EXCESS ENTHALPIES IN TERNARY SYSTEMS

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Abstract. A short review of the study of excess enthalpies (H^E) carried out in the Institute of Chemistry of the Estonian Academy of Sciences is given. As an example of these investigations, new excess enthalpy data for the system *tert*-butanol–isobutanol–*n*-heptane and for constituent binaries at 303.15 K are presented. To calculate ternary H^E, the Redlich–Kister equation, its modification, the group contribution method UNIFAC, and a version of the latter, UNIFAC(3Q), were applied.

Key words: excess enthalpy, ternary system, *tert*-butanol, isobutanol, *n*-heptane.

INTRODUCTION

The objective of this paper is to provide a short review of the investigations of excess enthalpies carried out in the Institute of Chemistry since 1978. These investigations were supported and directed by Prof. Olaf Eisen. It is our pleasure and privilege to dedicate this review to his memory.

The heat effects of mixing nonelectrolytes are of interest in process equipment design as well as in the thermodynamics of mixtures. These properties are useful for studying the solution chemistry and help to understand the states and structures of components in mixtures.

The earliest studies of quantitative heat effects for nonelectrolytes date to the beginning of this century when heats of mixing alcohols with water, hydrocarbons with halogenated ones, and different hydrocarbons between themselves were reported [1–3].

Heats of mixing are now referred to as excess molar enthalpies, H^E, related with other excess functions such as excess molar Gibbs energy, G^E, and excess entropy, S^E, through the well-known equation

$$G^E = H^E - TS^E,\qquad(1)$$

where T is temperature, K.

Excess molar enthalpies can be obtained from calorimetric measurements or the temperature effect of the excess molar Gibbs energy:

$$\left(\frac{\partial\left(\dfrac{G^E}{T}\right)}{\partial T}\right)_p = -\frac{H^E}{T^2}\qquad(2)$$

where G^E is usually obtained from phase equilibria measurements. However, the second way is very difficult and therefore it is not often used. The usefulness of Eq. (2) involves usually the reverse process: the temperature effect on G^E is calculated from H^E values obtained calorimetrically.

In view of the variety of compounds and mixtures, a large number of systems must be studied experimentally to obtain the required data. Although a large amount of data has been reported in the literature for binary systems, only a limited H^E database exists for ternary and higher multicomponent mixtures [4–7]. The experimental procedure is labor- and time-consuming, and as a consequence, researchers have turned to estimation and predictive methods as means for generating desired quantities.

Therefore, our studies usually consist of two parts. The first part is concerned with obtaining new H^E data to reduce the shortage of experimental data. The second part includes checking the possibilities of using estimation methods and developing some of them. This work summarizes the results of our investigations on the excess enthalpies in binary and ternary systems.

First, some preliminary experiments were performed to identify the structure effect on the enthalpy of mixing in binary systems containing isomers of alkenes [8], alkynes [9, 10], alkyl cyclenes [11], and aroma compounds [12, 13]. In recent years, our attention was focused on H^E of ternary systems containing components with hydroxyl groups. Excess enthalpies of ternary systems containing alcohols of different structure, phenols, and diols have been measured [14–19]. The information in the literature concerning these subjects is sketchy.

We made a limited selection from latest available thermodynamic models to calculate excess enthalpies. The models selected were the Redlich–Kister equation and the UNIFAC group contribution method [20]. The Redlich–Kister equation was chosen because of its suitability for reproducing the H^E dependence on concentration if binary H^E data are available in a ternary system [21]. Group contribution methods such as UNIFAC are effective tools for predicting phase equilibria. In order to calculate H^E, the original UNIFAC was also fitted to binary H^E data, and a special matrix of group interaction parameters was developed. We

have found that in most cases the triple values of group surface area parameters, Q_s, using simultaneously tripled values for all groups, give a good correlation [22]. In our matrix of group interaction parameters for the UNIFAC(3Q) version, the values of parameters are reconsidered and revised to calculate the H^E of mixtures [23].

As an example of our investigations, we present below excess enthalpies for the system *tert*-butanol–isobutanol–*n*-heptane and for three constituent binaries obtained calorimetrically at 303.15 K.

EXPERIMENTAL

The apparatus and procedure used have been basically the same in all our investigations. A Calvet-type differential calorimeter DAK-1-1 (made in the USSR) was used to determine the heats of mixing. An essential difference from the standard DAK-1-1 was in the construction of the calorimetric cell, which was modified to provide complete mixing [10]. It consists of two vessels, the external one made of stainless steel and the internal one of Teflon. Varying the size of the internal vessel makes it possible to change the mixture compositions determined from the masses of liquids to be mixed. 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 average volume of the mixture was about 5 cm³. The microcalorimeter was calibrated electrically, and the calibration was checked by determining the H^E of well-established literature data. In this work the calibration was checked by comparing with H^E data for hexane–*tert*-butanol obtained at 303.15 K by Recko and coworkers cited in [5]. Measurements 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. No significant impurities were detected by gas chromatography in the substances used.

n-Heptane ("puriss grade") was supplied by Reakhim (Khar'kov, Ukraine) and used without further purification. Alcohols, which were reagents of special commercial grade, were distilled in vacuum and protected from external moisture. Mass percentage purity levels as shown by GLC analysis were >99.8% for heptane and >99.5% for alcohols.

RESULTS AND CORRELATIONS

For the ternary system investigated we have found no data in the literature. Those for binaries *tert*-butanol–isobutanol and isobutanol–*n*-heptane were reported at temperatures differing from 303.15 K [5, 6], and for *tert*-butanol–*n*-heptane in the *n*-heptane rich composition range only [5].

Table 1. Experimental molar excess enthalpies, H^E, for binary systems at 303.15 K

tert-Butanol(1)–isobutanol(2)		tert-Butanol(1)–n-heptane(2)		Isobutanol(1)–n-heptane(2)	
x_1	H^E, J/mol	x_1	H^E, J/mol	x_1	H^E, J/mol
0.104	−146	0.172	720	0.108	605
0.216	−259	0.236	802	0.114	632
0.304	−346	0.335	935	0.198	815
0.387	−392	0.405	978	0.300	876
0.538	−413	0.472	952	0.397	891
0.655	−396	0.581	931	0.497	874
0.738	−348	0.761	700	0.597	754
0.791	−302	0.835	549	0.708	559
				0.798	420

The results of H^E measurements as a function of the mole fraction of the first component in binary systems are summarized in Table 1. A Redlich–Kister polynom of the type

$$H^E\left(J/mol\right) = x_1\left(1 - x_1\right)\sum_{i=0}^{k-1} A_i\left(2x_1 - 1\right)^i,\tag{3}$$

where x_1 is the mole fraction of the first component in binary mixtures, was fitted to each set of results by the least-squares regression with all points weighed equally. The values of coefficients A_i are given in Table 2 together with standard deviations $\sigma(H^E)$ defined by

$$\sigma\left(H^E\right) = \left(\sum_i \left(H_{exp}^E - H_{calc}^E\right)_i^2 (n-k)^{-1}\right)^{\frac{1}{2}},\tag{4}$$

where k is the number of coefficients needed to represent results adequately and the sum is taken over the set of n results.

Table 2. Coefficients A_i of Eq. (3) and standard deviations, $\sigma(H^E)$, for binary systems at 303.15 K

System	A_0	A_1	A_2	A_3	A_4	A_5	$\sigma(H^E)$
tert-Butanol(1)–isobutanol(2)	−1662.22	−9.12	−401.90	−1706.30	1072.74	2975.07	4
tert-Butanol(1)–n-heptane(2)	3838.34	−418.45	1454.48	−858.34	0	0	19
Isobutanol(1)–n-heptane(2)	3431.54	−1625.48	−113.98	−1096.32	3159.02	0	22

The experimental H^E values for the ternary system *tert*-butanol–isobutanol–*n*-heptane are presented in Table 3.

Table 3. Experimental molar excess enthalpies, H^E, for the ternary system *tert*-butanol(1)–isobutanol(2)–*n*-heptane(3) at 303.15 K

x_1	x_2	H^E, J/mol	x_1	x_2	H^E, J/mol
	$r_{12} = 0.5$*			$r_{12} = 2.0$*	
0.306	0.611	−117	0.615	0.307	−51
0.276	0.553	145	0.456	0.228	575
0.233	0.466	434	0.366	0.183	767
0.146	0.291	820	0.270	0.135	837
0.082	0.165	780	0.158	0.079	801
0.051	0.103	562	0.114	0.057	730
	$r_{12} = 1.0$*			$r_{13} = 1.0$*	
0.4565	0.4565	−73	0.328	0.343	566
0.424	0.424	124	0.266	0.468	431
0.370	0.370	399	0.173	0.654	242
0.252	0.252	810	0.098	0.804	148
0.2515	0.2515	816			
0.137	0.137	743		$r_{23} = 1.0$*	
0.112	0.112	736	0.183	0.409	705
			0.262	0.369	631
			0.451	0.275	517
			0.644	0.178	317

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

For the calculation of ternary H^E, we used the Redlich–Kister equation

$$H^E_{ikj} = H_{ik} + H_{ij} + H_{kj}, \tag{5}$$

where H_{ik} are the binary contributions to ternary H_{ikj} calculated by Eq. (3).

To improve the description of H^E concentration dependence in ternary systems, a new term was added to Eq. (5) (see Eq. (6)). The coefficients of this term were calculated from ternary experimental data. The optimum value of m in most cases was found to be 4 [18].

$$H^E = H_{12} + H_{23} + H_{31} + (A_0 + A_1 x_1^m + A_2 x_2^m + A_3 x_3^m) x_1 x_2 x_3. \tag{6}$$

Table 4 compares the results obtained by Eqs. (5) and (6) with those predicted by UNIFAC and UNIFAC(3Q) version, the last two with interaction parameters fitted to binary H^E data. Most of these data were taken from the literature. The notation used for alcohol groups is given in parentheses. The group interaction parameters used are published in our earlier papers [13, 23]. Table 4 gives the

absolute arithmetic mean deviation, δ, between the measured and calculated H^E in ternary systems studied here and earlier [14, 16].

Table 4. Mean percentage deviations, $\delta(H^E)$, between experimental ternary H^E data and those calculated by Eqs. (5) and (6), the UNIFAC model, and the UNIFAC(3Q) version

System	T, K	$\delta(H^E)$, %			
		Eq. (5)	Eq. (6)	UNIFAC	UNIFAC(3Q)
tert-Butanol–isobutanol–n-heptane (sec. OH, prim. OH)	303.15	14	8	40	34
1-Nonene–2-hexyn-1-ol–n-nonane (prim. OH)	298.15	15	5	9	8
1-Hexanol–2-hexyn-1-ol–n-nonane (prim. OH)	298.15	8	1	15	15
Pentyl ethanoate–1-hexanol–n-nonane (prim. OH)	298.15	13	3	7	8

As seen from Table 4, the predicted by the UNIFAC models H^E values in the systems with two alcohols differ much more from the experimental results than those calculated by Eqs. (5) and (6). For systems containing one alcohol, all four calculation results are comparable. However, Eqs. (5) and (6) require much more initial information obtained at the same conditions. The group contribution methods UNIFAC and UNIFAC(3Q) version are suitable for H^E estimation at arbitrary conditions for other binary as well as multicomponent systems including adequate group interactions.

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LIIGENTALPIAD KOLMIKSÜSTEEMIDES

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On esitatud lühikokkuvõte liigentalpiate (H^E) uurimisest Eesti Teaduste Akadeemia Keemia Instituudis (praegune Tallinna Tehnikaülikooli Keemia Instituut). Nende uuringute näitena on esitatud uued liigentalpia andmed kolmiksüsteemi *tert*-butanool–isobutanool–*n*-heptaan ja selles sisalduvate kaksiksüsteemide kohta temperatuuril 303,15 K. Kolmiksüsteemide H^E arvutamiseks on kasutatud Redlichi–Kisteri võrrandit, selle modifikatsiooni, UNIFAC'i grupimudelit ja selle versiooni UNIFAC(3Q).

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