEHAVIOUR OF MIXTURES OF *n*-ALCOHOL + ALIPHATIC ETHER: HEAT CAPACITIES AND VOLUMES AT 298.15 K *

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ABSTRACT

Molar excess volumes V^E at 298.15 K were obtained as a function of mole fraction for each of the binary mixtures formed from methyl *n*-butylether, 3,6-dioxaoctane, and 2,5,8-trioxanonane + methanol, and + ethanol, and also for 2,5,8-trioxanonane + 1-propanol. In addition, a Picker flow calorimeter was used to determine molar excess heat capacities C_p^E at 298.15 K for the same mixtures. All the excess heat capacities are positive and the excess volumes are negative. Values of V^E of mixtures with a given ether become less negative with increasing chain length of the alcohol.

INTRODUCTION

In this paper we report measurements of molar excess heat capacities and excess volumes of seven binary mixtures: methyl *n*-butylether [$CH_3O(CH_2)_3CH_3$] + methanol, + ethanol, 3,6-dioxaoctane [1,2-diethoxyethane, or ethyleneglycol diethylether, $CH_3CH_2O(CH_2)_2OCH_2CH_3$] + methanol, + ethanol, and 2,5,8-trioxanonane [diethyleneglycol dimethylether or diglyme, $CH_3O(CH_2)_2O(CH_2)_2OCH_3$] + methanol, + ethanol, and + 1-propanol. The results will enlarge the data basis for our current studies [1] concerning binary mixtures of ethers and alcohols, thus contributing to our efforts within the frame of the TOM project [2–4]. Excess enthalpies for these mixtures have been reported elsewhere [1].

EXPERIMENTAL

The pure substances used in this work were obtained as summarized previously together with their densities at 298.15 K [1]. Our measured molar heat capacities C_p at 298.15 K for the alcohols are in agreement, though higher, with the recent

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literature data [5,6]: we found values of 81.92, 113.75 and 146.88 J K^{-1} mole^{-1} for methanol, ethanol and 1-propanol, respectively. For the aliphatic ethers the following values were obtained: 192.48, 261.08 and 279.84 J K^{-1} mole^{-1} for methyl *n*-butyl ether, 3,6-dioxaoctane, and 2,5,8-trioxanonane, respectively; no literature data were found for comparison.

Binary mixtures were prepared by mass. Densities ρ were measured with a vibrating-tube densimeter [7] from Sodev (model 02D). Before each series of measurements the instrument was calibrated with doubly distilled and degassed water ρ (298.15 K) = 997.047 kg m^{-3} [8] and "vacuum". Molar excess volumes $V^E = V_m - xV_1 - (1-x)V_2$ were determined according to

$$V^E = xM_1(\rho_m^{-1} - \rho_1^{-1}) + (1-x)M_2(\rho_m^{-1} - \rho_2^{-1}) \qquad (1)$$

where V_i, M_i, ρ_i denote, respectively, the molar volume, the molar mass and the density of pure component i, x being the mole fraction of component 1; quantities with subscript m refer to the mixture.

Heat capacities per unit volume C_p/V were determined with a Picker flow calorimeter [9,10] from Setaram using the stepwise procedure. Excess heat capacities were calculated from

$$C_p^E = C_{p\,m} - xC_{p\,1} - (1-x)C_{p\,2} \qquad (2)$$

where C_p, with the appropriate subscript, is the molar heat capacity of pure component i or mixture m.

Details of the experimental technique and accuracy attainable with these instruments in the case of non-electrolyte mixtures may be found in previous publications [11,12] The imprecision of the values of the molar excess heat capacities is estimated to be about ± 0.03 J K^{-1} mole^{-1}; however, for mixtures with the more volatile liquids the imprecision is expected to be higher as shown by the standard deviation σ in Table 2.

RESULTS AND DISCUSSION

Results for the mixtures are contained in Table 1 along with the mole fraction x of the alcohol. For each mixture, the excess quantities were fitted with a smoothing function of type

$$Q^E = x(1-x)\sum_{i=0}^{n-1} A_i(1-2x)^i \qquad (3)$$

by the method of (unweighted) least squares, where either $Q^E = V^E$ (cm^3 mole^{-1}) or $Q^E = C_p^E$(J K^{-1} mole^{-1}). The coefficients A_i and the corresponding standard deviations are given in Table 2.

As expected for this type of mixture, C_p^E is positive and rather large. For a given alcohol, the curves become more symmetric when the number of ether oxygen groups is increased. For a given ether, there is a marked increase in C_p^E when going

TABLE 1

Molar excess volumes V^E and molar excess heat capacities C_p^E for alcohol+aliphatic ether at 298.15 K

x	V^E (cm^3 mole^{-1})	C_p^E (J K^{-1} mole^{-1})	x	V^E (cm^3 mole^{-1})	C_p^E (J K^{-1} mole^{-1})
x $CH_3OH+(1-x)$ $CH_3O(CH_2)_3CH_3$			x $CH_3CH_2OH+(1-x)$ $CH_3O(CH_2)_3CH_3$		
0.1149	−0.160	3.485	0.1182	−0.082	3.263
0.1701	−0.211	4.572	0.1573	−0.198	4.656
0.2548	−0.260	5.639	0.2627	−0.231	6.627
0.3406	−0.282	5.829	0.3781	−0.249	7.815
0.5396	−0.278	4.540	0.4621	−0.249	7.807
0.6585	−0.241	4.088	0.5613	−0.238	6.242
0.7497	−0.184	2.806	0.6568	−0.214	5.515
0.8414	−0.120	2.016	0.7578	−0.174	4.196
			0.8228	−0.139	3.310
x $CH_3OH+(1-x)$ $CH_3CH_2O(CH_2)_2OCH_2CH_3$			x $CH_3CH_2OH+(1-x)$ $CH_3CH_2O(CH_2)_2OCH_2CH_3$		
0.1587	−0.368	1.949	0.1556	−0.210	2.921
0.2789	−0.561	3.120	0.3201	−0.368	5.124
0.4193	−0.682	3.565	0.4326	−0.401	5.249
0.5184	−0.713	3.461	0.5099	−0.416	5.386
0.6125	−0.697	3.128	0.6031	−0.409	5.045
0.7373	−0.595	2.382	0.7276	−0.358	4.044
0.8361	−0.450	1.703			
0.9180	−0.257	0.955			
x $CH_3OH+(1-x)$ $CH_3O(CH_2)_2O(CH_2)_2OCH_3$			x $CH_3CH_2OH+(1-x)$ $CH_3O(CH_2)_2O(CH_2)_2OCH_3$		
0.1848	−0.337	2.532	0.1215	−0.079	1.430
0.3271	−0.509	3.528	0.2544	−0.156	3.007
0.4247	−0.580	3.663	0.3378	−0.199	3.862
0.5142	−0.644	3.696	0.4228	−0.224	4.307
0.6150	−0.655	3.406	0.5392	−0.248	4.655
0.7157	−0.609	2.863	0.6321	−0.248	4.447
0.8628	−0.430	1.700	0.7349	−0.228	3.722
			0.8601	−0.145	2.205
x $CH_3(CH_2)_2OH+(1-x)$ $CH_3O(CH_2)_2O(CH_2)_2OCH_3$					
0.1345	−0.027	1.672			
0.2185	−0.036	2.493			
0.3170	−0.049	3.372			
0.4131	−0.061	4.070			
0.4908	−0.066	4.407			
0.5883	−0.068	4.603			
0.6869	−0.079	4.391			
0.7942	−0.051	3.658			
0.8910	−0.031	2.618			

from methanol to ethanol, whereas the increment between ethanol and 1-propanol is almost zero.

Excess volumes are negative in all cases, becoming more negative the smaller the *n*-alcohol. This parallels to some extent the trend observed for the excess enthalpies,

TABLE 2

Coefficients A_i and standard deviations σ for least-squares representation by eqn (3) of V^E(cm^3 mole^{-1}) and C_p^E(J K^{-1} mole^{-1}) at 298.15 K

System	Function Q^E	A_0	A_1	A_2	A_3	σ
$(1-x)$ $CH_3O(CH_2)_3CH_3 + x$ CH_3OH	V^E(cm^3 mole^{-1})	−1.146	−0.294	−0.123	−0.325	0.0007
	C_p^E(J K^{-1} mole^{-1})	20.446	13.521	7.783		0.56
$(1-x)$ $CH_3O(CH_2)_3CH_3 + x$ CH_3CH_2OH	V^E(cm^3 mole^{-1})	−1.026	0.218			0.006
	C_p^E(J K^{-1} mole^{-1})	29.270	11.093	−3.895		0.10
$(1-x)$ $CH_3CH_2O(CH_2)_2OCH_2CH_3 + x$ CH_3OH	V^E(cm^3 mole^{-1})	−2.846	0.277	−0.367	0.200	0.0008
	C_p^E(J K^{-1} mole^{-1})	14.081	4.421	−1.144	−5.693	0.01
$(1-x)$ $CH_3CH_2O(CH_2)_2OCH_2CH_3 + x$ CH_3CH_2OH	V^E(cm^3 mole^{-1})	−1.673	0.174	−0.195		0.002
	C_p^E(J K^{-1} mole^{-1})	21.580	2.564			0.04
$(1-x)$ $CH_3O(CH_2)_2O(CH_2)_2OCH_3 + x$ CH_3OH	V^E(cm^3 mole^{-1})	−2.515	0.900	−0.766		0.002
	C_p^E(J K^{-1} mole^{-1})	14.785	2.237	1.958		0.01
$(1-x)$ $CH_3O(CH_2)_2O(CH_2)_2OCH_3 + x$ CH_3CH_2OH	V^E(cm^3 mole^{-1})	−0.984	0.334			0.003
	C_p^E(J K^{-1} mole^{-1})	18.519	−3.200	−4.510		0.01
$(1-x)$ $CH_3O(CH_2)_2O(CH_2)_2OCH_3 + x$ $CH_3(CH_2)_2OH$	V^E(cm^3 mole^{-1})	−0.273	0.108			0.001
	C_p^E(J K^{-1} mole^{-1})	17.646	−6.963	3.524		0.02

which are less positive for mixtures with methanol [1] than for mixtures with longer *n*-alcohols.

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REFERENCES

1 M A Villamañan, C Casanova, A H Roux and J -P E Grolier J Chem Thermodyn , 14 (1982)
2 H.V Kehiaian, Ber Bunsenges. Phys Chem 81 (1977) 908
3 H V Kehiaian, J -P.E Grolier and G C Benson, J Chim Phys , 75 (1978) 1031
4 H V. Kehiaian, J -P E Grolier, M R Kechavarz and G C Benson, Fluid Phase Equilibria 5 (1981) 159.
5 R C Wilhoit and B J Zwolinski, J Phys Chem Ref Data, 2 (1973) Supplement No 1
6 J -L Fortier, G C Benson and P Picker, J Chem Thermodyn 8 (1976) 289
7 P Picker, E Tremblay and J Jolicoeur, J Solution Chem , 3 (1974) 377
8 G S Kell, J Chem. Eng Data, 20 (1975) 97
9 P Picker, P.-A Leduc, P R Philip and J E Desnoyers, J Chem Thermodyn 3 (1971) 631
10 J -P E Grolier, G.C Benson and P Picker, J. Chem Eng Data 20 (1975) 243
11 E Wilhelm, J -P E Grolier and M H Karbalai Ghassemi, Monatsh Chem 109 (1978) 369
12 E Wilhelm, A Faradjzadeh and J -P E Grolier, J Chem Thermodyn 11 (1979) 979