

## EXCESS ENTHALPIES IN TERNARY SYSTEMS CONTAINING ALCOHOLS

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**Abstract.** New excess enthalpy data for the systems 2-methyl-1-propanol–2-butanol–*n*-heptane, 1-pentanol–3-methyl-2-butanol–*n*-heptane, 2-methyl-1-propanol–2-butanol, 1-pentanol–3-methyl-2-butanol, and 3-methyl-2-butanol–*n*-heptane were obtained at 298.15 K using a microcalorimeter DAK-1-1. The Redlich-Kister binary contribution method, the UNIFAC group-contribution model, and a version of the latter, UNIFAC(3Q), were applied to predict ternary excess enthalpies. The interaction parameters for groups CH<sub>2</sub>/OH(prim), CH<sub>2</sub>/OH(sec) and OH(prim)/OH(sec) were determined from binary excess enthalpy data taken from literature.

**Key words:** excess enthalpy, ternary and binary mixtures, Redlich-Kister equation, UNIFAC group contribution.

Excess enthalpy ( $H^E$ ) is of interest in process equipment design as well as in the thermodynamics of mixtures. Excess enthalpy studies can supply reliable data and empirical rules for technology and science, and help to investigate the states and structures of solutes and solvents in solution, as well as their interactions. In view of the variety of compounds and possible mixtures, a large number of systems needs to be studied experimentally to obtain the required data. Although a large amount of data has been reported in literature for binary systems, the data for ternary and higher multicomponent mixtures are scarce [1–3]. Therefore, the applicability of predictive methods is essential.

Some empirical predictive equations, such as the Redlich-Kister one, described in detail by Prchal et al. [4], were proposed to provide accurate excess enthalpy values just for ternary systems from the  $H^E$  of binary systems involved. In recent years, thermodynamic models have been employed to achieve the reliable prediction of  $H^E$ . The UNIFAC group contribution model [5] and its modifications [6–8] are the most widely used. The determination of the group interaction parameters is essential for the application of these methods. These parameters should be calculated from binary experimental  $H^E$  data on mixtures containing the adequate groups, in order to obtain the best  $H^E$  prediction results.

As a continuation of our studies on thermodynamic excess enthalpies for ternary systems, we have investigated, at 298.15 K, two ternary systems formed by *n*-heptane with alcohols of different structure: 2-methyl-1-propanol and 2-butanol, as well as 1-pentanol and 3-methyl-2-butanol.

The  $H^E$  data for three binary systems, 2-methyl-1-propanol—2-butanol, 1-pentanol—3-methyl-2-butanol, and 3-methyl-2-butanol—*n*-heptane, were also obtained in the present study, since these data are not available in literature.

The Redlich-Kister equation has been used to correlate the binary experimental data and to predict the  $H^E$  of ternary systems from binary data only. The ternary  $H^E$  data have also been predicted by the UNIFAC model and a version of it, UNIFAC(3Q) [9].

The purpose of the present work was to evaluate the influence of the alcohol structure on the excess enthalpy values, by comparing the results for two ternary systems, and to test the predictive ability of the aforementioned models.

## EXPERIMENTAL

2-Methyl-1-propanol and 3-methyl-2-butanol (special commercial grade reagents) were distilled, before use, in a teflon rotor column. 2-Butanol, 1-pentanol and *n*-heptane (puriss grade) were obtained from Reakhim (Kharkov, Ukraine) and used without further purification. The purity was found to be higher than 99.5% for alcohols and higher than 99.8% for *n*-heptane, as estimated by GLC. The  $H^E$  measurements were made at 298.15 K. Excess enthalpies were measured by direct mixing in the cells of a Calvet-type microcalorimeter DAK-1-1 [10]. The accuracy of the  $H^E$  results was estimated to be better than  $\pm 2$  per cent over most of the composition range.

## RESULTS

Experimental results for excess molar enthalpies of three binary mixtures at various composition are given in Table 1. They were fitted to the Redlich-Kister equation

$$H^E(\text{J mol}^{-1}) = x_1(1 - x_1) \sum_{i=1}^k A_i(2x_1 - 1)^{i-1}, \quad (1)$$

where  $x_1$  is the mole fraction of the first component in a binary system. The adjustable coefficients  $A_i$ , calculated by the least-square method, are given in Table 2, together with the standard deviations  $\sigma(H^E)$  of the results, defined by

$$\sigma(H^E) = \left[ \sum_i (H_{\text{exp}}^E - H_{\text{calc}}^E)_i^2 (n - k)^{-1} \right]^{\frac{1}{2}}, \quad (2)$$

where  $k$  is the number of coefficients needed to represent results adequately and the sum is taken over the set of  $n$  results. The calculation results are compared with the experimental data in Table 1. For these three binary systems, we found no previous results of  $H^E$  to compare with our ones.

The coefficients of Eq. (1) are presented in Table 2 also for other systems which are component binaries of the ternary systems studied. For  $A_i$  calculation, the experimental data from our earlier work [11] and literature [1] were used.

Experimental results for excess molar enthalpies of the ternary systems 2-methyl-1-propanol—2-butanol—*n*-heptane and 1-pentanol—3-methyl-2-butanol—*n*-heptane are given in Tables 3 and 4, respectively.



Table 1

Excess enthalpies  $H^E$  for binary systems at 298.15 K

$x_1$	$H^E$ , J mol <sup>-1</sup>		$x_1$	$H^E$ , J mol <sup>-1</sup>	
	exp	calc		exp	calc
2-Methyl-1-propanol(1)—2-butanol(2)					
0.098	-24	-24.2	0.583	-64	-63.2
0.121	-29	-29.1	0.657	-58	-58.1
0.154	-36	-35.5	0.778	-44	-44.0
0.295	-56	-55.8	0.861	-30	-30.2
0.418	-64	-64.5			
1-Pentanol(1)—3-methyl-2-butanol(2)					
0.171	-158	-157.9	0.553	-254	-256.6
0.258	-213	-212.9	0.676	-231	-232.0
0.478	-257	-262.1	0.757	-203	-205.4
0.532	-268	-259.0	0.782	-197	-194.9
3-Methyl-2-butanol(1)— <i>n</i> -heptane(2)					
0.111	417	413	0.480	1011	1015
0.203	661	679	0.565	1003	1033
0.293	837	843	0.745	784	764
0.360	965	923	0.826	451	458
0.460	1003	1004			

Table 2

Coefficients  $A_i$  of Eq. (1) and standard deviation  $\sigma(H^E)$  in J mol<sup>-1</sup> for binary systems at 298.15 K

System	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$\sigma(H^E)$	Source of exp. data
2-Methyl-1-propanol(1)—2-butanol(2)	-262.58	14.59	—	—	—	—	0.4	This work
1-Pentanol(1)—3-methyl-2-butanol(2)	-1045.56	103.69	-265.12	-401.68	—	—	5.6	This work
3-Methyl-2-butanol(1)— <i>n</i> -heptane(2)	4096.31	780.42	971.64	-3699.52	-4467.39	138.58	29.6	This work
2-Methyl-1-propanol(1)— <i>n</i> -heptane(2)	2866.52	-1215.71	756.03	-1455.15	1243.52	—	3.4	[1], p. 1864
2-Butanol(1)— <i>n</i> -heptane(2)	3626.43	-953.50	550.89	-2064.26	2480.76	—	24.3	[11]
1-Pentanol(1)— <i>n</i> -heptane(2)	2214.41	-819.50	164.45	-2009.42	1994.82	—	10.4	[1], p. 1925

Table 3

Excess enthalpies  $H^E$  at 298.15 K for the system  
2-methyl-1-propanol(1)—2-butanol(2)—*n*-heptane(3)

$x_1$	$x_2$	$x_3$	$H^E, \text{J mol}^{-1}$	$x_1$	$x_2$	$x_3$	$H^E, \text{J mol}^{-1}$
$x_{12}=1.00^a$				$x_{13}=1.00^a$			
0.092	0.092	0.816	650	0.132	0.736	0.132	314
0.104	0.104	0.792	713	0.303	0.394	0.303	580
0.122	0.122	0.756	757	0.366	0.268	0.366	642
0.149	0.149	0.702	780	$x_{23}=1.01^a$			
0.174	0.174	0.652	798	0.305	0.349	0.346	611
0.188	0.188	0.624	804	0.503	0.250	0.247	426
0.293	0.293	0.414	750	0.639	0.182	0.179	302
0.306	0.306	0.388	697	0.783	0.109	0.108	169
0.372	0.372	0.256	481	$x_{23}=0.50^a$			
0.420	0.420	0.160	341	0.546	0.152	0.302	526
$x_{12}=0.496^a$				0.668	0.111	0.221	396
0.045	0.090	0.865	748	$x_{23}=1.93^a$			
0.055	0.110	0.835	788	0.578	0.278	0.144	244
0.171	0.343	0.486	851	0.425	0.379	0.196	345
0.186	0.375	0.439	821	0.140	0.566	0.294	593
0.202	0.407	0.391	719	$x_{12}=2.01^a$			
0.299	0.603	0.098	219	0.109	0.054	0.837	630
$x_{12}=2.01^a$				0.188	0.094	0.718	713
0.109	0.054	0.837	630	0.599	0.299	0.102	162
0.188	0.094	0.718	713				
0.599	0.299	0.102	162				

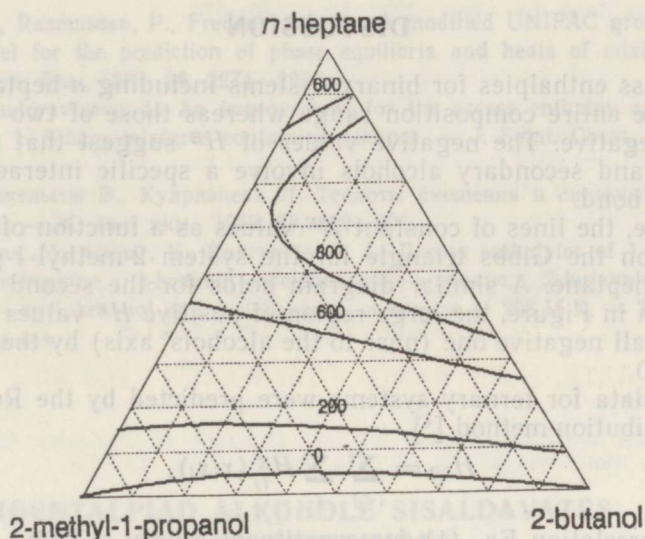
Table 4

Excess enthalpies  $H^E$  at 298.15 K for the system  
1-pentanol(1)—3-methyl-2-butanol(2)—*n*-heptane(3)

$x_1$	$x_2$	$x_3$	$H^E, \text{J mol}^{-1}$	$x_1$	$x_2$	$x_3$	$H^E, \text{J mol}^{-1}$
$x_{12}=1.00^a$				$x_{13}=1.00^a$			
0.060	0.060	0.880	516	0.147	0.706	0.147	234
0.106	0.106	0.788	603	0.260	0.480	0.260	353
0.210	0.210	0.580	653	0.332	0.336	0.332	421
0.322	0.322	0.356	442	0.396	0.208	0.396	480
$x_{12}=0.50^a$				$x_{23}=1.00^a$			
0.089	0.179	0.732	720	0.200	0.400	0.400	661
0.136	0.271	0.593	779	0.308	0.346	0.346	537
0.239	0.480	0.281	485	0.648	0.176	0.176	164
$x_{12}=2.00^a$							
0.236	0.120	0.644	632				
0.372	0.188	0.440	545				
0.429	0.217	0.354	386				

<sup>a</sup> Obtained by the mixing of pure component  $j$  with a binary mixture  $i+k$  in which the mole fraction relation is  $x_{i:k}=x_i/x_k$ .





The isoenthalpic curves of the excess enthalpy for the ternary system 2-methyl-1-propanol—2-butanol—*n*-heptane at 298.15 K.

Table 5

Mean percentage deviation  $\delta(H^E)$ , % between experimental and predicted by the Eq. (3), the original UNIFAC model and its version UNIFAC(3Q) excess enthalpies

System	$\delta(H^E)$ , %		
	Eq. (3)	UNIFAC	UNIFAC(3Q)
2-Methyl-1-propanol—2-butanol— <i>n</i> -heptane	13.8	26.8	14.2
1-Pentanol—3-methyl-2-butanol— <i>n</i> -heptane	23.0	11.5	22.8

Table 6

The UNIFAC and UNIFAC(3Q) group interaction parameters ( $a_{st}$ ), mean percentage deviations ( $\delta(H^E)$ , %) and the number of sets/points used for the correlation

Groups		UNIFAC			UNIFAC(3Q)			Number of sets/points
<i>s</i>	<i>t</i>	$a_{st}$	$a_{ts}$	$\delta(H^E)$	$a_{st}$	$a_{ts}$	$\delta(H^E)$	
CH <sub>2</sub>	OH(prim)	981.13	190.98	8.4	459.84	-169.83	16.4	10/122
	OH(sec)	748.65	187.78	29.3	486.54	-136.71	16.2	9/140
OH(prim)	OH(sec)	-19.93	-8.61	5.3	-70.02	80.99	18.2	4/72

## DISCUSSION

Table 8

The excess enthalpies for binary systems including *n*-heptane are positive over the entire composition range whereas those of two alcohol mixtures are negative. The negative values of  $H^E$  suggest that the mixtures of primary and secondary alcohols involve a specific interaction via the O...H—O bond.

In Figure, the lines of constant  $H^E$  values as a function of composition are drawn on the Gibbs triangle for the system 2-methyl-1-propanol—2-butanol—*n*-heptane. A similar diagram holds for the second ternary system. As seen in Figure, the large region of positive  $H^E$  values is separated from the small negative one (near to the alcohols' axis) by the isoenthalpic curve  $H^E=0$ .

The  $H^E$  data for ternary systems were predicted by the Redlich-Kister binary contribution method [4]

$$H_{ijk} = \sum_{i < j} \sum_j H_{ij}^E(x_i x_j), \quad (3)$$

using the correlation Eq. (1) for constituent binary systems.

Table 5 compares the  $H^E$  prediction results obtained by using Eq. (3), the UNIFAC model, and a version of the latter, UNIFAC(3Q). The notation used for main groups is shown in Table 6, together with the group interaction parameters  $a_{st}$  fitted to binary  $H^E$  data. The procedure of the  $a_{st}$  determination is described by Fredenslund et al. [5].

Table 5 shows that, for both ternary systems considered, Eq. (3) and UNIFAC(3Q) give similar prediction results which are better for 2-methyl-1-propanol—2-butanol—*n*-heptane and worse for 1-pentanol—3-methyl-2-butanol—*n*-heptane than those obtained by the original UNIFAC model.

When comparing the predictive methods used, the following should be noted. The application of Eq. (3) (the Redlich-Kister equations) for ternary systems requires the knowledge of experimental data for all three binary systems involved, and the measurements have to be carried through in the same conditions. The prediction of  $H^E$  for ternary and higher multicomponents systems using the group contribution methods does not require any experimental data for binary systems. The latter are often lacking, or they are obtained for temperatures different from the temperature at which the excess enthalpies should be calculated.

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## LIIGENTALPIAD ALKOHOLE SISALDAVATES KOLMIKSÜSTEEMIDES

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Mikrokalorimeetri DAK-1-1 abil on saadud uued andmed süsteemide 2-metüül-1-propanool—2-butanool—*n*-heptaan, 1-pentanool—3-metüül-2-butanool—*n*-heptaan, 2-metüül-1-propanool—2-butanool, 1-pentanool—3-metüül-2-butanool ja 3-metüül-2-butanool—*n*-heptaan liigentalpia kohta 298,15 K juures. Kolmiksüsteemide liigentalpiate ennustamiseks on kasutatud Redlichi-Kisteri võrrandit, UNIFAC'i grupimudelit ning selle modifikatsiooni UNIFAC(3Q). Binaarsete segude liigentalpiate kirjandusandmete alusel on määratud grupipaaride CH<sub>2</sub>/OH(prim), CH<sub>2</sub>/OH(sec) ja OH(prim)/OH(sec) vastastikmõju parameetrid.

## ИЗБЫТОЧНЫЕ ЭНТАЛЬПИИ ТРОЙНЫХ СИСТЕМ, СОДЕРЖАЩИХ СПИРТЫ

Мати КУУС, Хелле КИРСС, Энн СИИМЕР, Людмила КУДРЯВЦЕВА

С помощью микрокалориметра ДАК-1-1 получены новые данные об избыточных энтальпиях смешения в системах 2-метил-1-пропанол—2-бутанол—*n*-гептан, 1-пентанол—3-метил-2-бутанол—*n*-гептан, 2-метил-1-пропанол—2-бутанол, 1-пентанол—3-метил-2-бутанол и 3-метил-2-бутанол—*n*-гептан при температуре 298,15 К. Для предсказания избыточных энтальпий тройных систем использованы уравнение бинарных вкладов Редлиха—Кистера, групповая модель УНИФАК и ее модификация УНИФАК(3Q). Параметры взаимодействия групп CH<sub>2</sub>/OH(перв.), CH<sub>2</sub>/OH(втор.) и OH(перв.)/OH(втор.) определены по данным об избыточных энтальпиях бинарных систем, взятым из литературы.