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Excess Volumes of Binary Mixtures Containing Cyclic Ethers + Alkanols at 298.15 K

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Excess molar volumes (V^E) for binary mixtures containing cyclic ethers and 1-alkanols (C_6–C_9) have been measured at atmospheric pressure and 298.15 K by using a vibrating-tube densimeter. The experimental data were correlated by means of a polynomial function. The results are discussed in terms of molecular interactions between the components and the ring size of the ethers.

Introduction

This work is part of an extensive study of excess volumes of mixing for a large number of solvent pairs. As a complement to previous work (*1*) we report here the excess molar volumes V^E of binary mixtures of a cyclic ether (tetrahydrofuran or tetrahydropyran) + 1-alkanol (1-hexanol, 1-heptanol, 1-octanol, and 1-nonanol) at 298.15 K and atmospheric pressure, over the entire range of mole fractions.

The aim of these investigations is to correlate the experimental data with the factors affecting interactions between molecules in such mixtures.

Experimental Section

Materials. The sources and purities of the chemicals used were tetrahydrofuran (THF), Fluka, purum 99%; tetrahydropyran (THP), Fluka, puriss p.a. 99.5%; 1-hexanol, Fluka, puriss 99%; 1-heptanol, Fluka, puriss 99.5%; 1-octanol, Fluka, puriss 99.5%; and 1-nonanol, Sigma, 98%. All liquids were used without further purification, and before used were stored in the dark over molecular sieves (Union Carbide Type 4A) and partially degassed.

The purity of the solvents was ascertained by comparing their densities ρ at 298.15 K and atmospheric pressure (Table I) with the corresponding literature values (*2–7*).

Volumetric Measurements. Mixtures were prepared by mass using a Mettler H51 and air-tight stoppered bottles. The possible error in the mole fraction is estimated to be less than 10^{-4}. The 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 100-30). A Heto circulating thermostat (type 04 PT 623) maintained the temperature constant to within 0.01 K. Bidistilled degassed water and dry air were used as calibrating substances (*8, 9*).

Results and Discussion

The values of V^E for the binary mixtures are reported in Table II, and graphical representations are given in Figures 1 and 2.

The polynomial function

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1 x_2 \sum_{k\geq0} A_k (x_1 - x_2)^k \qquad (1)$$

was fitted to each set of results by the method of least squares with all points weighted equally.

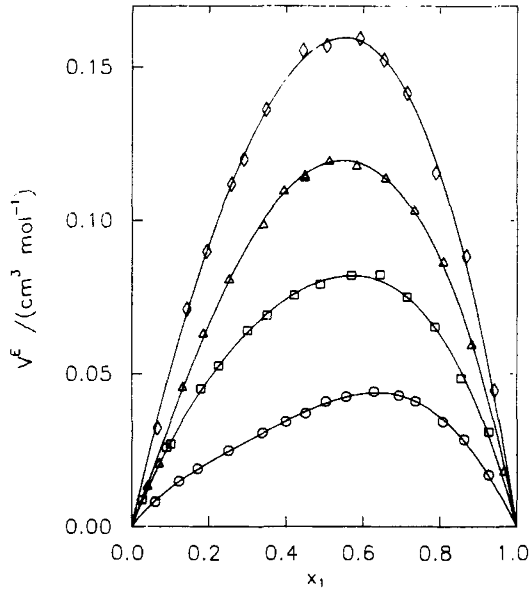

Figure 1. Excess molar volumes V^E at 298.15 K of tetrahydrofuran mixtures with ○, 1-hexanol; □, 1-heptanol, △, 1-octanol; and ◇, 1-nonanol.

Table I. Experimental Measurements of Liquid Density ρ

component	ρ/(g cm^{-3}) this work	ρ/(g cm^{-3}) lit.	ref
tetrahydrofuran	0.881 95	0.881 97	2
tetrahydropyran	0.878 91	0.877 2	3
1-hexanol	0.815 05	0.815 15	4
1-heptanol	0.818 78	0.818 6	5
1-octanol	0.821 61	0.821 77	6
1-nonanol	0.824 22	0.824 33	7

Table III summarizes the values of parameters A_k and the standard deviations. These coefficients were used to calculate the solid curves in Figures 1 and 2. The number of parameters A_k was selected for each set using the statistical *F*-test (*10*).

We have been unable to find any previously published values of V^E with which to compare our own results.

All mixtures exhibit positive V^E values, increasing their magnitude with the length of the hydrocarbonated chain of the alkanol for a given ether. The V^E–x curve presents a maximum that is shifted toward cyclic ether rich molar fractions, reflecting the strong self-association of alkanols. This association decreases with an increase in the molar mass of the 1-alkanol (*11, 12*), so the increase in V^E with the increase in the molar mass of the 1-alkanol implies that the cyclic ether–1-alkanol interaction is relatively weaker.

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Table II. Experimental Excess Molar Volumes V^E at 298.15 K

x_1	V^E/ ($cm^3\ mol^{-1}$)	x_1	V^E/ ($cm^3\ mol^{-1}$)	x_1	V^E/ ($cm^3\ mol^{-1}$)
Tetrahydrofuran (1) + 1-Hexanol (2)					
0.0611	0.0081	0.3997	0.0343	0.6948	0.0429
0.1227	0.0149	0.4519	0.0370	0.7375	0.0410
0.1712	0.0190	0.5046	0.0409	0.8071	0.0343
0.2514	0.0249	0.5575	0.0425	0.8622	0.0285
0.3387	0.0307	0.6292	0.0442	0.9265	0.0170
Tetrahydrofuran (1) + 1-Heptanol (2)					
0.0272	0.0088	0.3013	0.0641	0.6449	0.0823
0.0918	0.0259	0.3512	0.0690	0.7149	0.0750
0.1021	0.0270	0.4220	0.0756	0.7872	0.0653
0.1810	0.0451	0.4894	0.0792	0.8558	0.0485
0.2263	0.0526	0.5702	0.0821	0.9262	0.0310
Tetrahydrofuran (1) + 1-Octanol (2)					
0.0410	0.0136	0.3949	0.1099	0.7330	0.1034
0.0714	0.0208	0.4490	0.1149	0.8090	0.0865
0.1330	0.0457	0.4501	0.1142	0.8822	0.0597
0.1863	0.0633	0.5124	0.1196	0.9665	0.0183
0.2530	0.0810	0.5841	0.1180		
0.3410	0.0988	0.6585	0.1140		
Tetrahydrofuran (1) + 1-Nonanol (2)					
0.0661	0.0322	0.3484	0.1361	0.7145	0.1414
0.1433	0.0710	0.4438	0.1553	0.7901	0.1156
0.1946	0.0898	0.5056	0.1569	0.8678	0.0882
0.2591	0.1118	0.5917	0.1592	0.9421	0.0446
0.2912	0.1199	0.6539	0.1522		
Tetrahydropyran (1) + 1-Hexanol (2)					
0.0463	0.0129	0.4064	0.0600	0.7879	0.0741
0.1015	0.0196	0.4872	0.0695	0.8638	0.0637
0.1785	0.0323	0.5539	0.0755	0.9302	0.0387
0.2557	0.0411	0.6415	0.0802		
0.3364	0.0505	0.7122	0.0806		
Tetrahydropyran (1) + 1-Heptanol (2)					
0.0537	0.0217	0.3697	0.0927	0.7136	0.1155
0.1046	0.0366	0.4162	0.1017	0.7912	0.1021
0.1743	0.0538	0.4745	0.1104	0.8698	0.0772
0.2109	0.0593	0.5041	0.1128	0.9426	0.0421
0.2615	0.0732	0.5780	0.1200		
0.3333	0.0844	0.6424	0.1212		
Tetrahydropyran (1) + 1-Octanol (2)					
0.0426	0.0216	0.4248	0.1508	0.8236	0.1218
0.1073	0.0559	0.5020	0.1582	0.8560	0.1090
0.1946	0.0899	0.5723	0.1613	0.8777	0.0961
0.2739	0.1137	0.6495	0.1591	0.9618	0.0391
0.3266	0.1278	0.7204	0.1521		
0.3837	0.1417	0.7447	0.1484		
Tetrahydropyran (1) + 1-Nonanol (2)					
0.0373	0.0247	0.3561	0.1702	0.6997	0.1899
0.1115	0.0716	0.4414	0.1920	0.7622	0.1721
0.1956	0.1159	0.5113	0.1990	0.8197	0.1498
0.2528	0.1361	0.5629	0.2042	0.8958	0.1004
0.3292	0.1629	0.6330	0.1987	0.9491	0.9571

Table III. Coefficients A_k and Standard Deviations s for the Least-Squares Fits of Equation 1 at 298.15 K

mixture	A_0	A_1	A_2	A_3	s
tetrahydrofuran +					
1-hexanol	0.1607	0.0952	0.0481	−0.0493	0.0004
1-heptanol	0.3224	0.0772	0.0669		0.0011
1-octanol	0.4743	0.0882	0.0134	0.0722	0.0015
1-nonanol	0.6319	0.1238	0.0444		0.0020
tetrahydropyran +					
1-hexanol	0.2784	0.2060	0.1773		0.0015
1-heptanol	0.4485	0.2183	0.1472		0.0017
1-octanol	0.6313	0.1823	0.1832		0.0014
1-nonanol	0.7931	0.2190	0.1751		0.0016

For the two ethers we studied the excess volume increases with the growth of the hydrocarbonated chain of the ether.

In interpreting V^E in terms of molecular phenomena, positive values are explained by the breaking of chemical or nonchemical interactions among molecules in the pure components during the mixing process. A more efficient packing the mixture than in the pure liquids is considered the major contribution to negative V^E values.

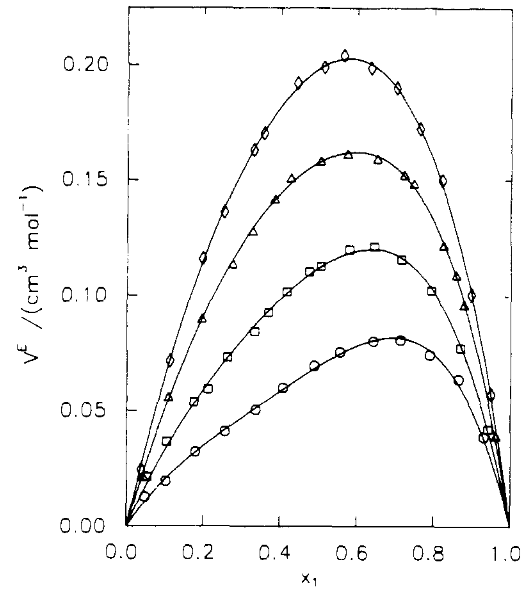

Figure 2. Excess molar volumes V^E at 298.15 K of tetrahydropyran mixtures with ○, 1-hexanol, □, 1-heptanol, △, 1-octanol; and ◇, 1-nonanol.

The cyclic ethers we studied are associated through dipole–dipole interactions, whereas 1-alkanols are associated through the hydrogen bonding of their hydroxyl groups. Then, in the mixing process, the positive contribution to V^E is due to the breaking of these two kinds of interactions. Values of the dipolar moment of the ethers (*3*) lead us to believe that the O–O interaction is stronger in the THF than in the THF and also that the THF–1-alkanol interactions are stronger than the THF–1-alkanol interactions, which implies that the negative contributions to V^E are larger in the mixtures with THF than in those with THP. This agrees with the values found experimentally, taking into account the signs of the contributions to the V^E of both effects.

Registry Numbers Supplied by Author. THF, 109-99-9; THP, 142-68-7; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 111-87-5; 1-nonanol, 143-08-8.

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