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Excess enthalpies for the ternary mixtures phenol–1-hexanol–*n*-heptane and phenol–cyclohexanol–*n*-heptane, and their constituent binaries at 318.15 K

H. Kirss, M. Kuus, E. Siimer, L. Kudryavtseva *

Institute of Chemistry, Estonian Academy of Sciences, Tallinn EE 0026, Estonia

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Abstract

Excess molar enthalpies H^E as a function of composition for the two ternary systems, phenol–1-hexanol–*n*-heptane and phenol–cyclohexanol–*n*-heptane, and five constituent binaries have been measured with a Calvet-type microcalorimeter at 318.15 K. All the excess enthalpies of binary systems containing *n*-heptane are positive, including those for a partially miscible system, phenol–*n*-heptane. The H^E values of phenol–alcohol systems are negative. The results have been used to predict ternary H^E data by the UNIFAC model and a version of this, the UNIFAC(3Q), both with enthalpy-fitted interaction parameters. It was found that the models could only qualitatively predict the ternary H^E values.

Keywords: Alcohol; Binary system; Excess enthalpy; Liquid mixture; Phenol; Ternary system

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1. Introduction

Continuing our studies of ternary mixtures containing compounds with the OH functional group, we have selected systems including phenol (hydroxybenzene). Few H^E measurements have been made for such systems. Methods which would permit additional H^E prediction for systems with phenolic compounds are highly desirable.

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* Corresponding author.

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Therefore, a version of the UNIFAC group contribution model, the UNIFAC(3Q) [1], used by us for ternary systems with two different alcohols [2–4], was applied in this work to mixtures containing phenol instead of one of the alcohols. The binary H^E data obtained in this work and measured earlier were used to calculate the interaction parameters for the UNIFAC and UNIFAC(3Q) models. Experimental H^E values were compared with those calculated with these models and also with the modified Redlich–Kister equation [5].

2. Experimental

Measurements were made in a Calvet-type differential microcalorimeter DAK-1-1 as described in an earlier paper [6]. For ternary measurements, one vessel was filled with a pure component, and the other with a homogeneous binary mixture of the other two components.

A chemical calibration was made by comparing our measured H^E results in the system 1-propanol–*n*-heptane at 318.15 K with those reported by Savini et al., taken from the Heats of Mixing Data Collection [7]. The accuracy of the observed H^E values was estimated to be better than 2.0%, based on both the electrical and chemical calibrations. *n*-Heptane (‘puriss.’ grade) was supplied by Reakhim (Kharkov, Ukraine) and used without further purification. Alcohols and phenol, which were special commercial grade reagents, were distilled in vacuum in a teflon rotor column and stored in special flasks to protect from external moisture and light. Analysis by GLC showed mass percentage purity levels to be >99.8% for *n*-heptane and >99.5% for alcohols and phenol. The densities (in kg m^{-3}) of the purified products measured at 318.15 K were: 1054.4 for phenol, 801.3 for 1-hexanol, 929.9 for cyclohexanol and 659.8 for *n*-heptane, in close agreement with the literature values.

The titration method was used to determine the binodal curves. Experiments were carried out in a 15-ml glass vessel supplied with a water jacket, an electromagnetic stirrer, a cap with a needle for displacement of air during sample addition, and a 2-ml syringe for adding a component. The temperature was kept at 45 ± 0.1°C by a VEB Prüfgeräte-Werk Medingen/Dresden, type U3 thermostat.

The boundaries of the binodal curve in the binary phenol–*n*-heptane system were found by titrating a pre-weighed amount of phenol with *n*-heptane until the cloud point was reached as determined visually. Then *n*-heptane was added until the turbidity disappeared. The procedure was repeated three times to guarantee finding reliable boundary points. The quantities of added substance were calculated by weighing the syringe before and after the experiments. The accuracy of the cloud points was estimated to be about 0.35 wt%.

Binodal curves in ternary systems were measured by titrating heterogeneous phenol–*n*-heptane mixtures with alcohol, 1-hexanol or cyclohexanol. The mixtures were prepared by weighing phenol and *n*-heptane into the vessel. The end points were checked by slight overtitration followed by back-titration from the one-phase to the two-phase region by addition of *n*-heptane.

3. Results and discussion

The results of H^E measurements (H^E as a function of mole fraction, x_i) are presented in Tables 1 and 2 for binary and ternary systems, respectively. No literature data were found for a comparison.

The expression

$$H^E/\mathrm{J\,mol^{-1}} = x_1 x_2 \sum_{i=0}^{k} A_i (x_1 - x_2)^i \tag{1}$$

where x_1 is the mole fraction of the first component, was fitted to each binary data set by the least squares regression, all points being weighted equally. Values of the

Table 1
The experimental excess ethalpy H^E in J mol^{-1} at 318.15 K for the binary systems

x_1	H^E
Phenol (1)–1-hexanol (2)	
0.135	−676
0.186	−843
0.215	−934
0.268	−1048
0.411	−1323
0.500	−1350
0.586	−1302
0.662	−1190
0.761	−937
0.860	−602
1-Hexanol (1)–*n*-heptane (2)	
0.103	719
0.174	815
0.192	831
0.252	857
0.304	868
0.322	860
0.438	832
0.460	797
0.478	769
0.500	750
0.546	686
0.584	651
0.653	586
0.806	344
Phenol (1)–cyclohexanol (2)	
0.252	−1179
0.286	−1319
0.303	−1362
0.442	−1615
0.500	−1625
0.595	−1584
0.644	−1546
0.736	−1303
0.849	−857
Cyclohexanol (1)–*n*-heptane (2)	
0.066	717
0.136	980
0.209	1100
0.265	1187
0.337	1252
0.439	1251
0.500	1227
0.507	1223
0.622	1080
0.729	876
0.853	516
Phenol (1)–*n*-heptane (2)	
0.107	780
0.197	1025
0.258*	1125
0.344*	1075
0.390*	1059
0.431*	1038
0.550*	991
0.591*	966
0.649*	959
0.680*	924
0.692*	915
0.741*	895
0.792	850
0.799	821
0.846	665
0.875	597
0.905	461

Table 2
Excess enthalpies H^E in J mol^{-1} at 318.15 K for the ternary systems

x_1	x_2	x_3	H^E_{exp}	Predicted by	
				UNIFAC	UNIFAC(3Q)
		Phenol (1)–1-hexanol (2)–n-heptane(3)			
			$r_{12} = 1.0$[a]		
0.370	0.370	0.260	−376	−496	−292
0.167	0.167	0.666	421	368	768
0.092	0.092	0.816	484	496	724
			$r_{23} = 1.0$[a]		
0.126	0.437	0.437	185	10	303
0.297	0.351	0.352	−147	−280	13
0.318	0.341	0.341	−153	−295	−12
0.418	0.291	0.291	−149	−315	−91
0.427	0.287	0.286	−185	−316	−98
0.484	0.258	0.258	−160	−300	−120
0.538	0.231	0.231	−245	−275	−133
0.642	0.179	0.179	−70	−209	−133
0.660	0.170	0.170	−117	−196	−131
			$r_{23} = 2.0$[a]		
0.145	0.573	0.282	−125	−266	−63
0.241	0.509	0.250	−380	−509	−309
0.294	0.473	0.233	−481	−590	−405
0.427	0.384	0.189	−563	−678	−549
0.550	0.301	0.149	−498	−643	−565
0.620	0.255	0.125	−492	−592	−540
0.692	0.206	0.102	−420	−509	−478
0.782	0.146	0.072	−309	−386	−375
			$r_{23} = 0.5$[a]		
0.186	0.271	0.543	300	123	522
0.252	0.249	0.499	216	80	478
0.337	0.221	0.442	230	74	430
0.440	0.186	0.374	292	109	384
0.562	0.146	0.292	336	158	321
0.757	0.081	0.162	287	194	203
			$r_{23} = 5.7$[a]		
0.206	0.675	0.119	−609	−702	−610
0.343	0.559	0.098	−884	−962	−905
0.454	0.464	0.082	−982	−1028	−1000
0.614	0.328	0.058	−892	−947	−940
			$r_{23} = 0.05$[a]		
0.473	0.026	0.501	1044	1102	1293
		Phenol (1)–cyclohexanol (2)–n-heptane(3)			
			$r_{12} = 1.0$[a]		
0.071	0.071	0.858	580	476	611
0.122	0.122	0.756	652	519	767
0.123	0.123	0.754	649	518	768
0.194	0.193	0.613	475	394	702
0.337	0.336	0.327	−163	−268	−98
0.443	0.443	0.114	−1073	−1057	−1048

Table 2 *(Continued)*

x_1	x_2	x_3	H^{E}_{exp}	Predicted by	
				UNIFAC	UNIFAC(3*Q*)
			$r_{12}=0.5$[a]		
0.103	0.206	0.691	658	477	706
0.165	0.328	0.507	358	233	476
0.222	0.443	0.335	62	−183	−7
0.302	0.601	0.097	−962	−1009	−970
			$r_{23}=1.0$[a]		
0.197	0.402	0.401	159	1	208
0.389	0.306	0.305	−232	−305	−156
0.459	0.271	0.270	−262	−344	−233
0.541	0.230	0.229	−261	−355	−287
0.710	0.145	0.145	−186	−290	−285
0.733	0.133	0.134	−157	−270	−275
			$r_{23}=0.5$[a]		
0.221	0.259	0.520	300	222	505
0.296	0.234	0.470	227	154	426
0.448	0.183	0.369	189	107	294
0.542	0.152	0.306	195	105	224
0.660	0.113	0.227	227	110	148
			$r_{23}=2.0$[a]		
0.123	0.585	0.292	268	−12	127
0.245	0.504	0.251	−252	−433	−305
0.346	0.436	0.218	−529	−640	−548
0.433	0.378	0.189	−655	−738	−682
0.678	0.215	0.107	−636	−699	−703
0.757	0.162	0.081	−504	−596	−602

[a] Obtained by mixing pure component j with a binary mixture $i+k$ in which the mole fraction ratio is $r_{ik}=x_i/x_k$.

coefficients A_i with the standard deviations, $\sigma(H^{E})$, are given in Table 3. The standard deviation is defined by

$$\sigma(H^{E})=\left[\sum(H^{E}_{exp}-H^{E}_{calc})^{2}/(n-m)\right]^{1/2} \tag{2}$$

where the sum was taken over the set of n results and m is the number of coefficients.

For the system phenol–*n*-heptane at 318.15 K, Eq.(1) was fitted to only the one-phase region H^{E} data. The region of immiscibility within the molar fraction of phenol between 0.238 and 0.745 shows a linear dependence of H^{E} on the total ("gross") mole fraction of the two liquids; these values in Table 1 are marked by an asterisk. All excess enthalpy values in the phenol–*n*-heptane system were measured directly.

Experimental data for the binodal curves at 318.15 K for the ternary systems studied are given in Table 4.

The ternary systems exhibit regions of both exothermic and endothermic mixing, separated by an isoenthalpic line $H^{E}=0$, as shown in Fig. 1 for the system phenol–cyclohexanol–*n*-heptane.

Table 3
Coefficients A_i of Eq. (1) and standard deviations $\sigma(H^E)$ for binary mixtures given in Table 1

System	A_0	A_1	A_2	A_3	A_4	A_5	$\sigma(H^E)$/J mol^{-1}
Phenol–1-hexanol	−5422.426	37.007	941.606	946.173	−1678.157	0	11.0
Phenol–cyclohexanol	−6523.234	−292.699	−1627.973	1136.012	7198.481	−7585.379	13.5
1-Hexanol–*n*-heptane	2998.548	−2298.182	2143.921	3597.751	−359.816	−11267.880	8.5
Cyclohexanol–*n*-heptane	4907.941	−1893.161	931.783	3142.461	2785.669	−9827.219	10.9
Phenol–*n*-heptane	4467.384	−304.595	2414.880	−1024.627	644.410	0	14.0

Table 4
The experimental data for the binodal curves at 318.15 K for ternary systems

x_1	x_2	x_3
	Phenol (1)–1-hexanol (2)–*n*-heptane (3)	
0.238	0	0.762
0.336	0.010	0.654
0.376	0.010	0.614
0.394	0.013	0.593
0.444	0.015	0.541
0.492	0.020	0.488
0.548	0.019	0.433
0.674	0.013	0.313
0.745	0	0.255
	Phenol (1)–cyclohexanol (2)–*n*-heptane (3)	
0.238	0	0.762
0.332	0.017	0.651
0.430	0.024	0.546
0.467	0.029	0.504
0.556	0.028	0.416
0.567	0.032	0.401
0.624	0.025	0.351
0.745	0	0.255

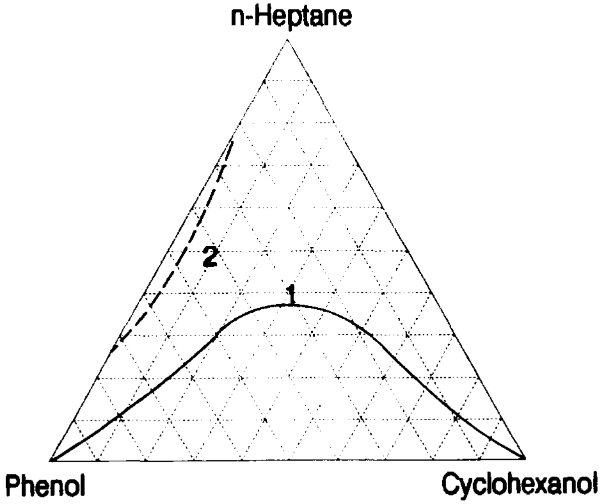

Fig. 1. The Gibbs triangle for the ternary system phenol–cyclohexanol–*n*-heptane at 318.15 K: 1, the isoenthalpic curve of $H^E = 0$; 2, the binodal curve.

The interaction parameters of the group-contribution models tested were determined using binary H^E data from this work and those found in the literature. The procedure was the same as described by Fredenslund et al. [8]. The sources of experimental H^E data used for the determination of interaction parameters for the

Table 5
H^E data used to calculate the group-interaction parameters of the phenolic OH group. Mean percentage deviation of the correlation, $\delta(H^E)/\%$, is given for the UNIFAC model (*) and its version UNIFAC (3Q) (**)

Groups	Systems	Number of sets/points	$\delta(H^E)/\%$ */**	Ref.
CH_2/OH(arom)	n-Hexane–phenol[a] ($T = 318.15$; 328.15 K)	5/38	18.0/15.9	Our data (unpubl.)
	n-Heptane–phenol[a] ($T = 318.15$ K)			This work
	n-Decane–phenol ($T = 353.15$ K)			[9]
	n-Decane–m-cresol[b] ($T = 353.15$ K)			[9]
cCH_2/OH(arom)	Cyclohexane–phenol ($T = 313.15$ K)	1/12	4.6/4.8	[10]
ACH/OH(arom)	Benzene–phenol ($T = 313.15$ K)	1/8	39.6/1.0	[10]
OH(prim)/OH(arom)	1-Hexanol–phenol ($T = 318.15$ K)	1/7	2.8/1.0	This work
cOH/OH(arom)	Cyclohexanol–phenol ($T = 318.15$ K)	1/8	2.4/1.1	This work

[a] H^E data for the completely miscible region only.

[b] m-Cresol is regarded as containing 1 CH_3, 4 ACH, 2 AC, 1 OH(arom).

Table 6
Group-interaction parameters of the UNIFAC (upper) and the UNIFAC(3Q) (lower) models based on the binary H^E data

	CH_2	cCH_2	ACH	OH(prim)	cOH	OH(arom)
CH_2	0	−30.26	93.20	981.13	512.13	931.97
		−35.15	46.98	459.84	328.41	464.13
cCH_2	71.94	0	231.72	1046.57	691.29	396.52
	52.31		44.76	375.81	416.44	328.15
ACH	70.99	−4.79	0	753.31	1144.79	681.40
	4.28	3.94		474.81	653.96	434.03
OH(prim)	190.98	321.87	59.31	0	54.17	−236.48
	−169.83	−154.29	−149.05		−16.89	−65.08
cOH	117.42	173.84	324.85	−51.42	0	−254.59
	−127.27	−144.75	−76.74	4.57		−114.60
OH(arom)	89.95	−3.25	190.43	−224.31	−283.90	0
	−130.99	−106.68	−87.89	−123.80	−138.39	

Table 7
Mean percentage deviations, $\delta(H^E)/\%$, between experimental values and those predicted by Eq. (2) (RK), the UNIFAC model (*) and its version the UNIFAC(3Q) (**) for excess enthalpies of the ternary systems

System	$\delta(H^E)/\%$		
	RK	*	**
Phenol–1-hexanol–*n*-heptane	105.6	49.5	38.9
Phenol–cyclohexanol–*n*-heptane	125.9	50.6	32.2

phenolic OH group (OH(arom)) are presented in Table 5. New parameters are presented in Table 6 together with the literature values [11–14] that were needed in this work for H^E predictions. The group surface area Q_s of OH(arom) for the original UNIFAC model was taken as 1.200. For the UNIFAC(3Q) version, trebled values of the original UNIFAC surface area parameters were used for all groups in mixtures.

The given values of the interaction parameters were used for prediction of excess enthalpy in ternary systems for all molar compositions used and the results are compared with the experimental H^E values in Table 2. Table 7 presents the mean percentage deviations between experimental H^E values and those predicted by the UNIFAC model, the UNIFAC(3Q) version, and the Redlich–Kister (RK) equation for ternary systems

$$H^E = H^E_{ik} + H^E_{ij} + H^E_{kj} \tag{3}$$

where H^E_{ik}, H^E_{ij} and H^E_{kj} are binary excess enthalpies presented by Eq. (1), the coefficients of which are given in Table 3, and x_i in Eq. (1) is taken as a mole fraction of the component i in a ternary mixture.

The results, given in Table 7, show that the Redlich–Kister equation gives poor predictions for both ternary systems. The UNIFAC(3Q) represents the H^E values better than the UNIFAC, although these predictions are only in qualitative agreement with the experiments.

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