J. Chem. Eng. Data **1998,** *43,* 351−353

Excess Enthalpies for the Systems *o*-Xylene + Cyclohexanol + Phenol and *o*-Xylene + Cyclohexanol + 1,3-Butanediol at 318.15 K

Mati Kuus, Helle Kirss, Enn Siimer, and Ludmilla Kudryavtseva*

Institute of Chemistry, EE-0026 Tallinn, Estonia

Excess molar enthalpies (H^E) at 318.15 K are reported for two ternary systems, *o*-xylene + cyclohexanol + phenol and *o*-xylene + cyclohexanol + 1,3-butanediol, and for two constituent binaries formed by *o*-xylene with phenol and 1,3-butanediol. The ternary system containing phenol exhibits regions of both exothermic and endothermic mixing, H^E for the other ternary system are endothermic. Owing to partial miscibility in the *o*-xylene + 1,3-butanediol system, the ternary system containing 1,3-butanediol includes a region with two coexisting liquid phases. A modified Redlich−Kister equation fitted to experimental results provides a satisfactory mathematical representation of H^E data for the *o*-xylene + cyclohexanol + 1,3-butanediol system.

Introduction

Very little information on excess enthalpies (H^E) in ternary systems containing phenols and diols is available. In our earlier works (Kirss et al., 1995, 1997; Kuus et al., 1996, Siimer et al., 1997), we reported H^E data for some ternary systems composed of phenols and diols with alcohols and alkanes. A continuing development of solution models for describing the thermodynamic properties of ternary systems requires a large experimental database.

The present paper reports our results on H^E in the ternary systems *o*-xylene + cyclohexanol + phenol and *o*-xylene + cyclohexanol + 1,3-butanediol. There appears to be no data for excess enthalpies of these systems in the literature.

Additionally, no H^E data have been previously reported for the binary systems *o*-xylene + phenol and *o*-xylene + 1,3-butanediol at 318.15 K. *o*-Xylene + phenol is completely miscible, but *o*-xylene + 1,3-butanediol is a partially miscible system. Existing measurements of mutual solubilities in binary glycols + aromatic hydrocarbons systems are limited to systems containing benzene, *p*-xylene, and toluene (Mandik and Lešek, 1982). Our measurements were used to further test the descriptive abilities of the modified Redlich−Kister equation reported earlier (Siimer et al., 1997).

Experimental Section

A Calvet-type microcalorimeter DAK-1-1 and the static apparatus for mutual solubility measurements as well as experimental procedures have been fully described (Kuus et al., 1996) and were unchanged for this work. All mixtures were prepared by mass. The possible errors in mole fraction and excess enthalpy are estimated to be less than 0.0005 and ±2%, respectively. The last value is a result of the chemical and electrical calibration procedures (Kirss et al., 1996).

The purities of chemicals supplied by Reakhim (Ukraine) were tested chromatographically, and they were found to be more than 99.5%. The densities were measured by means of a capillary pycnometer with an accuracy of $\pm 2.0 \times 10^{-1}$ kg·m^{-3}. As seen from Table 1, the measured densities are in good agreement with the literature data.

Table 1. Densities (*d*) of Pure Compounds

compound	*T*/K	*d*/kg·m^{-3} obsvd	*d*/kg·m^{-3} lit.
o-xylene	293.15	880.1	880.1[a]
cyclohexanol	303.15	941.5	941.6[b]
phenol	314.15	1057.1	1057.6[b]
1,3-butanediol	293.15	1005.3	1005.3[b]

[a] TRC d-3290, 1996. [b] Dean, 1992.

Table 2. Measured Excess Enthalpy for Binary Systems *o*-Xylene (1) + Phenol (2) and *o*-Xylene (1) + 1,3-Butanediol (2) at 318.15 K

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
	o-Xylene (1) + Phenol (2)		
0.154	407	0.746	1026
0.268	650	0.795	929
0.383	890	0.878	752
0.508	1051	0.906	625
0.640	1089		
	o-Xylene (1) + 1,3-Butanediol (2)		
0.055	290	0.640[a]	383
0.104	484	0.729[a]	359
0.212[a]	508	0.815[a]	335
0.313[a]	461	0.871[a]	313
0.400[a]	443	0.945[a]	280
0.496[a]	430		

[a] Total mole fraction of two liquids.

Cyclohexanol, 1,3-butanediol, and phenol were stored in a drybox and protected from light.

The binodal curve in the ternary system *o*-xylene + cyclohexanol + 1,3-butanediol was measured by titrating *o*-xylene + 1,3-butanediol with cyclohexanol. *o*-Xylene + 1,3-butanediol mixtures were prepared by adding known masses of components into the vessel. The accuracy of cloud points was estimated to be about 0.35 mass %. The temperature of the water bath was controlled at 318.15 K within ±0.1 K.

We could not determine cloud points in the *o*-xylene + 1,3-butanediol system in the *o*-xylene-rich region.

---

* To whom correspondence should be addressed. E-mail: siimer@argus.chemnet.ee.

S0021-9568(97)00267-7 CCC: $15.00

Table 3. Coefficients A_i of the Redlich−Kister (Eq 2) and Standard Deviations $\sigma(H^E)$ for Binary Systems at 318.15 K

system	A_0	A_1	A_2	A_3	A_4	A_5	$\sigma(H^E)$/J·mol^{-1}
o-xylene + phenol	4185.916	1823.77	−88.97	1167.48	2709.92	0	12.1
o-xylene + 1,3-butanediol	1735.56	320.27	645.48	−6661.63	5241.77	7594.02	24.0

Table 4. Experimental Excess Enthalpies for the Ternary Systems *o*-Xylene (1) + Cyclohexanol (2) + Phenol (3) and *o*-Xylene (1) + Cyclohexanol (2) + 1,3-Butanediol (3) at 318.15 K

x_1	x_2	x_3	H^E/J·mol^{-1}	x_1	x_2	x_3	H^E/J·mol^{-1}
o-Xylene (1) + Cyclohexanol (2) + Phenol (3)							
$x_1/x_2 = 1.00$				$x_1/x_3 = 2.00$			
0.444	0.444	0.112	763	0.581	0.129	0.290	395
0.384	0.384	0.232	90	0.480	0.280	0.240	155
0.287	0.287	0.426	−449	0.379	0.432	0.189	236
0.150	0.150	0.700	−465	0.142	0.787	0.071	280
$x_1/x_2 = 0.33$				$x_2/x_3 = 1.00$			
0.206	0.617	0.177	−82	0.906	0.047	0.047	510
0.154	0.462	0.384	−908	0.798	0.101	0.101	577
0.093	0.279	0.628	−1058	0.660	0.170	0.170	483
0.050	0.149	0.801	−690	0.102	0.449	0.449	−1175
$x_1/x_2 = 2.00$				$x_2/x_3 = 0.67$			
0.546	0.273	0.181	419	0.808	0.077	0.115	561
0.449	0.224	0.327	40	0.655	0.138	0.207	486
0.203	0.102	0.695	−83	0.522	0.191	0.287	230
0.097	0.048	0.855	−37	0.133	0.347	0.520	−1005
$x_1/x_3 = 1.00$				$x_2/x_3 = 2.00$			
0.434	0.133	0.433	229	0.849	0.101	0.050	713
0.358	0.284	0.358	−268	0.756	0.163	0.081	769
0.278	0.445	0.277	−327	0.610	0.260	0.130	619
0.124	0.752	0.124	−78	0.516	0.323	0.161	452
$x_1/x_3 = 0.50$				0.115	0.590	0.295	−877
0.286	0.142	0.572	−46				
0.257	0.230	0.513	−470				
0.216	0.351	0.433	−715				
0.055	0.834	0.111	−304				
o-Xylene (1) + Cyclohexanol (2) + 1,3-Butanediol (3)							
$x_1/x_2 = 1.00$				$x_2/x_3 = 1.00$			
0.442	0.442	0.116	1598	0.844	0.078	0.078	1035
0.346	0.345	0.309	1455	0.742	0.129	0.129	1360
0.250	0.249	0.501	1242	0.716	0.142	0.142	1423
0.096	0.096	0.808	631	0.670	0.165	0.165	1491
$x_1/x_2 = 4.00$				0.648	0.176	0.176	1522
0.700	0.175	0.125	1530	0.602	0.199	0.199	1526
0.698	0.175	0.127	1548	0.234	0.383	0.383	1191
0.609	0.152	0.239	1486	0.105	0.448	0.447	774
0.525	0.131	0.344	1358[a]	$x_2/x_3 = 2.00$			
0.386	0.097	0.517	1057[a]	0.751	0.166	0.083	1431
0.232	0.058	0.710	765[a]	0.560	0.293	0.147	1509
$x_1/x_2 = 2.00$				0.234	0.511	0.255	1165
0.584	0.292	0.124	1644	0.128	0.581	0.291	819
0.474	0.237	0.289	1545	$x_2/x_3 = 0.25$			
0.341	0.171	0.488	1339	0.779	0.044	0.177	794[a]
0.139	0.069	0.792	782	0.559	0.088	0.353	1008[a]
$x_1/x_2 = 0.50$				0.293	0.142	0.565	1235[a]
0.300	0.601	0.099	1346	0.259	0.149	0.592	1180
0.241	0.482	0.277	1241	0.191	0.162	0.647	1005
0.171	0.342	0.487	1060				
0.110	0.221	0.669	780				

[a] Total molar fraction of two liquid phases.

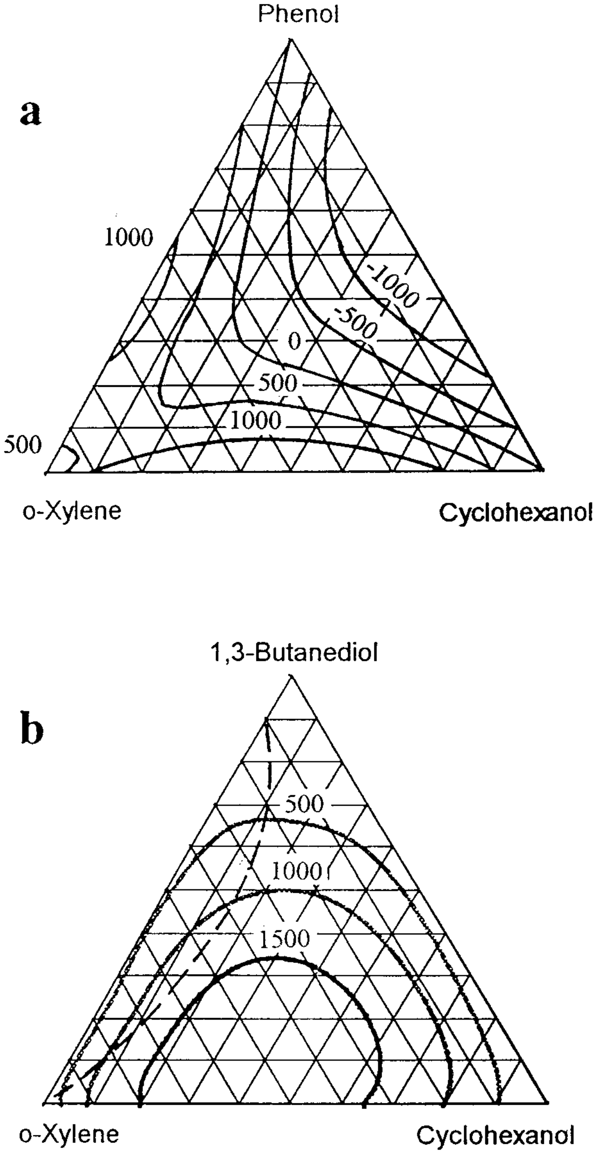

Figure 1. Isoenthalpic curves (H^E = const) of ternary systems at 318.15 K: (a) *o*-xylene + cyclohexanol + phenol, the graphical presentation of experimental data; (b) *o*-xylene + cyclohexanol + 1,3-butanediol, calculated by eq 4. The dashed line, drawn by the graphical interpolation of experimental data, separates the two-phase liquid system (left) from the one-phase system.

Table 5. Binodal Curve for *o*-Xylene (1) + Cyclohexanol (2) + 1,3-Butanediol (3) at 318.15 K

x_1	x_2	x_3	x_1	x_2	x_3
0.112		0.888	0.412	0.154	0.434
0.114	0.014	0.872	0.511	0.144	0.345
0.142	0.057	0.801	0.590	0.131	0.279
0.174	0.091	0.735	0.685	0.114	0.201
0.222	0.122	0.656	0.816	0.079	0.105
0.242	0.129	0.629	0.914	0.038	0.048
0.270	0.143	0.587	0.947	0.023	0.030
0.323	0.153	0.524			

Results

The experimental data of the excess enthalpy for the binary systems *o*-xylene + phenol and *o*-xylene + 1,3-butanediol are given in Table 2.

The binary H^E values were fitted to the Redlich−Kister equation (eq 1)

$$H^E/\text{J}\cdot\text{mol}^{-1} = x_1x_2\sum_{i=0}^{n-1}(x_1 - x_2)^i A_i \qquad (1)$$

where x_1 and x_2 are the mole fractions of the first and the second component, respectively, and n is the number of coefficients A_i.

The values of parameters A_i and standard deviations are listed in Table 3. In each case, the optimum number of

Table 6. Mean Relative Error between Experimental and Calculated by Eq 4 Ternary Excess Enthalpies, and Values of Coefficients A_i at $m = 4$

system	mean relative error, %	coefficients of eq 4			
		A_0	A_1	A_2	A_3
o-xylene + cyclohexanol + phenol	22.6	−16 414.36	−196 904.30	0	0
o-xylene + cyclohexanol + 1,3-butanediol	5.6	11 638.47	18 906.53	28 427.30	−100 480.80

coefficients was obtained through testing the standard deviation

$$\sigma(H^E) = [\sum(H^E_{calc} - H^E_{exp})^2/(N - n)]^{1/2} \qquad (2)$$

where N and n are the numbers of experimental points and coefficients of eq 1, respectively.

Superscript *a*'s of *o*-xylene + 1,3-butanediol composition (Table 2) refer to the total ("gross") mole fraction of two coexisting liquid phases. The immiscibility in the composition range (at x_1 values higher than 0.11) of this system shows a linear dependence of H^E on the total mole fraction of two liquids:

$$H^E/J\cdot mol^{-1} = 563.6 - 288.0\cdot x_1{}^a \qquad (3)$$

with $\sigma(H^E) = 7.4\ J\cdot mol^{-1}$.

The experimental results for the excess enthalpies of ternary systems at 318.15 K are listed in Table 4. We used the same experimental technique described earlier (Kuus et al., 1996), starting with a homogeneous binary liquid with mole ratio of components (x_i/x_k) shown in Table 4. The ternary system *o*-xylene + cyclohexanol + phenol exhibits regions of both exothermic and endothermic mixing, whereas the H^E values of *o*-xylene + cyclohexanol + 1,3-butanediol are endothermic over the entire composition range. The last system has both one-phase and two-phase liquids separated by a binodal curve; these measurements are given in Table 5.

The isoenthalpic lines H^E = const of the systems *o*-xylene + cyclohexanol + phenol and *o*-xylene + cyclohexanol + 1,3-butanediol are compared in parts a and b of Figure 1, respectively.

The isoenthalpic lines of the first system were determined by graphical interpolation of experimental data, whereas those of the second one were calculated using the equation reported and tested in our previous work (Siimer et al., 1997)

$$H^E = H_{12} + H_{23} + H_{31} + (A_0 + A_1x_1{}^m + A_2x_2{}^m + A_3x_3{}^m)x_1x_2x_3 \qquad (4)$$

where H_{ik} are contributions to the ternary H^E values from constituent binaries calculated by eq 1 and x_i is the mole fraction of component *i* in the ternary mixture. Of course, in principle, eq 4 cannot correctly reproduce excess enthalpy in the two-phase liquid region.

The values of parameters A_i of eq 4 and mean relative errors between experimental and calculated H^E for both systems are given in Table 6. As seen from Table 6, the equation gives a quite satisfactory description of excess enthalpy for the system *o*-xylene + cyclohexanol + 1,3-butanediol only. For the second ternary system eq 4 does not give fully satisfactory results. It is very difficult to describe excess enthalpy in such systems, having both exothermic and endothermic mixing, as we have mentioned earlier (Siimer et al., 1997).

Acknowledgment

Support of this work by the Estonian Scientific Foundation under Grant No. 1806 is gratefully acknowledged.

Literature Cited

Dean, J. A. *Lange's Handbook of Chemistry*, 14th ed.; McGraw-Hill, Inc.: New York, 1992.

Kirss, H.; Kuus, M.; Siimer, E.; Kudryavtseva, L. Excess Enthalpies for the Ternary Mixtures Phenol-1-Hexanol−*n*-Heptane and Phenol−Cyclohexanol−*n*-Heptane, and their Constituent Binaries at 318.15 K. *Thermochim. Acta* **1995**, *265*, 45−54.

Kirss, H.; Kudryavtseva, L.; Kuus, M.; Siimer, E. Excess Enthalpies for Ternary Mixtures Phenol−3-Methylphenol−1-Hexanol, 3-Methylphenol−1-Hexanol−Cyclohexanol and Their Constituent Binaries. *Chem. Eng. Commun.* **1996**, *146*, 139−147.

Kirss, H.; Kuus, M.; Siimer, E.; Kudryavtseva, L. Excess Enthalpies of 3- Methylphenol−*n*-Heptane, 3-Methylphenol−Phenol−*n*-Heptane and 3−Methylphenol−1-Hexanol−*n*-Heptane at 318.15 K. *Chem. Eng. Commun.* **1997**, *162*, 15−22.

Kuus, M.; Kirss, H.; Siimer, E.; Kudryavtseva, L. Excess Enthalpies for the Systems 1,3-Butanediol + Cyclohexanol + Decane and 1,2-Propanediol + 1,3-Butanediol + Cyclohexanol and for Constituent Binaries at 318.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1206−1209.

Mandik, M,; Lešek, F. Liquid−Liquid Equilibrium in Binary Glycols−Toluene and Glycols−Xylene Systems. *Collect. Czech. Chem. Commun.* **1982**, *47*, 1686−1694.

Siimer, E.; Kirss, H.; Kuus, M.; Kudryavtseva, L. Excess Enthalpies for the Systems *o*-Xylene + Cyclohexanol + Nonane at 298.15 K and 318.15 K and 3-Methylphenol + 1-Hexanol + Heptane at 298.15 K and for Constituent Binaries. *J. Chem. Eng. Data* **1997**, *42*, 619−622.

TRC Thermodynamic Tables−Hydrocarbons, d-3290, 1996. Thermodynamic Research Center: Texas A&M University System, College Station, TX, extant 1996.

Received for review November 11, 1997. Accepted January 22, 1998.

JE970267M