J. Chem. Eng. Data **1997,** *42,* 619−622 **619**

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

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

Institute of Chemistry, EE-0026 Tallinn, Estonia

Excess enthalpies (H^E) were determined for two ternary systems, *o*-xylene + cyclohexanol + nonane and 3-methylphenol + 1-hexanol + heptane, and for their constituent binaries at 298.15 K and for the first ternary system also at 318.15 K. The ternary H^E as a function of the composition was described by a new modification of the Redlich− Kister equation and presented in the form of isoenthalpic (H^E = const) curves.

Introduction

This paper forms a part of our program on the measurement of the excess enthalpy (H^E) of ternary systems containing different alcohols and phenols. We report here experimental excess enthalpies for *o*-xylene + cyclohexanol + nonane at two temperatures (298.15 K and 318.15 K), for 3-methylphenol + 1-hexanol + heptane at 298.15 K, and for the constituent binaries.

A survey of the literature showed that excess enthalpies for binary mixtures of all three xylene isomers with different alkanols have been measured at 298.15 K (Rodriguez-Nuñez *et al.*, 1984, 1985; Letcher *et al.*, 1990). Comelly *et al.* (1988) have determined H^E of binary mixtures of *m*- and *p*-xylenes with cyclohexanol at 313.15 K. In our earlier works (Kirss *et al.*, 1996a,b, 1995a) we have reported H^E data for the systems 3-methylphenol + 1-hexanol + heptane, 3-methylphenol + 1-hexanol, 1-hexanol + heptane at 318.15 K, and cyclohexanol + nonane at 298.15 K. Reliable H^E exist for 1-hexanol + heptane at 288.15 K and 303.15 K (Belousov *et al.*, 1981).

Mathematical description of H^E in ternary systems whose components are associated and/or have a strong interaction is complicated. Unsatisfactory results of the prediction of H^E for such systems, *e.g.* by the UNIFAC models, are not surprising. We have found that the description of H^E by different equations of the polynomial type (for example, the modified Redlich−Kister equations) gives, in some cases, inadequate results although ternary excess enthalpy experimental data are used for the correlation (Kirss *et al.*, 1996b).

The choice of the correlation relationship for ternary H^E data remains uncertain. Prchal *et al.* (1983) have tested the representation of ternary H^E data on nine systems, using different prediction and correlation equations (among them more often used Scatchard and Tsao ones) and compared them. For systems characterized by a strong interaction between molecules, the search for a better description of ternary H^E values seems to be reasonable.

For the description of binary H^E data, the Redlich−Kister equation is popular:

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

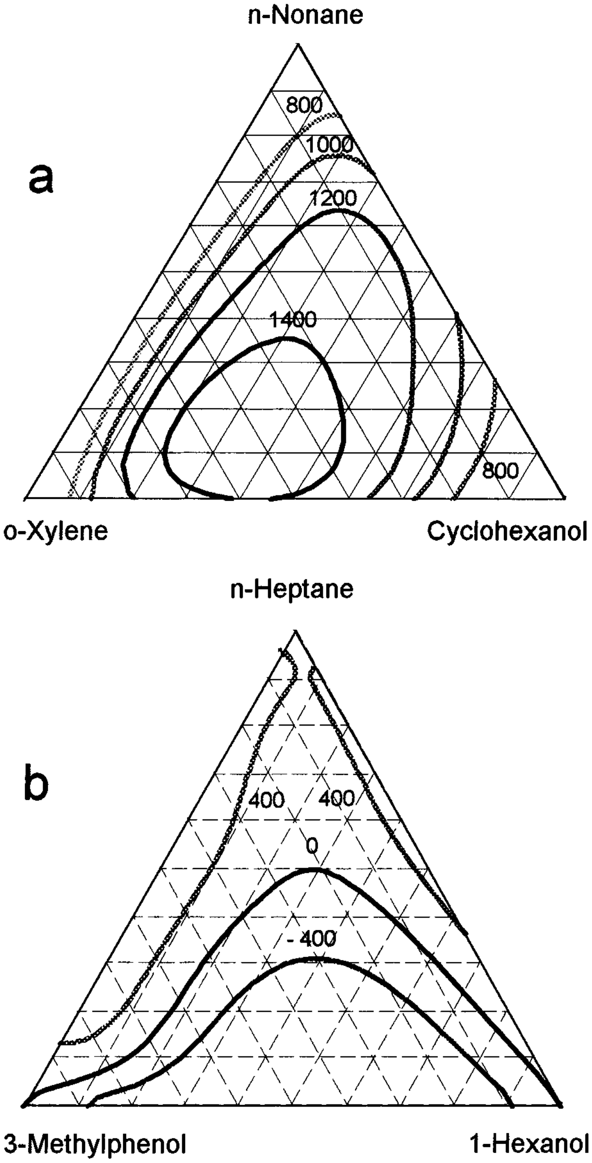

Figure 1. Isoenthalpic curves (H^E = const) of ternary systems at 298.15 K, calculated by eq 7: (a) *o*-xylene + cyclohexanol + nonane; (b) 3-methylphenol + 1-hexanol + heptane.

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.

---

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

S0021-9568(96)00396-2 CCC: $14.00

Table 1. Physical Properties of Pure Compounds, Density (d) and Refractive Index (n_D)

		density (d/kg·m^{-3})		n_D	
compound	T/K	obs	lit.	obs	lit.
heptane	293.15	683.8	683.69[a]	1.3876	1.38764[a]
nonane	293.15	717.6	717.72[a]	1.4055	1.40542[a]
o-xylene	293.15	880.1	880.1[a]	1.5055	1.50545[a]
1-hexanol	293.15	818.7	819.8[a]	1.4183	1.4181[a]
cyclohexanol	303.15	941.5	941.56[b]	1.4621	1.4629[b]
3-methylphenol	293.15	1034.2	1033.9[a]	1.5437	1.5414[a] (293.65 K) 1.5438[b]

[a] TRC, 1996. [b] Dean, 1992.

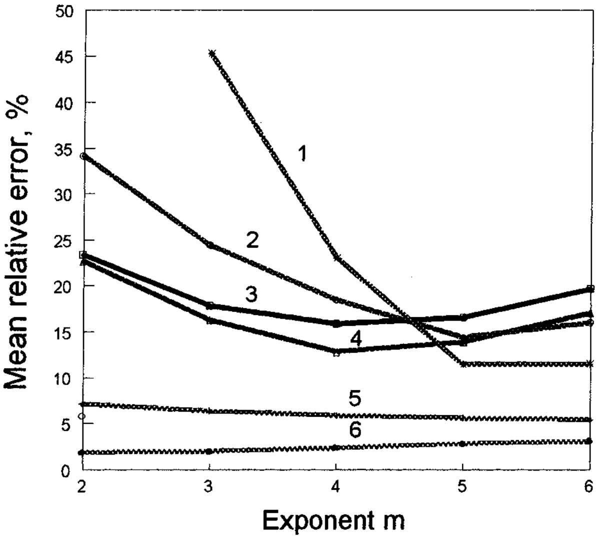

Figure 2. Dependence of relative error between experimental and calculated H^E for ternary systems on exponent m in eq 7: (1) 3-methylphenol + 1-hexanol + heptane at 298.15 K (this work); (2) the same system at 318.15 K (Kirss *et al.*, 1996b); (3) phenol + 1-hexanol + heptane at 318.15 K (Kirss *et al.*, 1995b); (4) phenol + cyclohexanol + heptane at 318.15 K (Kirss *et al.*, 1995b); (5) 1-butanol + 2-butanol + heptane at 298.15 K (Kirss *et al.*, 1995a); (6) *o*-xylene + cyclohexanol + nonane at 298.15 K (this work).

For the prediction of ternary H^E data, the modification of the Redlich–Kister equation has the form

$$H^E/\text{J}\cdot\text{mol}^{-1} = H_{ik} + H_{ij} + H_{jk} \tag{2}$$

where H_{ik}, H_{ij}, and H_{jk} are contributions to the ternary H^E value from the constituent binaries calculated by eq 1 and x_i is the mole fraction of component i in the ternary mixtures (for calculation 4–6 coefficients are used for each contribution term).

To have a better description of the excess enthalpy in ternary mixtures, a new term H_{ijk} is usually added to eq 2 (see eq 3). Coefficients of this term are calculated from ternary experimental H^E data. In this case the description of H^E is obtained by the correlation of experimental results.

$$H^E/\text{J}\cdot\text{mol}^{-1} = H_{ik} + H_{ij} + H_{jk} + H_{ijk} \tag{3}$$

The last term in eq 3 usually has the form $F(x_i,x_j,x_k)$, which is a polynomial expression with six empirical coefficients.

$$H_{ijk} = F(x_i,x_j,x_k) \times x_i x_j x_k \tag{4}$$

In this paper, we propose a new, more simple form of eq 4 which gave a remarkable improvement of H^E representation for ternary systems, particularly for those containing different components with hydroxyl groups.

Table 2. Measured Excess Enthalpy for Binary System Constituents of Ternary Systems *o*-Xylene (1) + Cyclohexanol (2) + Nonane (3) and 3-Methylphenol (1) + 1-Hexanol (2) + Heptane (3)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
o-Xylene (1) + Cyclohexanol (2)			
T = 298.15 K			
0.165	652	0.578	1405
0.256	931	0.645	1382
0.309	1082	0.699	1341
0.463	1332	0.806	1178
0.500	1379	0.923	758
T = 318.15 K			
0.107	565	0.566	1765
0.200	998	0.620	1745
0.315	1375	0.651	1731
0.422	1637	0.719	1651
0.496	1702	0.801	1456
0.530	1743	0.898	1063
o-Xylene (1) + Nonane (2)			
T = 298.15 K			
0.162	213	0.632	416
0.261	316	0.692	403
0.310	336	0.757	352
0.372	372	0.843	253
0.420	411	0.882	190
0.547	440	0.891	185
T = 318.15 K			
0.159	212	0.585	433
0.225	277	0.698	379
0.308	346	0.798	304
0.413	389	0.895	188
0.485	430		
Cyclohexanol (1) + Nonane (2)			
T = 318.15 K			
0.100	488	0.691	1376
0.195	847	0.733	1324
0.359	1256	0.772	1241
0.471	1403	0.839	1155
0.576	1453	0.933	797
0.674	1407		
3-Methylphenol (1) + 1-Hexanol (2)			
T = 298.15 K			
0.017	−95	0.484	−1226
0.143	−653	0.593	−1163
0.244	−948	0.610	−1156
0.302	−1050	0.729	−901
0.453	−1244	0.838	−630
0.457	−1245	0.910	−392
0.471	−1232		
3-Methylphenol (1) + Heptane (2)			
T = 298.15 K			
0.033	316	0.524	858
0.136	594	0.556	831
0.173	657	0.604	796
0.235	765	0.655	753
0.299	782	0.698	700
0.333	812	0.770	631
0.382	833	0.824	516
0.425	841	0.875	382
0.459	852		
1-Hexanol (1) + Heptane (2)			
T = 298.15 K			
0.119	472	0.476	545
0.122	475	0.527	515
0.234	549	0.672	363
0.236	552	0.714	331
0.307	573	0.770	265
0.420	558	0.896	100

Experimental Section

Measurements of H^E were carried out by a Calvet-type microcalorimeter DAK-1-1 (made in USSR). The apparatus and experimental procedures have been described in the previous papers (Otsa *et al.*, 1979; Kuus *et al.*, 1996).

Table 3. Coefficients A_i of the Redlich−Kister Equation (1) and Standard Deviations $\sigma(H^E)$ for Binary Systems

system	T/K	A_0	A_1	A_2	A_3	A_4	A_5	$\sigma(H^E)$/J·mol^{-1}
o-xylene + cyclohexanol	298.15	5507.37	1486.80	646.93	803.99	2994.68	3232.32	6.5
	318.15	6885.92	1784.10	1533.81	881.21	2215.38	3108.88	10.8
o-xylene + nonane	298.15	1727.90	420.51	29.90	−419.92	0	0	7.6
	318.15	1709.93	287.95	−74.09	−91.06	391.24	0	8.3
cyclohexanol + nonane	318.15	5762.91	−1493.17	14.87	1648.87	5757.29	−7218.06	14.8
3-methylphenol + 1-hexanol	298.15	−4939.49	381.54	718.35	799.13	1496.05	−1154.51	12.2
3-methylphenol + heptane	298.15	3411.80	−941.69	461.91	4696.88	2646.49	−9812.82	22.8
1-hexanol + heptane	298.15	2109.98	1342.70	35.78	479.97	2061.98	−3351.63	6.1

Table 4. Experimental Excess Enthalpies for Ternary Systems *o*-Xylene (1) + Cyclohexanol (2) + Nonane (3) at 298.15 K and 318.15 K and 3-Methylphenol (1) + 1-Hexanol (2) + Heptane (3) at 298.15 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) + Nonane (3)							
T = 298.15 K							
$x_1/x_2 = 1.00$				$x_2/x_3 = 1.00$			
0.422	0.422	0.156	1496	0.785	0.107	0.108	1056
0.375	0.375	0.250	1469	0.472	0.264	0.264	1445
0.268	0.267	0.465	1344	0.266	0.367	0.367	1405
0.194	0.193	0.613	1153	0.110	0.445	0.445	1249
$x_1/x_2 = 0.50$				$x_2/x_3 = 0.50$			
0.292	0.584	0.124	1300	0.796	0.068	0.136	929
0.262	0.525	0.213	1361	0.608	0.131	0.261	1239
0.192	0.384	0.424	1319	0.497	0.167	0.336	1322
0.128	0.256	0.616	1187	0.141	0.286	0.573	1228
$x_1/x_2 = 2.00$				$x_2/x_3 = 2.00$			
0.580	0.289	0.131	1446	0.880	0.080	0.040	844
0.531	0.265	0.204	1450	0.717	0.189	0.094	1269
0.361	0.180	0.459	1265	0.391	0.406	0.203	1487
0.239	0.120	0.641	1014	0.165	0.557	0.278	1254
$x_1/x_3 = 1.00$							
0.400	0.199	0.401	1345				
0.318	0.364	0.318	1457				
0.180	0.639	0.181	1171				
T = 318.15 K							
$x_1/x_2 = 1.00$				$x_1/x_3 = 0.50$			
0.404	0.403	0.193	1853	0.276	0.177	0.547	1542
0.325	0.325	0.350	1817	0.218	0.348	0.434	1730
0.275	0.275	0.450	1697	0.113	0.662	0.225	1319
0.170	0.170	0.660	1424				
0.163	0.163	0.674	1394				
$x_1/x_2 = 2.01$				$x_1/x_3 = 2.00$			
0.595	0.297	0.108	1781	0.533	0.200	0.267	1694
0.444	0.221	0.335	1733	0.341	0.488	0.171	1779
0.361	0.180	0.459	1596	0.268	0.598	0.134	1598
0.334	0.166	0.500	1557	0.148	0.778	0.074	1078
0.207	0.103	0.690	1287				
$x_1/x_3 = 1.01$				$x_2/x_3 = 1.00$			
0.349	0.304	0.347	1811	0.778	0.111	0.111	1294
0.279	0.443	0.278	1786	0.582	0.209	0.209	1722
0.188	0.625	0.187	1513	0.462	0.269	0.269	1797
0.062	0.877	0.061	612	0.314	0.343	0.343	1806
3-Methylphenol (1) + 1-Hexanol (2) + Heptane (3)							
T = 298.15 K							
$x_1/x_2 = 1.00$				$x_1/x_3 = 1.00$			
0.374	0.374	0.252	−503	0.383	0.234	0.383	−168
0.311	0.311	0.378	−218	0.227	0.546	0.227	−453
0.296	0.296	0.408	−151	0.107	0.786	0.107	−338
0.154	0.154	0.692	241	0.098	0.804	0.098	−325
0.149	0.149	0.702	258	$x_2/x_3 = 1.02$			
0.102	0.102	0.796	268	0.945	0.028	0.027	−31
$x_1/x_2 = 0.50$				0.522	0.241	0.237	−342
0.284	0.568	0.148	−694	0.198	0.404	0.398	−121
0.201	0.402	0.397	−136	0.164	0.421	0.415	−53
0.102	0.204	0.694	246				
0.062	0.124	0.814	309				
$x_1/x_2 = 2.00$							
0.564	0.282	0.154	−567				
0.520	0.260	0.220	−346				
0.330	0.164	0.506	167				
0.288	0.144	0.568	232				

Heptane and nonane ("puriss grade", supplied by Reakhim) were used without further purification, their purity was 99.8−99.9%, as determined by gas chromatographic analysis. Cyclohexanol, 1-hexanol, and 3-methylphenol were dried with fresh ignited CaO and distilled in a high-efficiency Teflon rotor column. Purification was continued until trace impurities were no longer detectable by GLC. Alcohols and 3-methylphenol were stored in a drybox and protected from light. The density and refractive index values of the materials are given in Table 1 and compared with literature data.

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, carried out at both 298.15 K and 318.15 K, described in our recent paper (Kirss *et al.*, 1996a).

Results

The experimental data for the excess enthalpy for the binary systems are given in Table 2. The system cyclohexanol + nonane at 298.15 K has been studied earlier (Kirss *et al.*, 1995a).

The positive excess enthalpies have been measured over the entire composition range of all binary systems except for the system 3-methylphenol + 1-hexanol. The binary H^E values were fitted to the Redlich−Kister equation (eq 1). The values of parameters A_i and standard deviations are listed in Table 3. In each case, the optimum number of coefficients was obtained through testing the standard deviation

$$\sigma(H^E) = [\sum(H^E{}_{calc} - H^E)^2/(N - n)]^{1/2} \tag{5}$$

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

As seen in Table 4 and Figure 1 the excess enthalpies of the ternary system *o*-xylene + cyclohexanol + nonane are also positive for each composition, whereas the system 3-methylphenol + 1-hexanol + heptane exhibits regions of both exothermic and endothermic mixing. The latter system is complicated, at least three main processes take place at mixing, all being equilibrium ones: dissociation of hydrogen bonds in 3-methylphenol, the same in 1-hexanol, formation of new hydrogen bonds between 3-methylphenol and 1-hexanol.

Prediction of H^E by eq 2 gave relatively satisfactory results for the ternary system *o*-xylene + cyclohexanol + nonane at both temperatures used, but very poor results for the system 3-methylphenol + 1-hexanol + heptane. The mean relative error of calculated H^E may sometimes exceed even 100%, and in this case the use of eq 3 substantially improved the description of H^E. For example, for the system 3-methylphenol + 1-hexanol + heptane at 318.15 K, using in eq 3 the last term $H^E{}_{123}$ with six coefficients, reduced the mean relative error from 117.2% to 34.5% (Kirss *et al.*, 1996b). The last result, however, is also considered unsatisfactory. We propose using the next simple form of eq 4 (the last term of eq 3), being strictly empirical:

$$H_{123} = (A_0 + A_1x_1{}^m + A_2x_2{}^m + A_3x_3{}^m)x_1x_2x_3 \tag{6}$$

where coefficients A_0, A_1, A_2, and A_3 are calculated by the

Table 5. Mean Relative Error between Experimental and Calculated by Modified Redlich−Kister Equations (Eqs 3 and 7) Ternary Excess Enthalpies, and Values of Coefficients Used in Eq 7 (at $m = 4$)

	mean relative error, %			coeff of eq 7 at $m = 4$			
		calcd by eq 7					
system	calcd by eq 3	at optimum m value[a]	at $m = 4$	A_0	A_1	A_2	A_3
o-xylene + cyclohexanol + nonane at 298.15 K	11.9	2.2 (2)	2.3	3659.59	41928.99	−8944.28	30587.77
o-xylene + cyclohexanol + nonane at 318.15 K	13.0	1.8 (2)	2.3	4842.56	45573.51	−8348.52	69228.32
3-methylphenol + 1-hexanol + heptane at 298.15 K	158.0	11.4 (5)	23.0	−10763.09	102579.70	15304.04	−82136.18
3-methylphenol + 1-hexanol + heptane at 318.15 K (Kirss *et al.*, 1996b)	117.2	14.4 (4)	18.4	−7535.61	1760.68	9284.03	−144786.70
phenol + 1-hexanol + heptane at 318.15 K (Kirss *et al.*, 1995b)	105.6	15.8 (4)	15.8	−6696.97	2722.16	−22199.16	−126738.00
phenol + cyclohexanol + heptane at 318.15 K (Kirss *et al.*, 1995b)	125.9	12.8 (4)	12.8	−9931.63	9050.37	−4767.31	−125330.70
1-butanol + 2-butanol + heptane at 298.15 K (Kirss *et al.*, 1995a)	29.5	5.3 (7)	5.8	−1986.35	−5893.02	−4183.69	−22592.78

[a] Optimal values of m are given in parentheses.

least squares method by solving the system of normal equations obtained by considering the differences between experimental and calculated by eq 2 H^E values. The exponent m is the fifth parameter, but in many cases (for systems of similar type) the constant integer (*e.g.*, $m = 4$) can be used.

Concretely, eq 3 can here be expressed as follows:

$$H^E = H_{12} + H_{13} + H_{31} + (A_0 + A_1x_1^{\,m} + A_2x_2^{\,m} + A_3x_3^{\,m})x_1x_2x_3 \quad (7)$$

In Figure 2, the mean relative error of H^E calculation as a function of exponent m is presented for six ternary systems studied by us. As seen in the figure, for systems 1−4, the optimum value of m is about 4−5 but for system 6 the lower m value gives somewhat better results. The last system (*o*-xylene + cyclohexanol + nonane) in Figure 2 is presented only at 298.15 K because the results for this system at 318.15 K are practically identical, with the mean relative error 2−3%.

In Table 5 the results of H^E calculations for some ternary systems are compared. A significant improvement of H^E description has been achieved. In all cases, eq 7, with a constant m exponent, $m = 4$, guarantees a closer estimate of the experimental value than does eq 3. The values of coefficients A_0, ..., A_3 of eq 7 are also included in Table 5.

The isoenthalpic curves given in Figure 1 were calculated using eq 7. These curves are quite similar to those obtained by the graphical interpolation of the experimental data.

Literature Cited

Belousov, V. P.; Morachevsky, A. G.; Panov, M. Yu. *Heat Properties of Nonelectrolyte Solutions*; Khimiya: Leningrad, 1981.

Comelly, F.; Francesconi, R.; Arcelly, A. Isobaric Vapor-Liquid Equilibrium and Liquid-Phase Enthalpy of Mixing Data for the Binary Mixtures of *m*- or *p*-Xylene with Cyclohexanol. *Can. J. Chem. Eng.* **1988**, *66*, 644−650.

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 of 1-Butanol - 2-Butanol - *n*-Heptane, 1-Hexanol - Cyclohexanol - *n*-Nonane, 2-Butanol - *n*-Heptane, 1-Hexanol - Cyclohexanol and Cyclohexanol - *n*-Nonane at 298.15 K. *Thermochim. Acta* **1995a**, *255*, 63−69.

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* **1995b**, *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.* **1996a**, *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.* **1996b**, in press.

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.

Letcher, T. M.; Prasad, A. K.; Schoonbaert, F. E. Z.; Mercer-Chalmers, J. Excess Enthalpies of (a Xylene + an Alkanol) at 298.2K. *J. Chem. Thermodyn.* **1990**, *22*, 765−770.

Otsa, E.; Mihkelson, V.; Kudryavtseva, L. Heats of Mixing in *n*-Alkane - *n*-Alkyne Systems. *Zh. Fiz. Khim.* **1979**, *57*, 899−901.

Prchal, M.; Dohnal, V.; Veselý, F. Prediction and Representation of Ternary Excess Enthalpy Data. *Collect. Czech. Chem. Commun.* **1983**, *48*, 1104−1114.

Rodriguez-Nuñes, E.; Paz-Andrade, M. I.; Navarro, J. M. Thermodynamic Properties of (a Xylene + an *n*-Alkanol). 1. Excess Molar Enthalpies at 298.15 K for 1-Hexanol, 1-Heptanol and 1-Octanol. *J. Chem. Thermodyn.* **1984**, *16*, 385−389.

Rodriguez-Nuñes, E.; Paz-Andrade, M. I.; Jimenez, E.; Bravo, R. Thermodynamic Properties of (a Xylene + an *n*-Alkanol). II. Excess Molar Enthalpies at 298.15 K for 1-Propanol, 1-Butanol, and 1-Pentanol. *J. Chem. Thermodyn.* **1985**, *22*, 765−770.

TRC Databases for Chemistry and Engineering. Thermodynamic Tables, Version 1996-2S; Thermodynamics Research Center: Texas A&M University System, College Station, TX, 1996.

Received for review December 9, 1996. Accepted February 20, 1997.[⊗] This work has been supported by the Estonian Scientific Foundation under Grant No. 1806.

JE960396N

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.