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Thermodynamic Evidence for Complex Formation between Tetrahydrofuran and Aromatic Hydrocarbons

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The excess enthalpies and excess volumes of mixtures of tetrahydrofuran with benzene, toluene, and xylenes were measured at 298.15 K as a function of composition. H^E and V^E values have been found to be negative for these systems. These results are consistent with complex formation between the unlike molecules and provide further evidence for electron donor capacity of ethers with aromatic hydrocarbons.

Introduction

The existence of specific interactions in binary liquid mixtures containing ethers as one of the components has been established (*2, 7, 13, 14, 18*) from thermodynamic measurements. The electron donor capacity of ethers is well known (*2, 3, 5, 6, 8, 9, 15*) and it has been pointed out that in tetrahydrofuran and benzene systems such interactions may involve a charge-transfer type of mechanism (*2*) between the lone pair of electrons on the oxygen atom of tetrahydrofuran and benzene. As part of an investigation of the thermodynamic properties of such systems we have measured H^E and V^E of tetrahydrofuran with benzene, toluene, and xylenes to further support the presence of such interactions between tetrahydrofuran and aromatic hydrocarbons.

Experimental Section

The materials were purified, and their purity was checked as described earlier (*11, 12*). Excess volumes were measured dilatometrically (*17*) as a function of composition. The dilatometer was similar to that used by Brown and Smith (*4*) but with slight modifications. Our dilatometer dispensed with the use of a hypodermic syringe. This improvement eliminates completely the vapor phase, which otherwise had been a potential source of error.

Excess enthalpies were measured in a calorimeter designed in our laboratory (*16*) (Figure 1). It consists of a double-walled glass mixing vessel having B-7 and B-12 standard joints at its ends. The liquid components of the binary mixture were kept separated with mercury taking care to avoid any vapor space in the two chambers of the calorimeter. The capillary tube, fused to the middle of the mixing vessel, was partly filled with mercury in order to avoid the liquids coming in direct contact with the atmosphere. This capillary provides an air space which, while remaining out of contact with the liquids, ensures that the volume change on mixing causes no change of pressure in the calorimeter. The calorimeter heater of constantan wire was wound around a very thin glass tube fused with a B-12 standard joint. A thermistor is passed through the glass tube to record the change in temperature. The empty space between the thermistor and glass tube was filled with mercury to ensure good thermal contact.

Table I. Excess Volumes of Mixtures Containing Tetrahydrofuran at 298.15 K

Mole fraction x_1	V^E, cm^3 mol^{-1}	Mole fraction x_1	V^E, cm^3 mol^{-1}
Tetrahydrofuran (1) + Benzene (2)			
0.0704	−0.055	0.5509	−0.213
0.1946	−0.140	0.6155	−0.204
0.3481	−0.198	0.6991	−0.184
0.4349	−0.212	0.7957	−0.148
0.4953	−0.216	0.8890	−0.089
Tetrahydrofuran (1) + Toluene (2)			
0.1625	−0.195	0.5088	−0.344
0.2048	−0.228	0.5610	−0.345
0.2664	−0.272	0.6851	−0.325
0.3594	−0.316	0.7885	−0.268
0.4108	−0.331	0.8501	−0.220
		0.9399	−0.123
Tetrahydrofuran (1) + *o*-Xylene (2)			
0.1725	−0.149	0.5120	−0.288
0.2786	−0.215	0.6352	−0.280
0.3250	−0.238	0.6996	−0.258
0.4011	−0.265	0.7601	−0.225
0.4519	−0.279	0.8969	−0.123
Tetrahydrofuran (1) + *m*-Xylene (2)			
0.1751	−0.129	0.4632	−0.232
0.2508	−0.172	0.5506	−0.233
0.3056	−0.193	0.6779	−0.214
0.3286	−0.202	0.8166	−0.157
0.3901	−0.221	0.9011	−0.099
Tetrahydrofuran (1) + *p*-Xylene (2)			
0.1101	−0.131	0.5099	−0.347
0.2250	−0.238	0.5842	−0.344
0.2831	−0.276	0.6345	−0.334
0.3628	−0.318	0.8167	−0.233
0.4384	−0.339	0.8950	−0.136

The loaded calorimeter was clamped in a water thermostat which in turn was placed in another water thermostat, the temperature of which was controlled to better than ±0.01 K. The contents were allowed to attain equilibrium. The outer jacket was then evacuated. Liquid components were mixed by repeatedly tilting the glass vessel, and current was passed through the calorimeter heater for compensation (in the case of endothermic mixing). Readings of the galvanometer spot were taken continuously. Again at a particular time, current was passed through the heater and readings of the galvanometer spot were taken. The heat of mixing was then calculated using the relationship

$$H^E(\text{J mol}^{-1}) = (C^2Rt_1 + C^2Rt_2(\Delta h_1/\Delta h_2))/(n_1 + n_2) \qquad (1)$$

where C is the current in amperes, R is the resistance of

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Table II. Excess Enthalpies of Mixtures Containing Tetrahydrofuran at 298.15 K (1 cal = 4.184 J)

Mole fraction x_1	H^E, cal mol^{-1}	Mole fraction x_1	H^E, cal mol^{-1}
Tetrahydrofuran (1) + Benzene (2)			
0.2081	−65.7	0.5967	−91.3
0.3616	−89.0	0.6180	−89.5
0.4081	−92.3	0.7034	−80.5
0.4869	−94.1	0.7776	−67.5
0.5091	−94.6	0.8591	−45.6
Tetrahydrofuran (1) + Toluene (2)			
0.1749	−49.8	0.5480	−84.3
0.2433	−62.0	0.5600	−84.0
0.3125	−72.3	0.6321	−78.5
0.4052	−81.1	0.7220	−68.6
0.4556	−84.7	0.8601	−43.0
Tetrahydrofuran (1) + *o*-Xylene (2)			
0.1195	−22.2	0.4975	−52.2
0.2219	−34.8	0.5483	−51.8
0.3262	−44.6	0.6683	−47.0
0.3899	−48.5	0.7464	−40.6
0.4622	−51.9	0.8312	−30.1
Tetrahydrofuran (1) + *m*-Xylene (2)			
0.1443	−18.7	0.4734	−46.0
0.1955	−24.5	0.5506	−46.0
0.2713	−32.8	0.6016	−44.7
0.3805	−42.3	0.7218	−37.3
0.4444	−45.3	0.7810	−31.5
Tetrahydrofuran (1) + *p*-Xylene (2)			
0.1583	−30.3	0.4471	−60.0
0.2195	−34.0	0.5011	−62.3
0.2875	−47.0	0.5600	−62.2
0.3297	−52.0	0.6911	−55.1
0.3950	−57.6	0.8647	−29.7

calorimeter heater in ohms, t_1 is the time for which the current was passed during compensation, t_2 the time for which the current was passed during calibration, and $\Delta h_1/\Delta h_2$ was the factor used to calculate the amount of heat required for exact compensation. Δh_1 and Δh_2 has the same significance as described by Adcock and McGlashan (*1*). In the case of the exothermic reaction for which no heating was required for compensation, t_1 becomes zero.

Results and Discussion

The excess volumes and excess enthalpies are given in Tables I and II, respectively, and were fitted by the method of least squares to the general equation

$$X^E = x_1(1 - x_1)\{A + B(1 - 2x_1) + C(1 - 2x_1)^2 + D(1 - 2x_1)^3\} \qquad (2)$$

where X^E is the excess thermodynamic function and x_1 is the mole fraction of tetrahydrofuran. The values of the coefficients *A*, *B*, *C*, and *D* for each mixture evaluated by fitting the experimental values of X^E/x_1x_2 to eq 2 by the method of least squares along with standard deviations[10] $\delta(V^E)$ and $\delta(H^E)$ are given in Tables III and IV, respectively. The values of H^E and V^E are reproducible to within 1.0 cal mol^{-1} and 0.003 cm^3 mol^{-1}.

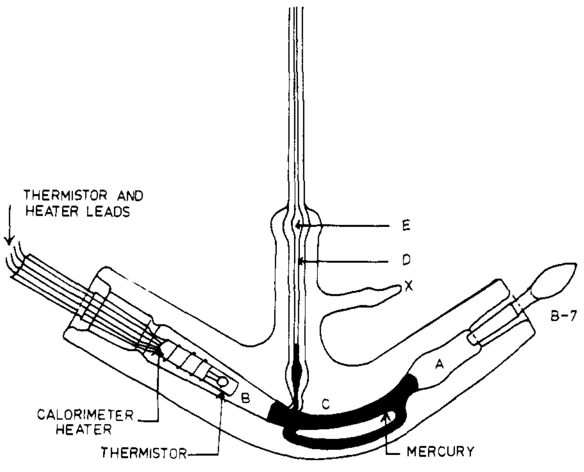

Figure 1.

The excess volumes for tetrahydrofuran + benzene have been obtained previously by Geier (*7*) and Meyer (*13*) at 298.15 K; their V^E values for equimolar compositions are 0.211 and 0.250 cm^3 mol^{-1}, respectively. Our values are in excellent agreement with the values reported by Geier. However, the values of V^E reported by Meyer are consistently more negative than ours, the greatest difference being 0.03 cm^3 mol^{-1}. The literature (*7*) value of H^E for tetrahydrofuran + benzene is −102 cal mol^{-1} at 294.15 K whereas our H^E value is −95 cal mol^{-1} at 298.15 K at equimolar composition.

The values of V^E and H^E are negative for the entire composition range for all five mixtures. The magnitude of H^E at equimolar composition follows the sequence benzene > toluene > xylenes. The relative position of methyl groups in xylene effects the magnitude of V^E and H^E and follows the sequence *p*-xylene > *o*-xylene > *m*-xylene. The exothermic mixing together with the negative excess volumes of tetrahydrofuran + benzene systems provides good evidence of moderately strong interactions between unlike molecules in the liquid state. This is further supported from the exothermic mixing of tetrahydrofuran with toluene and xylenes because toluene and xylenes have their molar volumes 40% larger than that of tetrahydrofuran and one would expect endothermic mixing if no interactions are present in these systems. It seems that the lone pair of electrons on the oxygen atom of tetrahydrofuran forms charge-transfer complexes (*2*) of decreasing stability with

Table III. Values of the Constants in Equation 2 for $X^E = V^E$/cm^3 mol^{-1} and Standard Deviations $\delta(V^E)$

System	*A*	*B*	*C*	*D*	$\delta(V^E)$/cm^3 mol^{-1}
Tetrahydrofuran + benzene	−0.8631	0.0141	−0.0671	−0.0750	0.001
Tetrahydrofuran + toluene	−1.3779	−0.1236	−0.4176	−0.2016	0.002
Tetrahydrofuran + *o*-xylene	−1.1452	−0.1916	−0.0375	0.0208	0.002
Tetrahydrofuran + *m*-xylene	−0.9367	−0.0705	−0.0888	−0.1217	0.001
Tetrahydrofuran + *p*-xylene	−1.3970	−0.1221	−0.0400	0.0738	0.003

Table IV. Values of the Constants in Equation 2 for $X^E = H^E$/cal mol^{-1} and Standard Deviations $\delta(H^E)$

System	*A*	*B*	*C*	*D*	$\delta(H^E)$/cal mol^{-1}
Tetrahydrofuran + benzene	−379.0	−1.0	−40.4	43.1	0.7
Tetrahydrofuran + toluene	−338.3	−3.0	−16.7	−12.1	0.7
Tetrahydrofuran + *o*-xylene	−208.1	−17.9	−2.2	26.5	0.4
Tetrahydrofuran + *m*-xylene	−185.1	−17.8	−41.0	−9.1	0.2
Tetrahydrofuran + *p*-xylene	−248.6	−31.9	17.9	19.4	1.0

benzene, toluene, and xylenes.

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Experimental Heats of Mixing of Some Miscible and Partially Miscible Nonelectrolyte Systems

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The isothermal dilution calorimeter has been modified by some improvements in the electronics of temperature control and heat addition, to facilitate the ease of measurements. Endothermic heats of mixing are shown to be in good agreement with existing data for two test systems; new results are reported for eight additional binary mixtures: hexane–nitrobenzene at 25 and 50 °C; hexane–nitroethane at 35 and 50 °C; cyclohexane–aniline at 35 and 50 °C; acetone–ethanol at 25 and 50 °C; chlorobenzene–1-nitropropane at 25 and 50 °C; ethanol–chlorobenzene at 25 and 50 °C; cyclohexane–furfural at 75 °C; and methylcyclohexane–furfural at 75 °C.

Although traditional methods of solution thermodynamics have primarily been centered on the determination of activity coefficients through phase equilibrium measurements, the prediction and correlation of the heat of mixing are now being recognized as an important step toward a generally valid representation of liquid mixture nonidealities. As a direct measure of the temperature dependence of the excess Gibbs energy, the heat of mixing can be used to evaluate semitheoretical Gibbs energy expressions; it can also be viewed as a potential alternative to classical vapor–liquid equilibria measurements. Until the development of the Van Ness-type isothermal dilution calorimeter (*11*, *15*), reliable heat of mixing measurements were often considered exceptionally difficult and were attempted only infrequently. On the other hand, no theoretical expression suggested the possibility of simultaneously representing or cross-predicting heats of mixing and vapor–liquid equilibria until the appearance of the Wilson equation (*13*) and other local composition models that followed (*1*, *5*, *10*).

As part of our effort to establish a data base for the evaluation of different liquid models, an isothermal dilution calorimeter of the Van Ness (*11*, *15*) type was developed and data were obtained for three miscible and five partially miscible nonelectrolyte systems. These results have been combined elsewhere (*8*, *9*) with phase equilibria and additional heats of mixing from the literature and used to investigate the utility of local composition equations in representing, extrapolating, and cross-predicting the different types of binary data. The combination of heats of mixing and activity coefficients at infinite dilution, the latter measured directly with a newly developed technique (*3*), has been found sufficient to describe completely the nonideality of miscible systems over a reasonable temperature range.

Apparatus

The calorimeter is shown schematically in Figures 1 and 2. The mixing occurs in a Dewar flask sealed by a moving Teflon piston. One component is weighed into the flask and then all vapor is eliminated through a vent as the piston is lowered. With the vent closed, the piston is raised to draw in the second component, which flows into the vessel through a stainless steel capillary tube and a mercury seal, under the pressure of a mercury column. Heat is added quantitatively at the same time to compensate for the endothermic mixing so that the system is kept isothermal. The composition of the mixture after each addition of the second component is determined by weighing into the solute reservoir a volume of mercury equal to that of the liquid added to the mixture.

Several advantages accrue from this type of calorimeter. The complete absence of a vapor space eliminates the necessity for any heat of vaporization correction, a substantial source of uncertainty in older calorimeter designs. In addition, the semicontinuous introduction of the solute, compared to various diaphragm-rupturing arrangements, permits the determination of as many data points as needed during a run and of all the data for a binary system in two runs. The measurement of the heat of mixing at very dilute concentrations is also facilitated. Finally, the isothermal operation of the instrument minimizes heat losses or gains through the calorimeter piston and, above all, obviates any absolute measurements other than those of the heat added quantitatively and the gravimetric determinations of composition.

The calorimeter was designed to combine simplicity of construction and operation and accuracy of better than 1%. The Dewar mixing vessel is 8 in. high and has a 2-in. inner diameter of precision bore tubing. It is held stationary relative to the solute reservoir which is about 4 in. high and 2 in. in diameter with a 16 in. high, 0.3 in. diameter column at its center where mercury is contained. The column broadens into a

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