Excess Enthalpies and Excess Volumes of Binary Mixtures Containing Toluene + Cyclic Ethers at 298.15 K

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The excess molar enthalpies H^E and the excess molar volumes of mixing V^E of binary liquid systems containing toluene + cyclic ethers (1,4-dioxane, oxane, 1,3-dioxolane, or oxolane) were determined at atmospheric pressure and 298.15 K by using an isothermal flow microcalorimeter and a digital densimeter. The experimental data were correlated by means of a polynomial function, and the influence of ring size and proximity of oxygen atoms in diethers on H^E and V^E has been discussed.

Introduction

As an extension of our systematic studies (*1-3*) reporting the excess molar enthalpies H^E for binary mixtures of cyclic ethers + 1-chloronaphthalene, + halothane, and + 1-methylnaphthalene, we have determined in this paper the excess molar enthalpies H^E and the excess molar volumes V^E of toluene + four cyclic ethers, namely, 1,4-dioxane, oxane, 1,3-dioxolane, or oxolane. The aim of these investigations is to correlate the experimental data and to stress the factors affecting interactions between molecules in such mixtures.

We are not aware of any previous investigations of the excess properties of these systems with the exception of H^E of toluene + 1,4-dioxane at 300.05 K (*4*).

Experimental Section

Materials and Density Measurements. Toluene (component 1), a Fluka product, analytical grade 99.8%, was used without further purification. The sources and purities of the cyclic ethers (component 2) were the same as in refs 1-3.

Before use, all liquids were stored in the dark over molecular sieves (Union Carbide Type 4A, $^1/_{16}$-in. pellets).

Table I reports the experimental densities ρ of pure components, at 298.15 K and atmospheric pressure and compared with literature values (*5-9*).

The procedure used for the preparation of the samples of mixing was described in ref 10.

Calorimetric Measurements. Measurements of excess molar enthalpy H^E were carried out in a flow microcalorimeter, model 2107 (LKB, Produkter AB, Bromma, Sweden). The apparatus and operating procedure are described elsewhere (*11, 12*).

Table I. Densities ρ of Pure Components at 298.15 K and Comparison with Literature Data

component	ρ/(g cm^{-3}) this work	ρ/(g cm^{-3}) lit.
toluene	0.862 149	0.862 19 (*5*)
0.879 16	0.879 103	0.879 16 (*6*)
1,4-dioxane	1.028 284	1.027 97 (*7*)
oxolane	0.882 339	0.882 698 (*8*)
1,3-dioxolane	1.058 827	1.058 65 (*9*)

Table II. Experimental Excess Molar Enthalpies H^E for Binary Mixtures of Toluene (1) + Cyclic Ethers (2) at 298.15 K

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
		Toluene + Oxane			
0.0368	-23.8	0.3143	-204.3	0.7334	-177.0
0.0710	-48.6	0.3793	-224.3	0.7857	-146.3
0.1326	-97.0	0.4783	-237.1	0.8462	-103.1
0.1865	-137.1	0.5790	-231.1	0.9167	-48.9
0.2340	-165.3	0.6471	-214.1	0.9565	-20.1
		Toluene + 1,4-Dioxane			
0.0318	9.4	0.3484	124.4	0.8279	56.1
0.0626	24.5	0.4451	129.1	0.8652	43.4
0.1179	50.2	0.5461	121.6	0.9059	29.2
0.1670	74.0	0.6160	110.9	0.9506	14.6
0.2109	91.0	0.7064	92.8		
0.2862	112.2	0.7624	76.3		
		Toluene + Oxolane			
0.0308	-30.7	0.3371	-311.9	0.8207	-153.2
0.0598	-62.7	0.4328	-337.1	0.8592	-109.1
0.1128	-126.9	0.5337	-334.2	0.9115	-55.1
0.1602	-182.4	0.6041	-315.3	0.9482	-22.5
0.2027	-223.7	0.6959	-264.2		
0.2761	-279.7	0.7532	-218.9		
		Toluene + 1,3-Dioxolane			
0.0517	31.2	0.3038	166.5	0.7971	86.1
0.0984	66.7	0.3956	180.6	0.8397	66.1
0.1406	95.2	0.4955	177.8	0.8871	44.1
0.1791	119.0	0.5670	167.1	0.9402	22.3
0.2466	149.8	0.6626	141.2		
		0.7236	117.0		

The microcalorimeter was calibrated by using the standard cyclohexane + hexane mixture (*13*), and the discrepancy between the measured and published values was less than 0.5% over the central range of concentration. The calorimetric experiments were performed at 298.15 ± 0.005 K (IPTS-68). The estimated accuracy of the calorimetric data is better than 1%.

Volumetric Measurements. Excess molar volumes V^E were measured at constant atmospheric pressure and at 298.15 K in a digital densimeter (Anton Paar DMA 60/602). The temperature was measured with a digital thermometer (DT 100-25/Anton Paar). A Colora ultrathermostat bath maintained the temperature constant to within 0.01 K. Bidistilled degassed water and dry air were used as calibrating substances. The mole fractions of samples were obtained with all weighings

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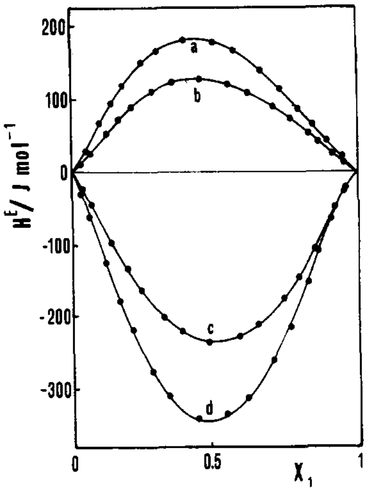

Figure 1. Excess molar enthalpies H^E of toluene (1) + 1,3-dioxolane (2) (a), + 1,4-dioxane (2) (b), + oxane (2) (c), and + oxolane (2) (d) at 298.15 K as a function of the mole fraction x_1 of toluene. The solid curves are least-squares representations of results by eq 1.

Table III. Experimental Excess Molar Volumes V^E of Binary Mixtures of Toluene (1) + Cyclic Ethers (2) 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})
Toluene + Oxane					
0.0045	−0.0030	0.3541	−0.1470	0.7496	−0.1175
0.0434	−0.0261	0.3893	−0.1525	0.8335	−0.0863
0.9304	−0.0574	0.4232	−0.1556	0.9074	−0.0520
0.1450	−0.0817	0.4718	−0.1596	0.9313	−0.0396
0.2172	−0.1114	0.5363	−0.1573	0.9939	−0.0032
0.2761	−0.1297	0.6079	−0.1508		
0.3108	−0.1388	0.7025	−0.1314		
Toluene + 1,4-Dioxane					
0.0401	0.0010	0.3916	−0.0086	0.6699	−0.0220
0.0788	0.0016	0.4626	−0.0113	0.7514	−0.0223
0.1647	0.0009	0.5004	−0.0152	0.8481	−0.0196
0.2151	−0.0005	0.5381	−0.0184	0.8944	−0.0150
0.2670	−0.0037	0.5982	−0.0196	0.9875	−0.0021
Toluene + Oxolane					
0.0049	n−0.0080	0.3765	−0.3521	0.6524	−0.3256
0.0534	−0.0818	0.4356	−0.3647	0.7085	−0.2936
0.0900	−0.1311	0.4853	−0.3679	0.7898	−0.2330
0.1338	−0.1841	0.5170	−0.3652	0.8588	−0.1676
0.1932	−0.2436	0.5592	−0.3594	0.9036	−0.1201
0.2316	−0.2764	0.5675	−0.3562	0.9878	−0.0168
0.3223	−0.3315	0.6131	−0.3421		
Toluene + 1,3-Dioxolane					
0.0040	−0.0016	0.2820	−0.0919	0.6172	−0.1216
0.0264	−0.0110	0.3460	−0.1075	0.6909	−0.1123
0.0769	−0.0301	0.3706	−0.1098	0.7710	−0.0961
0.1099	−0.0422	0.3986	−0.1151	0.8421	−0.0726
0.1996	−0.0710	0.4501	−0.1209	0.9141	−0.0445
0.2463	−0.0834	0.5218	−0.1243	0.9703	−0.0164

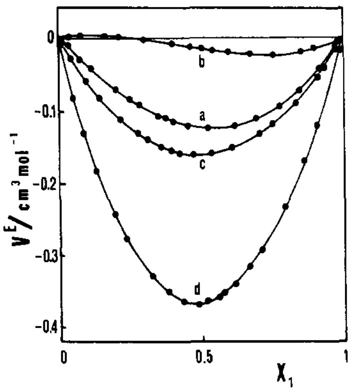

Figure 2. Excess molar volumes V^E of toluene (1) + cyclic ethers (2) at 298.15 K as a function of the mole fraction x_1 of toluene. The same letters are used as in Figure 1.

corrected for buoyancy and evaporation of components.

The equipment and the procedure for determining V^E measurements are described well in ref 10. The precision of the measured densities is of the order 1 × 10^{-6} g cm^{-3}.

Results and Discussion

The values of H^E and V^E for the four binary mixtures are reported in Tables II and III, respectively, and a graphical representation is given in Figures 1 and 2.

The polynomial function

$$Q^E_{calc} = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \qquad (1)$$

where Q^E is either H^E (J mol^{-1}) or V^E (cm^3 mol^{-1}), was fitted to each set of results by the method of least-squares with all points weighted equally.

Table IV summarizes the values of parameters a_k and the standard deviations $\sigma(Q^E)$ defined as

$$\sigma(Q^E) = \{\sum (Q^E_{calc} - Q^E)^2/(N - n)\}^{0.5} \qquad (2)$$

where N is the number of experimental points and n the number of coefficients a_k.

As can be seen from Figure 1, the H^E's for the systems containing diethers are positive whereas the corresponding systems with monoethers show negative H^E. Furthermore, the maximum absolute values of H^E are lower for the diethers, a behavior which was observed also for the mixtures of 1-methylnaphthalene with the same cyclic ethers (*1*).

As for the V^E vs x_1 curves, Figure 2, they always show volume contraction, with the exception of the system with 1,4-dioxane, explaining a feeble trend to inversion of sign toward solvent-poor mixtures.

Diethers show lower maximum absolute values of V^E than monoethers, as appeared for H^E.

Table IV. Coefficients a_k, Equation 1, and Standard Deviation $\sigma(Q^E)$, Equation 2, for Representation of Excess Functions of Toluene + Cyclic Ethers at 298.15 K

ether	Q^E	a_0	a_1	a_2	a_3	a_4	$\sigma(Q^E)$
oxane	H^E	−948.7	124.1	518.7			0.73
	V^E	−0.6368	0.0244				0.0007
1,4-dioxane	H^E	506.5	−166.5	158.5	−253.0		0.92
	V^E	−0.0595	−0.1129	−0.0214			0.0006
oxolane	H^E	−1349.7	153.1	256.3	881.3		0.94
	V^E	−1.4684	0.1268	−0.0385			0.0007
1,3-dioxolane	H^E	707.6	−204.0	−235.2	−292.1	386.0	0.70
	V^E	−0.4951	−0.0843				0.0006

Registry No. Toluene, 108-88-3; 1,4-dioxane, 123-91-1; oxane, 142-68-7; 1,3-dioxolane, 646-06-0; oxolane, 109-99-9.

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Separation of Phenol from Its Mixture with *o*-Cresol by Adductive Crystallization

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A ternary solid-liquid diagram of the system phenol, *o*-cresol, and 2-methyl-2-propanol is prepared. 2-Methyl-2-propanol can be used as an extraneous agent for the separation of phenol from its mixture with *o*-cresol by adductive crystallization in a multistage process. The boiling points of these compounds in the mixture differ by 9 °C and the melting points by 10 °C.

Introduction

The process of extractive or adductive crystallization appears attractive over the conventional separation methods used in the chemical industry for separation of organic isomeric or nonisomeric close boiling components from a mixture (*1-6*). The purpose of the present study was to select a suitable solvent for separation of components from a mixture of phenol-*o*-cresol by adductive crystallization, the boiling point and melting point differences between these two components being 9 and 10 °C, respectively. 2-Methyl-2-propanol is considered as a possible solvent for this system as it is a good solvent for many other separations (*6*). Its suitability was also judged by empirical measurements of enthalpy changes on complex formation for binary mixtures. After the favorable indication a detailed ternary solid-liquid equilibrium diagram was developed and the feasibility of the process demonstrated.

Solvent Selectivity by Calorimetry

In an adductive crystallization process the solvent usually forms a weak molecular compound, having a different melting point, with either one or both of the components to be separated. The data on enthalpy changes on complex formation were determined calorimetrically using the apparatus and procedure similar to those previously reported (*5*). The calorimeter consisted of a standard Dewar flask of ~0.2-L capacity and was mounted in a well-insulated constant-temperature bath with a water circulation pump. The thick and tightly fitting polypropylene lid had three holes, one for the tip of the jacketed buret through which the second liquid component was added, another for a thermometer graduated up to 0.1 °C, and the third for an electrically driven stirrer. The change in temperature was observed at steady state after mixing two components maintained at a constant temperature. Radiation corrections were applied and water equivalents of calorimeter determined repeatedly by the electrical method. All AnalaR grade chemicals were used during this investigation and further purified by conventional methods whenever it was necessary. The results for the two binaries of the present system are reported in Table I and also plotted in Figure 1, indicating that 2-methyl-2-propanol has greater interaction and more complex formation with phenol than *o*-cresol. The adduct-forming system usually showed enthalpy changes more than ~400 J/mol, and therefore the present calorimeter provided sufficient accuracy for the measurement. The working of the calorimeter was tested with the standard system (chloroform-acetone), yielding reasonably precise and comparable data (with less than ±2% error in measurement of enthalpy changes). Using the two-parameter chemical theory of solution (*7*), the apparent activity coefficient and selectivity values were determined and are shown in Figure 2. 2-Methyl-2-propanol appears to be a favorable solvent for separation of the eutectic of phenol and *o*-cresol.

Table I. Enthalpy of Mixing, $-\Delta H$, Data for Binary Systems at 50 °C

phenol (1) + 2-methyl-2-propanol (2)		*o*-cresol (1) + 2-methyl-2-propanol (2)	
x_2	$-\Delta H$, J/mol	x_2	$-\Delta H$, J/mol
0.098	661	0.105	415
0.192	1337	0.207	972
0.298	1904	0.291	1338
0.399	2179	0.396	1509
0.497	2192	0.496	1603
0.585	2049	0.596	1581
0.702	1520	0.682	1323
0.801	874	0.803	945
0.900	418	0.912	518

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