Thermodynamic Properties of Tetrahydropyran + 1-Alkanol Mixtures

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Excess molar enthalpies (H^E) at a temperature of 298.15 K and excess molar volumes (V^E) at temperatures of 288.15 and 308.15 K are reported for the binary mixtures tetrahydropyran + 1-hexanol, + 1-heptanol, and + 1-octanol at atmospheric pressure. Values of H^E were determined using a Calvet microcalorimeter and of V^E from densities measured with a vibrating-tube densimeter. The H^E and V^E values are all positive, increasing with the length of the hydrocarbon chain of the alkanol.

Introduction

Continuing a series of investigations into the thermodynamic behavior of binary mixtures of a cyclic ether + an *n*-alkane or a 1-alkanol *(1,2)*, the present paper reports the experimental excess molar enthalpies H^E at a temperature of 298.15 K and the excess molar volume V^E at temperatures of 288.15 and 308.15 K for the binary mixtures tetrahydropyran (THP) + 1-hexanol, + 1-heptanol, and + 1-octanol at atmospheric pressure.

There exist strong interactions between the hydroxyl group of an alkanol and the O atom of an ether. Our aim in the present study is to measure the excess properties of these systems in order to analyze the influence of the hydrocarbon chain of the alkanol and the chemical structure of the cyclic ether upon the excess enthalpies and excess volumes. Our results have been supplemented with those of other researchers *(3–5)* to enable a detailed interpretation of the behavior of this class of mixture.

Experimental Section

Materials. Tetrahydropyran, 1-hexanol, 1-heptanol, and 1-octanol were supplied by Fluka (puriss p.a. 99.5%). All liquids were used without further purification and before use were stored, in the dark, over molecular sieves (Union Carbide Type 4A) and partially degassed.

Densities of the pure liquids are listed in Table 1 together with the corresponding literature values *(6–10)*.

Mixtures were prepared by mass using a Mettler AT201 balance and were stored in air-tight stoppered bottles. The uncertainty in the mole fractions is estimated to be less than 10^{-4}. All molar quantities are based on the 1975 IUPAC recommendations *(11)*.

Calorimetric Measurements. Excess molar enthalpies were determined using a Calvet microcalorimeter linked to a data acquisition system, and their temperature was maintained constant to within 0.01 K. The microcalorimeter was calibrated electrically using an EJP-30 (Setaram) stabilized current source. The calibration was checked by determining the excess molar enthalpy of x $CH_3(CH_2)_4CH_3$ + $(1 - x)$ c-C_6H_{12} at $T = 298.15$ K. Our results differ by less than 1% from those of Arenosa *(12)*. The corrections for the vapor space are negligible, and the accuracy in excess molar enthalpies is better than 10^{-2}.

Table 1. Experimental Measurements of Liquid Density ϱ

component	T/K	ϱ/(g·cm^{-3}) this work	ϱ/(g·cm^{-3}) lit.	ref
tetrahydropyran	288.15	0.888 92		
	298.15	0.878 91	0.877 2	6
	308.15	0.868 82		
1-hexanol	288.15	0.822 33	0.822 52	7
	298.15	0.815 05	0.815 15	8
	308.15	0.808 00	0.808 08	7
1-heptanol	288.15	0.825 77	0.825 92	7
	298.15	0.818 78	0.818 6	9
	308.15	0.811 61	0.811 80	7
1-octanol	288.15	0.828 49	0.828 77	7
	298.15	0.821 61	0.821 77	10
	308.15	0.814 62	0.814 73	7

Table 2. Experimental Excess Molar Enthalpies H^E at 298.15 K

x	H^E/(J·mol^{-1})	x	H^E/(J·mol^{-1})	x	H^E/(J·mol^{-1})
		Tetrahydropyran (1) + 1-Hexanol (2)			
0.1187	358	0.4049	943	0.7555	852
0.1672	492	0.4478	989	0.8012	755
0.2348	651	0.5473	1017	0.8377	643
0.2998	778	0.6361	986	0.8542	604
0.3322	845	0.7217	895	0.9263	358
		Tetrahydropyran (1) + 1-Heptanol (2)			
0.1368	421	0.4937	1051	0.8130	759
0.1867	547	0.5490	1065	0.8602	619
0.2577	733	0.6380	1028	0.8828	546
0.3225	863	0.6783	999	0.9258	372
0.3909	964	0.7660	860		
		Tetrahydropyran (1) + 1-Octanol (2)			
0.0678	211	0.4170	1011	0.8010	824
0.1564	490	0.4742	1069	0.8975	512
0.2041	629	0.5949	1098	0.9338	352
0.2906	819	0.6373	1060		
0.3512	931	0.7101	999		

Volumetric Measurements. Densities were measured by an Anton Paar digital precision densimeter (model DMA 60/602) operated in the static mode and capable of a precision of better than 3×10^{-3} kg·m^{-3}. The temperature was measured with a digital thermometer (Anton Paar DT 100). A Heto (Birkerød, Denmark) circulating thermostat (type 04 PT 623) maintained the temperature constant to within better than 0.01 K. Bidistilled degassed water and dry air were used as calibrating substances *(13, 14)*. Densities were measured with a precision of ±0.01 kg·m^{-3}, and the results for V^E are estimated to be accurate to better than 0.002 cm^3·mol^{-1}.

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Table 3. Experimental Excess Molar Volumes V^E at 288.15 and 308.15 K

x	$V^E/(cm^3 \cdot mol^{-1})$	x	$V^E/(cm^3 \cdot mol^{-1})$	x	$V^E/(cm^3 \cdot mol^{-1})$
		Tetrahydropyran (1) + 1-Hexanol (2)			
		$T = 288.15$ K			
0.0518	0.0076	0.4687	0.0640	0.7943	0.0691
0.1577	0.0231	0.5027	0.0679	0.8755	0.0541
0.2046	0.0296	0.6044	0.0763	0.9523	0.0249
0.2731	0.0388	0.6400	0.0776		
0.3519	0.0497	0.7734	0.0720		
		$T = 308.15$ K			
0.0664	0.0175	0.3567	0.0569	0.6412	0.0842
0.1068	0.0237	0.3580	0.0571	0.7003	0.0860
0.1286	0.0273	0.4373	0.0667	0.8032	0.0800
0.2294	0.0421	0.4810	0.0716	0.8682	0.0655
0.2958	0.0499	0.5902	0.0820	0.9538	0.0295
		Tetrahydropyran (1) + 1-Heptanol (2)			
		$T = 288.15$ K			
0.0813	0.0185	0.4613	0.1033	0.8051	0.0922
0.1803	0.0401	0.5146	0.1107	0.8648	0.0722
0.1916	0.0429	0.5837	0.1158	0.9632	0.0225
0.2500	0.0601	0.6638	0.1154		
0.3544	0.0841	0.7157	0.1100		
		$T = 308.15$ K			
0.0428	0.0208	0.4190	0.1091	0.8157	0.1033
0.0935	0.0386	0.5004	0.1185	0.8688	0.0836
0.2571	0.0789	0.5606	0.1227	0.9491	0.0407
0.3379	0.0956	0.6504	0.1244		
0.3522	0.0981	0.7154	0.1211		
		Tetrahydropyran (1) + 1-Octanol (2)			
		$T = 288.15$ K			
0.0267	0.0093	0.4351	0.1430	0.7904	0.1227
0.1459	0.0549	0.5353	0.1558	0.8915	0.0727
0.2262	0.0835	0.5820	0.1581	0.9373	0.0446
0.3412	0.1202	0.6603	0.1534		
0.3753	0.1307	0.7306	0.1403		
		$T = 308.15$ K			
0.0196	0.0123	0.4368	0.1558	0.8066	0.1406
0.0698	0.0416	0.4947	0.1634	0.8292	0.1314
0.2885	0.1253	0.5718	0.1698	0.9504	0.0507
0.3490	0.1394	0.6514	0.1700		
0.3527	0.1402	0.7179	0.1632		

Table 4. Coefficients A_k and Standard Deviations s for the Least-Squares Fits of Eq 1

mixture	A_1	A_2	A_3	A_4	s^a
	H^E ($T = 298.15$ K)				
tetrahydropyran +					
1-hexanol	4044	768	249	447	7
1-heptanol	4218	795	244	642	4
1-octanol	4333	925	393	522	7
	V^E ($T = 288.15$ K)				
tetrahydropyran +					
1-hexanol	0.2701	0.2093	0.1008		0.0006
1-heptanol	0.4363	0.2450	−0.0008		0.0009
1-octanol	0.6137	0.2263	−0.0392		0.0010
	V^E ($T = 308.15$ K)				
tetrahydropyran +					
1-hexanol	0.2924	0.2164	0.2141		0.0006
1-heptanol	0.4704	0.2015	0.2165		0.0011
1-octanol	0.6571	0.2291	0.2666		0.0006

[a] $s(H^E)/(J \cdot mol^{-1})$, $s(V^E)/(cm^3 \cdot mol^{-1})$.

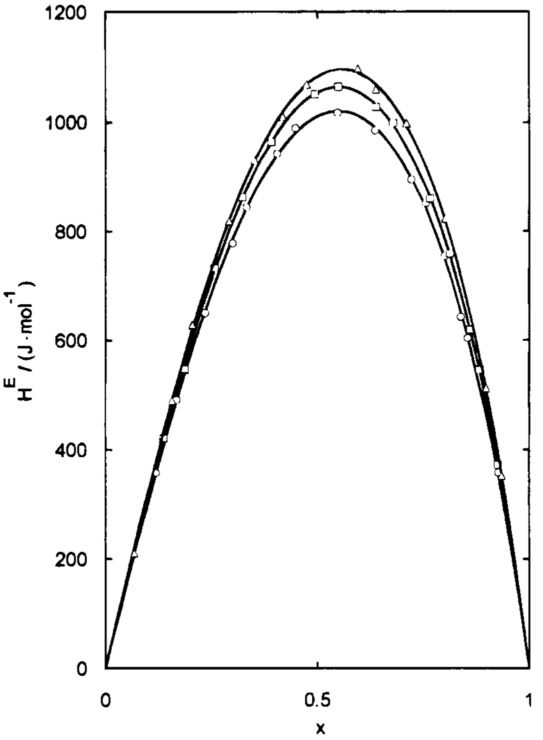

Figure 1. Excess molar enthalpies H^E at 298.15 K of tetrahydropyran mixtures with (○) 1-hexanol, (□) 1-heptanol, and (△) 1-octanol, plotted against x of the ether.

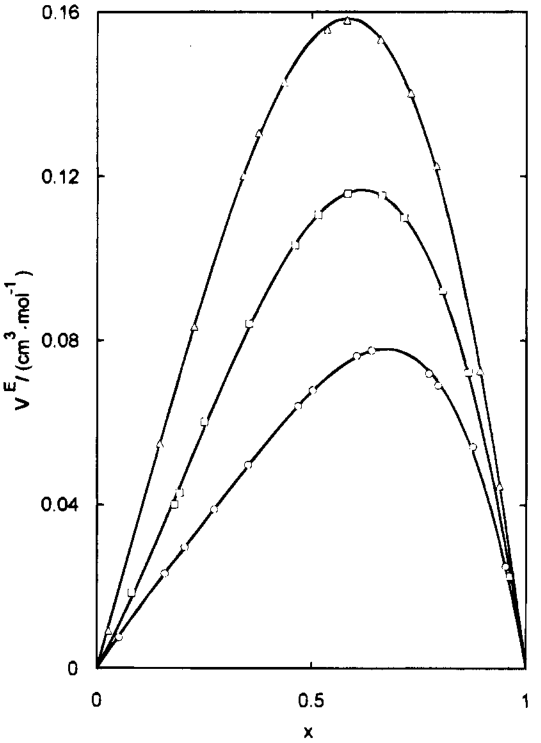

Figure 2. Excess molar volumes V^E at 288.15 K of tetrahydropyran mixtures with (○) 1-hexanol, (□) 1-heptanol, and (△) 1-octanol, plotted against x of the ether.

Results and Discussion

The H^E and V^E results are listed in Tables 2 and 3, respectively. For each mixture, Redlich–Kister functions of the form

$$X^E = x(1-x)\sum_{k=1}^{m} A_k(2x-1)^k \qquad (1)$$

where $X^E = H^E/(J \cdot mol^{-1})$ and $X^E = V^E/(cm^3 \cdot mol)$, were evaluated.

The coefficients A_k and standard deviations $s(X^E)$ listed in Table 4 were estimated by the unweighted least-squares method, and degree of the polynomial being optimized by means of the F test *(15)*.

Figures 1–3 show the experimental values and fitted curves for both excess quantities. The H^E and V^E values

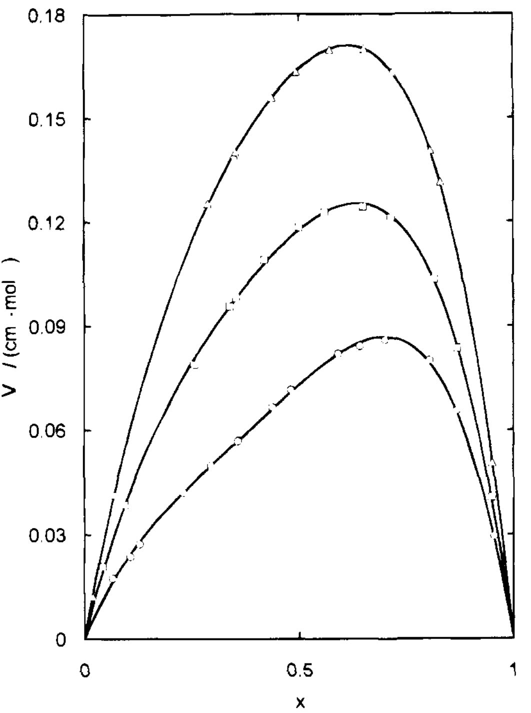

Figure 3. Excess molar volumes V^E at 308.15 K of tetrahydropyran mixtures with (○) 1-hexanol, (□) 1-heptanol, and (△) 1-octanol, plotted against x of the ether.

are all positive, increasing with the length of the hydrocarbon chain of the alkanol.

As expected with systems containing an associated liquid like alcohol, the H^E curves (see Figure 1) present a maximum shifted toward THP-rich molar fractions. Nevertheless, these curves are more symmetrical than those for alkanol + n-alkane mixtures *(16)*. This fact can be explained by taking into account that cyclic ether molecules are associated through dipole interactions and 1-alkanols through the hydrogen bonding of their hydroxyl groups. Therefore, the excess enthalpies for THP + 1-alkanols depend on the balance between two opposite contributions: a positive effect due to the rupture of alkanol–alkanol hydrogen bonds and THP–THP dipole interactions and to physical interactions among like molecules and a negative effect of the formation of $O-H\cdots OC_5H_{10}$ hydrogen-bonded complexes.

In general, the excess molar volumes of these mixtures exhibit the same trend as excess enthalpies, reflecting the strong self-association of alkanols. The fact that H^E and V^E increase with the length of the alkanol chain implies that the breaking of alkanol–alkanol bonds predominates over the formation of $O-H\cdots OC_5H_{10}$ bonds (though both effects decrease with increasing alkanol chain length.)

Figure 4 shows how V^E ($x = 0.5$) of the mixtures depends on the length of the alkanol chain and on the temperature. In this figure we include our previous results at the temperature 298.15 K *(2)*.

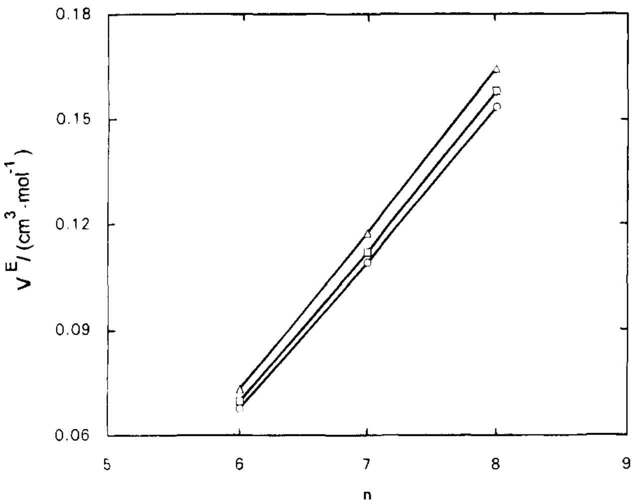

Figure 4. Excess molar volumes of 0.5 $c\text{-}C_5H_{10}O$ + 0.5 $CH_3(CH_2)_{n-2}CH_2OH$ plotted against the number of atom carbons in the alkanol: (○) this work at T = 288.15 K, (□) ref 1 at T = 298.15 K, (△) this work at T = 308.15 K.

Registry Numbers Supplied by Author. THP, 142-68-7; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 143-08-8.

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