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Thermodynamic Studies of Binary Mixtures of Tetrahydrofuran with Some Oxygen- and Nitrogen-Containing Solvents: Molar Excess Volumes

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Molar excess volumes of binary mixtures of tetrahydrofuran with 1,4-dioxane, cyclohexanone, triethylamine, tripropylamine, and aniline at 298.15 K have been calculated from the experimental density data. The results have been discussed in terms of the specific interactions between the functional groups and the steric effects arising from the geometric arrangement of component molecules in the binary mixtures.

Introduction

In the earlier papers from this laboratory, we reported the excess volumes for the binary mixtures of tetrahydrofuran (THF) with hydrocarbons (*1*), alcohols (*2*), amides (*3*), and various aliphatic compounds having different functional groups (*4*). As an extension of that work, we have determined the molar excess volumes for the binary mixtures of THF with some oxygen- or nitrogen-containing common organic solvents. The solvents studied are 1,4-dioxane, cyclohexanone, triethylamine, tripropylamine, and aniline. The purpose of these investigations is to provide some information about the thermodynamic properties of these mixtures with a view to understanding the factors determining the unlike interactions between the molecules in such mixtures.

Experimental Section

Fisher ACS certified grade tetrahydrofuran was fractionally distilled before use. The sample of 1,4-dioxane supplied by Aldrich was refluxed over sodium wire for 3-4 h, distilled, and the middle fraction collected. It was then kept over 8-12 mesh molecular sieves and fractionally distilled immediately before use in a spinning band still with a reflux ratio of ~1:20. The first and the last fraction were discarded. Triethylamine (Fisher ACS certified grade) was purified by following the procedure described elsewhere (*5*). The samples of tripropylamine (Eastman Kodak Co.), cyclohexanone (Aldrich), and aniline (Fisher ACS certified grade) were purified according to standard procedures (*6*). The densities and refractive indexes of the solvents agreed closely with the accepted literature values (Table I).

The molar excess volumes of mixing have been calculated from the experimental density data. The solutions for the measurement of densities were prepared by weight and corrections for buoyancy were applied. The densities were measured with a vibrating flow densimeter (Sodev, Inc.). The details of the experimental technique for the preparation of solutions and measurement of densities have been described elsewhere (*5*). Each data point reported is an average of at least two different measurements. Duplicate densities of liquids and liquid mixtures studied agreed to within 2×10^{-5} g·cm^{-3}. This propagates a maximum uncertainty of about ± 0.008 cm^3·mol^{-1} in molar excess volumes.

Table I. Densities and Refractive Indexes of Liquids Used at 298.15 K

	density, g.cm^{-3}		refractive index	
liquid	our value	lit.	our value	lit.
tetrahydrofuran	0.88193	0.88195 (*8*)	1.4049	1.40474 (*8*)
1,4-dioxane	1.02644	1.02797 (*6*)	1.4167	1.42025 (*6*)
cyclohexanone	0.94247	0.94207[a]	1.4108	1.41061[a]
triethylamine	0.72291	0.7230 (*6*)	1.3980	1.3980 (*6*)
tripropylamine	0.75227	0.7524 (*7*)	1.4146	1.4141 (*7*)
aniline	1.01706	1.01750 (*6*)	1.5823	1.58364 (*6*)

[a] Extrapolated value from data of ref *6*.

Table II. Molar Excess Volumes, V^E (cm^3•mol^{-1}), for the Binary Mixtures at 298.15 K

X_1	V^E	X_1	V^E	X_1	V^E
THF (1) + 1,4-Dioxane (2)					
0.0694	-0.089	0.4237	-0.005	0.7505	0.007
0.1803	-0.086	0.5113	0.035	0.8222	-0.005
0.2707	-0.068	0.6139	0.038	0.8688	-0.004
0.3560	-0.051	0.6813	0.020		
THF (1) + Cyclohexanone (2)					
0.0894	0.015	0.3419	-0.078	0.7050	-0.192
0.1728	0.012	0.3865	-0.106	0.7526	-0.175
0.2302	-0.018	0.4454	-0.134	0.8604	-0.122
0.2800	-0.045	0.6211	-0.191	0.9179	-0.079
THF (1) + Triethylamine (2)					
0.1083	-0.022	0.4665	-0.101	0.7017	-0.115
0.2499	-0.054	0.5450	-0.116	0.7676	-0.099
0.3645	-0.077	0.6334	-0.119	0.8852	-0.061
THF (1) + Tripropylamine (2)					
0.0987	0.108	0.4076	0.307	0.7953	0.229
0.2130	0.216	0.5302	0.329	0.8586	0.172
0.3239	0.271	0.6631	0.301	0.9217	0.094
THF (1) + Aniline (2)					
0.0929	-0.231	0.4284	-0.847	0.8395	-0.630
0.1922	-0.463	0.5494	-0.940	0.9263	-0.336
0.2470	-0.573	0.6837	-0.907		
0.3508	-0.747	0.7619	-0.802		

Table III. Values of the Parameters of Eq 1 and Standard Deviations $\sigma(V^E)$ of Experimental Results at 298.15 K

THF +	A_0	A_1	A_2	$\sigma(V^E)$/ (cm^3· mol^{-1})
1,4-dioxane	0.1117	0.5235	-1.2706	0.007
cyclohexanone	-0.6334	-0.7809	0.3360	0.002
triethylamine	-0.4311	-0.2559	0.0315	0.002
tripropylamine	1.3179	0.0966	-0.0425	0.002
aniline	-3.6698	-1.3065	-0.2214	0.003

Results and Discussion

The molar excess volumes, V^E, for the binary mixtures at 298.15 K are recorded in Table II and plotted as a function of solution composition in Figure 1. Each set of results were fitted with a polynomial form

$$V^E/(\mathrm{cm^3\ mol^{-1}}) = x(1 - x)\sum_{i=0}^{n-1} A_i(2x - 1)^i \qquad (1)$$

where x is the mole fraction of tetrahydrofuran. Values of the coefficients A_i were determined by the method of (unweighted) least squares. It was found that the best fit was obtained by using three parameters in the equation. The values of these

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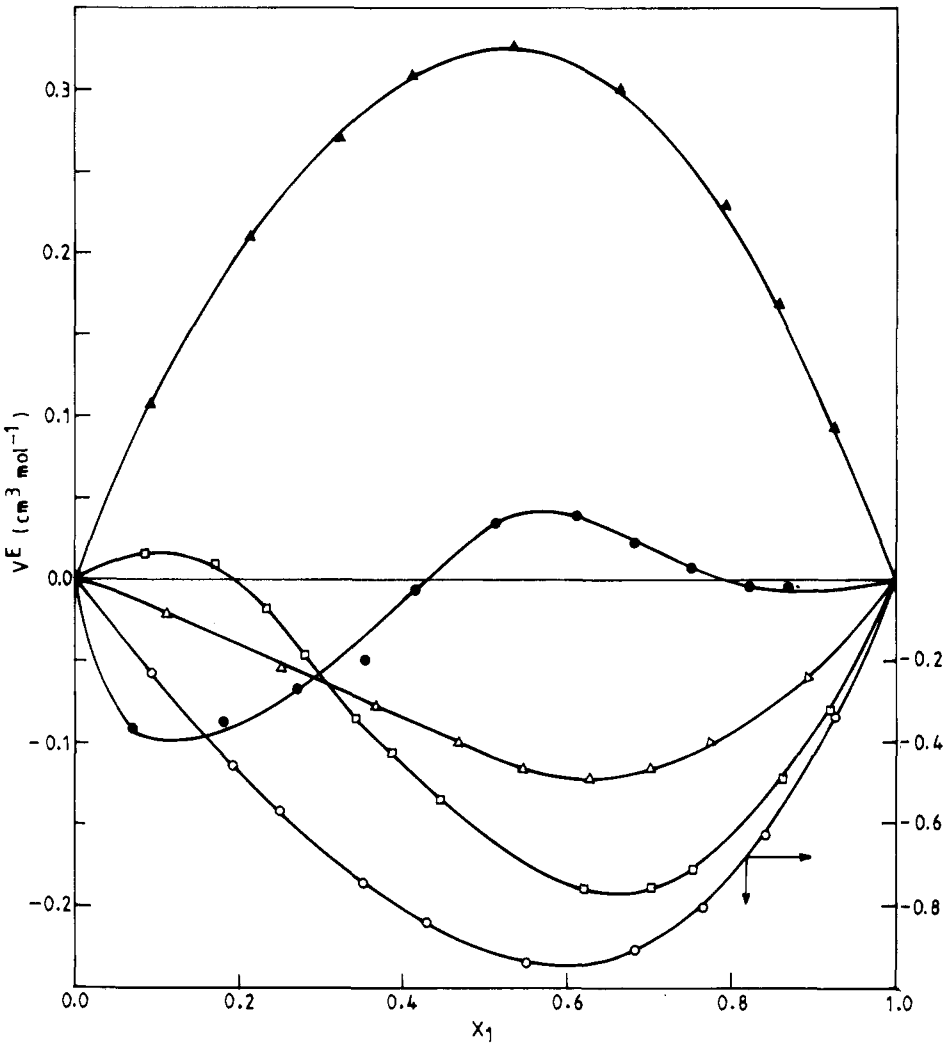

Figure 1. Molar excess volumes, V^E, at 298.15 K for the binary mixtures of tetrahydrofuran with (●) 1,4-dioxane; (□) cyclohexanone; (△) triethylamine; (▲) tripropylamine; and (○) aniline.

parameters along with the standard deviation for the molar excess volumes $\sigma(V^E)$ are listed in Table *III*. Since $\sigma(V^E)$ values for all the binary mixtures studied are less than the estimated experimental uncertainty, the constants of eq 1 can be taken to represent the experimental results. For the binary mixtures of THF and *p*-dioxane, our data are in poor agreement with those reported by Landauer et al. (*9*) who have reported a positive V^E over the entire composition range. A relatively higher uncertainty in their data renders it difficult for us to make any comment about it. To the best of our knowledge, no V^E data has been reported in literature for other binary mixtures considered here.

It is established that the sign and magnitude of V^E gives a good estimate of the strength of the unlike interactions in the binary mixtures. Large positive V^E values are taken as indicative of weak intermolecular interactions whereas large negative values of V^E are usually found when these interactions are strong and intermolecular "complexes" are believed to be present.

A comparison of the V^E values for the binary mixtures of THF and *p*-dioxane with the data reported in literature for the binary mixtures of THF + cyclohexane (*1*) reveals that the observed volumetric effects in the former system are very small. A sharp decrease in V^E values on going from cyclohexane to *p*-dioxane is indicative of a strong specific *n*-*n*-type interaction in the binary mixtures of THF and *p*-dioxane. The unsymmetrical nature of the curve appears to be due to the steric factors arising from a change in the proportion of the two geometric forms (namely "chair" and "boat" forms) with change in mole fraction of *p*-dioxane in the binary mixtures. In binary mixtures of THF with cyclohexanone, the specific interactions of the type $\rangle C{=}O\cdots O\langle$ are responsible for negative excess volumes and support the viewpoint of Bolinaga et al. (*10*). The relatively smaller volumetric effects for cyclohexanone solutions as compared to those of acetone solutions (*4*) may be attributed to the steric factors facilitating the packing of the cyclohexanone molecule in the THF lattice. For trialkylamine solutions also, the specific n–n interactions are responsible for the volumetric effects. These interactions are rendered weak in tripropylamine solutions due to relatively lower electron-donating power of the propyl group and results in an increase in V^E.

The specific n–π interactions between THF and the aromatic ring has been well documented (*1*, *11*). In aniline, the presence of $-NH_2$ group increases the π-electron density in the aromatic ring resulting in stronger n–π interactions and hence a large negative V^E as compared to benzene. Further work on such systems is underway.

Registry No. THF, 109-99-9; dioxane, 123-91-1; cyclohexanone, 108-94-1; aniline, 62-53-3; tripropylamine, 102-69-2; triethylamine, 121-44-8.

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Excess Molar Volumes of Ethyl Formate or Ethyl Acetate + 1-Chloroalkane at 298.15 K

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Excess molar volumes at 298.15 K of ethyl formate or ethyl acetate with 1-chloroalkanes (from C_5 to C_8) were calculated indirectly from densities. The V^E_m values were positive over the concentration range, increasing, for any one ester, with the length of the chain of the 1-chloroalkane and being smaller for the acetate than for ethyl formate.

Introduction

In order to understand the effect caused by the structure of compounds on the thermodynamic properties of solutions, systematic information on the behavior of substances with different structural characteristics is required. The literature includes several studies of the behavior of different families carrying some of the compounds studied here, such as those of chloroalkane + *n*-alkane (*1*), chloroalkane + 1-alkanol (*1*), ester + *n*-alkane (*2*, *3*), and ester + 1-alkanol (*4*, *5*) by means of different thermodynamic functions. However, few data are available for the systems ester + chloroalkane. This work presents excess molar volume data for the binary mixtures of ethyl formate and ethyl acetate with 1-ClC_nH_{2n+1} (n = 5, 6, 7, 8) at a constant temperature of 298.15 K, as part of the study in order to observe the interaction of the carbonyl group of the ester $\rangle C{=}O$ with other nonelectrolyte liquids containing structural groups such as CH_2, OH, and Cl.

Experimental Section

The materials used in this work, together with the specifications given by the manufacturer, are listed in Table I. All the products were used without further purification except the ethyl formate which was first washed with 2N sodium carbonate in order to remove the acid material, then stirred with calcium chloride for several hours to extract the ethyl alcohol and, finally, dried with potassium carbonate and distilled in a rectification column with a height equivalent to 120 theoretical plates. The final purity proved to be above 99 mol % verified by gas chromatography. However, before use, all the products were degassed in vacuo and dried with a molecular sieve, Type 4A, from Fluka. The experimental values and those taken from the literature for the refractive index and density of each of the substances chosen in this work are given in Table I. The agreement between the experimentally determined values and those found in the literature was considered to be satisfactory, since the greatest deviation found was smaller than 0.1%.

Excess volumes were determined from the density values of the mixtures, previously prepared by weighing. Densities were measured with an accuracy of ±0.01 kg·m^{-3} with an Anton Paar DMA-55 vibrating tube densimeter. Before each series of measurements, the apparatus was calibrated at atmospheric pressure by using bidistilled and degassed water and *n*-nonane, as recommended by the authors in an earlier work (*9*). The samples were thermostated in the densimeter cell at ±0.01 K using a Heto Birkeroad ultrathermostat together with a Anton Paar digital thermometer, Model DT 100-30. The mean error in the V^E_m was smaller than ±0.0003 cm^3·mol^{-1}.

Table I. Materials Employed and Their Characteristics at 298.15 K

		n_D		ρ, kg·m^{-3}	
material	supplier and specificns	expt	lit.	expt	lit.
ethyl formate	Aldrich >97 mol %	1.3576	1.35774 (6)[a]	915.87	916.03 (6)[a]
ethyl acetate	Fluka, puriss p.a. >99.5 mol %	1.3701	1.36979 (6)	894.34	894.55 (6)
1-chloropentane	Fluka, puriss >99 mol %	1.4099	1.4100 (6)	876.92	876.9 (6)
1-chlorohexane	Fluka, puriss >99 mol %	1.4174	1.4179 (8)[a]	873.33	874.5 (7)
1-chloroheptane	Alfa, >99 mol %	1.4232	1.4235 (7)[a]	870.56	871.5 (7)
1-chlorooctane	Fluka, >98 mol %	1.4280	1.4278 (7)[a]	868.65	869.5 (7)

[a] Value calculated by using the data shown in the mentioned reference.

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