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

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Excess enthalpies (H^E) were determined for two ternary systems, 1,3-butanediol + cyclohexanol + decane and 1,2-propanediol + 1,3-butanediol + cyclohexanol, and for their five constituent binaries at 318.15 K with a Calvet-type microcalorimeter. The ternary liquid−liquid coexistence curve for the first ternary system was measured at 318.15 K by the titration method. From the experimental results for binary systems, parameters of the Redlich−Kister equation were obtained and used to predict the ternary H^E results.

Introduction

Mixtures of diols with other organic compounds are of considerable interest because of the presence of specific interaction and the structure in the liquid state, as well as the reconstruction during the thermal motion. At the same time, diols represent a class of technically important compounds used in industry for the synthesis of polyesters. Information about the structure and thermodynamics of diols and their solutions is scarce. The presence of two hydroxyl groups in a molecule of a diol leads to formation of associates with a spatial structure (Zhuravlev *et al*., 1985). Because of that, solutions of diols may be regarded and used as model systems to study thermodynamic properties of liquids with intermolecular hydrogen bonds having a high viscosity. Experimental information about these systems helps to evaluate models and to test their applicability.

As seen from data collections (Francis, 1956; Wisniak and Tamir, 1980; Gmehling and Holderbaum, 1988), liquid−liquid equilibrium (LLE) and excess enthalpy (H^E) data for binary systems are limited mainly to diol + water and diol + 1-alkanol mixtures, containing as a diol 1,2-ethanediol. The LLE for diol + water + aromatic hydrocarbons has been investigated by Mandrík and Lešek (1982) and Lešek *et al*. (1985). Results of these works included LLE data for binary systems containing 1,2-propanediol and 1,3-butanediol. The excess enthalpy for the system 1,2-ethanediol + heptane with a split liquid phase has been measured by Belousov and Shutin (1985) at the temperatures 298.15, 303.15, and 318.15 K.

Reliable H^E data exist for the cyclohexanol + alkane systems, among them for cyclohexanol + decane at 298.15 K obtained by Kaur *et al*., 1989. We have measured H^E for the systems cyclohexanol + heptane at 318.15 K (Kirss *et al*., 1995a) and cyclohexanol + nonane at 298.15 K (Kirss *et al*., 1995b).

We report here experimental excess enthalpies (H^E) for ternary systems 1,3-butanediol + cyclohexanol + decane, 1,2-propanediol + 1,3-butanediol + cyclohexanol, and their constituent binaries at 318.15 K. At this temperature we have not found any experimental H^E values for the systems studied here. For the system 1,3-butanediol + cyclohexanol + decane, the LLE coexistence curve is also reported at the same temperature. The temperature 318.15 K was chosen for the experiments because of the melting point of cyclohexanol and to have the possibility of comparing interactions in diol-containing mixtures with phenol-containing ones, measured also at 318.15 K and reported earlier (Kirss *et al*., 1995a, 1996).

Table 1. Calibration Check of Calorimeter Comparing Measured and Literature Excess Enthalpies for the Systems Benzene (1) + Cyclohexane (2) at 298.15 K and 1-Propanol (1) + Heptane (2) at 318.15 K

benzene (1) + cyclohexane (2)			1-propanol (1) + heptane (2)		
	H^E/J·mol^{-1}			H^E/J·mol^{-1}	
x_1	this work	Stokes[a]	x_1	this work	Savini[b]
0.115	312	318.4	0.092	706	705.5
0.197	494	496.1	0.194	874	878.1
0.339	700	707.5	0.329	963	960.9
0.375	738	741.7	0.491	919	916.5
0.448	786	786.9	0.703	655	642.6
0.467	799	793.3	0.760	551	554.6
0.472	795	794.6	0.891	272	269.9
0.599	776	776.8			
0.703	688	685.9			
0.735	635	643.5			
0.877	364	365.5			

[a] Stokes *et al*., 1969; smoothed by eq 1 data. [b] Savini *et al*., 1976; smoothed by eq 1 data.

This work is a part of a systematic study of organic mixtures containing OH groups (Kirss *et al*., 1995a,b, 1996; Kuus *et al*., 1994) with an effort to predict ternary H^E data from H^E binary data alone. Experimental H^E data were used for determination of coefficients in the Redlich−Kister equation and to reproduce ternary H^E data by the modified Redlich−Kister equation.

Experimental Section

A Calvet-type differential microcalorimeter DAK-1-1 (made in USSR) (Kiryanov, 1983) was used to determine the excess enthalpy. An essential difference from a standard microcalorimeter DAK-1-1 was in the construction of the calorimetric cell. The latter consists of two vessels, an external one made of stainless steel and an internal one of Teflon. The bottom of the internal vessel is closed with a Teflon plug. When the plug is raised from the bottom by the help of a rod, two liquids, separate before mixing, are joined, and mixing is accomplished by means of a blade fixed to the lower end of the rod.

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Table 2. Physical Properties of Pure Compounds, Density (*d*) and Refractive Index (n_D)

	d/kg·m^{-3}		n_D	
compound	obs	lit. (Dean, 1992)	obs	lit. (Dean, 1992)
1,3-butanediol (T = 293.15 K)	1005.3	1005.3	1.4401	1.441
1,2-propanediol (T = 293.15 K)	1036.5	1036.4	1.4324	1.4331
decane (T = 293.15 K)	730.0	730.1	1.4120	1.4119
cyclohexanol (T = 303.15 K)	941.6	941.6	1.4621	1.4629

Table 3. Measured Excess Enthalpy for Binary System Constituents of Ternary Systems 1,3-Butanediol (1) + Cyclohexanol (2) + Decane (3) and 1,2-Propanediol (1) + 1,3-Butanediol (2) + Cyclohexanol (3) at 318.15 K

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
1,3-Butanediol (1) + Cyclohexanol (2)			
0.101	137	0.480	356
0.174	196	0.626	333
0.270	261	0.796	236
0.339	304	0.855	194
0.466	351	0.920	131
1,3-Butanediol (1) + Decane (2)			
0.050*	34.4	0.555*	38.9
0.075*	34.7	0.790*	41.0
0.135*	35.2	0.861*	41.6
0.380*	37.4	0.955*	42.4
Cyclohexanol (1) + Decane (2)			
0.092	854	0.459	1497
0.163	1181	0.508	1474
0.196	1278	0.574	1412
0.340	1476	0.720	1138
0.401	1498	0.808	875
0.435	1501	0.925	406
1,2-Propanediol (1) + Cyclohexanol (2)			
0.101	329	0.542	682
0.221	554	0.578	665
0.302	639	0.604	648
0.412	694	0.698	554
0.451	700	0.814	394
0.499	696	0.894	229
1,2-Propanediol (1) + 1,3-Butanediol (2)			
0.127	66	0.375	144
0.146	74	0.495	150
0.181	92	0.523	151
0.227	111	0.610	147
0.252	119	0.697	135
0.270	125	0.820	92
0.302	133	0.832	85
0.323	136		

[a] Asterisks refer to the total mole fraction of the two liquid phases.

Varying the size of the internal vessel makes it possible to change the mixture compositions, which were determined from the masses of liquids to be mixed. The average volume of the mixture was about 5 cm^3. A description of the cell construction and an operating procedure have been described in detail elsewhere (Otsa *et al.*, 1979).

For H^E measurements on ternary mixtures, one vessel was filled with a pure component, and the other with a binary mixture of the other two components. The microcalorimeter was calibrated electrically, and the calibration was checked by determining the H^E of benzene + cyclohexane mixtures at 298.15 K and comparing results with well-established literature data (Stokes *et al.*, 1969). The results are shown in Table 1. The calibration was also checked at 318.15 K by comparing with H^E data for 1-propanol + heptane mixtures obtained by Savini *et al.*, 1976. Measurements in both cases were reproduced within ±2%. The inaccuracy of the results could be expected to be ±2%. The mole fraction x was determined with an accuracy of ±0.0005.

The binodal curve was determined by a titration method. Experiments were carried out in a 15 mL glass vessel supplied with a water jacket, an electromagnetic stirrer, a cap with a hollow needle for displacement of air during sample addition, and a 0.5 mL syringe for adding a liquid. The temperature was kept at (318.1 ± 0.1) K by a VEB Prüfgeräte-Werk Medingen/Dresden type U3 thermostat.

The binodal curve in the ternary system was measured by titrating cyclohexanol + decane mixtures with 1,3-butanediol. Mixtures were prepared by adding known masses of cyclohexanol and decane into the vessel. The end points were checked by a slight overtitration followed by a back-titration from the two-phase region to the one-phase one by adding cyclohexanol. Quantities of added substance were calculated from the mass of the syringe before and after experiments. The accuracy of cloud points was estimated to be about 0.35 mass % (conditioned by the mass of one drop in the drop by drop addition of a component to the binary mixture).

It appeared impossible to obtain reproducible results in the determination of cloud points in the binary 1,3-butanediol + decane system.

Decane (“puriss grade”) was supplied by Reakhim (Kharkov, Ukraine) and used without further purification. Both diols and cyclohexanol were dried with fresh ignited CaO and distilled at subatmospheric pressure in a high-efficiency Teflon rotor column. Purities were checked by gas chromatography. Purification was continued until trace impurities were no longer detectable. Diols and cyclohexanol were stored under an argon atmosphere in a drybox and protected from light. Pure component refractive indexes (n_D) and densities (kg·m^{-3}) are compared with the literature data in Table 2. Refractive indexes were measured with a calibrated Abbe refractometer; densities, with a water-calibrated pycnometer.

Results

Experimental excess enthalpies for binary mixtures are shown in Table 3. They were fitted to the Redlich–Kister equation

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

where x_1 and x_2 are the mole fractions of the first component and the second one, respectively, and n is the number of coefficients A_i. Values of coefficients A_i and standard deviations $\sigma(H^E)$ are given in Table 4. The standard

Table 4. Coefficients A_i of the Redlich–Kister Equation (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	$\sigma(H^E)$
1,3-butanediol + cyclohexanol	1425.254	88.597	−517.144	42.436	1247.811	1.11
cyclohexanol + decane	5915.253	−1169.240	1893.274	−2314.563	1884.300	0.89
1,2-propanediol + 1,3-butanediol	602.765	22.758	281.910	−59.326	−581.753	0.67
1,2-propanediol + cyclohexanol	2780.884	−382.049	389.68	−575.425	0	3.52

Table 5. Experimental and Calculated by Eq 1 Excess Enthalpies for 1,3-Butanediol (1) + Cyclohexanol (2) + Decane (3) and 1,2-Propanediol (1) + 1,3-Butanediol (2) + Cyclohexanol (3) at 318.15 K

		H^E/J·mol^{-1}				H^E/J·mol^{-1}	
x_1	x_2	exp	calc	$x_1{}^a$	$x_2{}^a$	exp	calc
1,3-Butanediol (1) + Cyclohexanol (2) + Decane (3)							
$r_{12} = 0.25^b$				$r_{23} = 0.5^b$			
0.169	0.675	891	748	0.075	0.308	1383	1285
0.113	0.451	1367	1237	0.152*	0.282*	1261	1107
0.089	0.357	1401	1286	0.184*	0.272*	1213	1039
0.066	0.262	1340	1254	0.235*	0.255*	988	934
0.039	0.157	1158	1083				
				$r_{23} = 1.0^b$			
$r_{12} = 0.5^b$				0.079	0.460	1408	1309
0.305	0.609	716	552	0.165	0.417	1335	1137
0.283	0.565	936	710	0.236*	0.382*	1215	1004
0.231	0.461	1206	978	0.278*	0.361*	1164	929
0.194*	0.387*	1239	1083				
0.179*	0.357*	1265	1107	$r_{23} = 2.3^b$			
				0.152	0.590	1138	989
$r_{12} = 1.0^b$				0.189	0.565	1131	940
0.456	0.457	768	529	0.211	0.549	1132	913
0.413*	0.413*	872	666	0.286	0.497	1096	821
0.358*	0.358*	887	792	0.334*	0.464*	1053	763
0.273*	0.274*	862	896	0.350*	0.453*	1012	744
				0.407*	0.413*	894	677
$r_{12} = 2.0^b$							
0.633*	0.316*	564	383				
0.609*	0.304*	573	425				
0.551*	0.276*	584	510				
0.234*	0.117*	591	640				
1,2-Propanediol (1) + 1,3-Butanediol (2) + Cyclohexanol (3)							
$r_{12} = 1.0^b$				$r_{23} = 1.0^b$			
0.395	0.395	464	438	0.426	0.149	646	630
0.270	0.269	609	574	0.360	0.281	587	563
0.177	0.176	539	526	0.267	0.467	481	450
0.111	0.110	396	417	0.114	0.772	234	223
$r_{12} = 2.0^b$				$r_{23} = 1.0^b$			
0.597	0.298	342	321	0.146	0.427	482	481
0.515	0.257	493	482	0.359	0.320	553	534
0.362	0.181	643	620	0.532	0.234	504	491
0.248	0.124	608	591	0.798	0.101	279	265
$r_{12} = 0.5^b$							
0.307	0.615	267	250				
0.265	0.530	415	390				
0.175	0.351	521	516				
0.113	0.227	470	454				

[a] Asterisks refer to the total mole fraction in two coexisting liquid phases. [b] Obtained by mixing pure component *j* with a binary mixture *i* + *k* in which the mole fraction ratio is $r_{ik} = x_i/x_k$.

deviation was calculated by

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

where *N* is the number of experimental points.

The immiscibility in the composition range of 1,3-butanediol + decane shows a linear dependence of H^E on the total ("gross") mole fraction of two liquids:

$$H^E = 34.01 + 8.82x_1{}^* \qquad (3)$$

with a standard deviation of 0.033. Total mole fractions in Tables 3 and 5 are marked by an asterisk. All excess enthalpy values for 1,3-butanediol + decane were measured directly, provided complete mixing was assured.

In Figure 1 the experimental and calculated by eq 1 H^E results for four binary systems are compared.

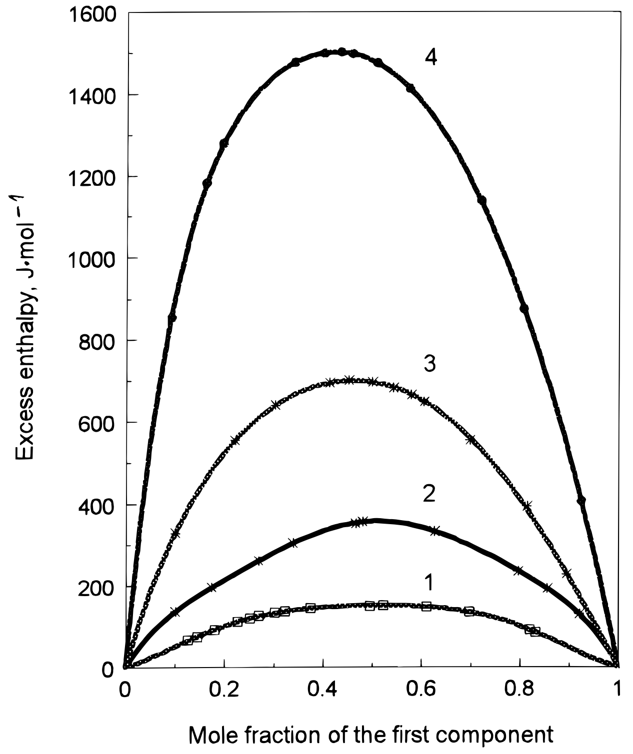

Figure 1. Excess enthalpy for binary systems at 318.15 K: (1) 1,2-propanediol (1) + 1,3-butanediol (2); (2) 1,3-butanediol (1) + cyclohexanol (2); (3) 1,2-propanediol (1) + cyclohexanol(2); (4) cyclohexanol (1) + decane (2). Experimental points are compared with calculated ones by eq 1 curves (coefficients are given in Table 4).

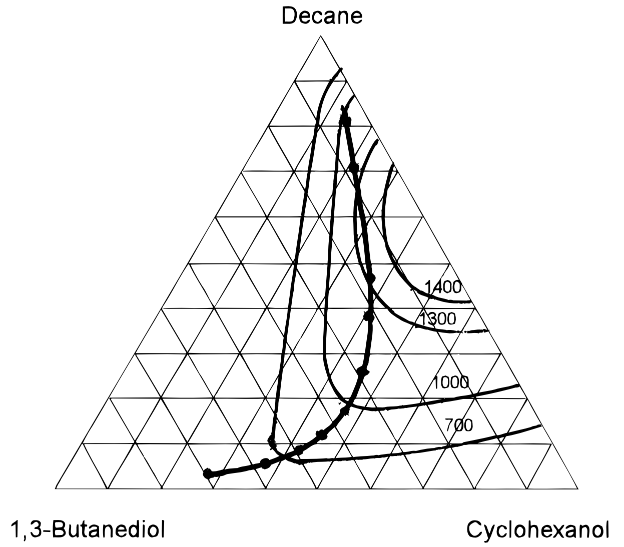

Figure 2. Isoenthalpic curves for the ternary system 1,3-butanediol + cyclohexanol + decane at 318.15 K. The binodal curve (— • —) is presented by the experimental points.

Experimental results for two ternary systems are presented in Table 5. Similarly to monofunctional alcohols, diols in the liquid state are self-associated. The decomposition of associates results in the positive contribution to H^E. This effect becomes dominant in both systems. Excess enthalpies of all binaries involved are endothermic. A significant difference between H^E in the decane mixtures with cyclohexanol and 1,3-butanediol may be attributed mainly to the different structure of alcohol and diol associates.

The ternary system 1,3-butanediol + cyclohexanol + decane exhibits regions of both one-phase and two-phase liquids separated by a binodal curve on the Gibbs triangle (Figure 2). Experimental data for the binodal curve at 318.15 K are given in Table 6.

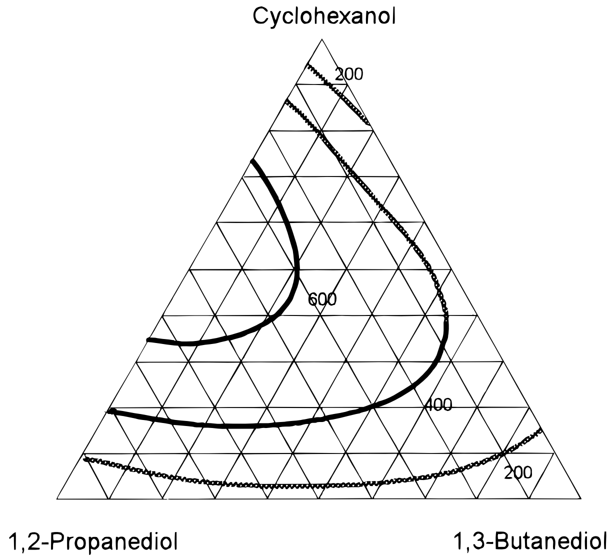

Figure 3. Isoenthalpic curves for the ternary system 1,2-propanediol + 1,3-butanediol + cyclohexanol at 318.15 K.

Table 6. Binodal Curve for 1,3-Butanediol (1) + Cyclohexanol (2) + Decane (3) at 318.15 K

x_1	x_2	x_3	x_1	x_2	x_3
0.683	0.281	0.036	0.206	0.398	0.396
0.561	0.377	0.062	0.161	0.353	0.486
0.487	0.424	0.089	0.112	0.290	0.598
0.428	0.446	0.126	0.066	0.205	0.729
0.356	0.469	0.175	0.033	0.127	0.840
0.280	0.455	0.265			

The H^E data for both ternary systems were reproduced by the expression

$$H^E/\mathrm{J{\cdot}mol^{-1}} = H^E_{12} + H^E_{13} + H^E_{23} \qquad (4)$$

where H^E_{ik} are the binary contributions calculated by eq 1 with coefficients from Table 4 for mole fractions x_i and x_k of the ternary mixture. The system 1,3-butanediol + decane was assumed to have a homogeneous liquid phase. The coefficients A_i of eq 1 were calculated on the basis of eq 3 ($A_0 = 158.744$, $A_1 = 8.934$, $A_2 = 10.430$, $A_3 = 61.188$, $A_4 = 635.638$, $\sigma(H^E) = 0.87$). The H^E calculation by eq 4 results are given in Table 5. The relative mean deviation between calculated and experimental results for the systems 1,3-butanediol + cyclohexanol + decane and 1,2-propanediol + 1,3-butanediol + cyclohexanol were equal to 16.2% (15.4% for homogeneous and 17.0% for heterogeneous liquid regions) and 4.0%, respectively. The isoenthalpic lines H^E = const in Figure 3 are calculated for the latter system by eq 4, whereas those of 1,3-butanediol + cyclohexanol + decane in Figure 2 are determined by graphical interpolation of experimental data.

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