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# 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

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## Abstract

Excess enthalpies for two ternary systems (1-butanol–2-butanol–*n*-heptane and 1-hexanol–cyclohexanol–*n*-nonane) and three binary systems (2-butanol–*n*-heptane, 1-hexanol–cyclohexanol and cyclohexanol–*n*-nonane) at 298.15 K have been measured with a Calvet-type microcalorimeter. The Redlich–Kister equation and the UNIFAC(3Q), a version of UNIFAC, fitted to binary $H^E$ data, have been applied in predicting ternary excess enthalpies. New group interaction parameters of this version have been determined.

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

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## 1. Introduction

Systems composed of alcohols with other organic compounds are of considerable theoretical interest and practical importance. Researches on the molar excess enthalpy ($H^E$) of these systems provide reliable data for testing model theories of mixtures, for improving group contribution methods and for promoting the understanding of the states, structure and interactions of components in solution.

We have continued our studies of excess enthalpy for ternary systems containing alkanols [1,2] by investigating at 298.15 K the two ternary systems (1-butanol–2-

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Table 1

Excess enthalpies $H^{E}$ for 2-butanol(1)–*n*-heptane(2), 1-hexanol(1)–cyclohexanol(2) and cyclohexanol(1)–*n*-nonane(2) at 298.15 K

| | $H^{E}$/(J mol$^{-1}$) | | | $H^{E}$/(J mol$^{-1}$) | |
|---|---|---|---|---|---|
| $x_1$ | Exp | Calc | $x_1$ | Exp | Calc |
| 2-Butanol(1)–*n*-heptane(2) | | | | | |
| 0.073 | 508 | 507 | 0.592 | 810 | 816 |
| 0.165 | 755 | 760 | 0.694 | 709 | 689 |
| 0.296 | 921 | 910 | 0.800 | 507 | 517 |
| 0.382 | 943 | 944 | 0.895 | 295 | 293 |
| 0.502 | 891 | 902 | | | |
| 1-Hexanol(1)–cyclohexanol(2) | | | | | |
| 0.170 | 139 | 136 | 0.516 | 176 | 173 |
| 0.199 | 142 | 147 | 0.540 | 174 | 170 |
| 0.260 | 163 | 163 | 0.655 | 140 | 148 |
| 0.266 | 170 | 164 | 0.783 | 101 | 104 |
| 0.353 | 171 | 175 | 0.815 | 97 | 90 |
| 0.373 | 172 | 176 | 0.841 | 74 | 77 |
| 0.495 | 179 | 174 | | | |
| Cyclohexanol(1)–*n*-nonane(2) | | | | | |
| 0.098 | 615 | 615 | 0.479 | 1119 | 1111 |
| 0.230 | 964 | 966 | 0.589 | 1044 | 1024 |
| 0.251 | 1000 | 998 | 0.663 | 892 | 920 |
| 0.313 | 1071 | 1068 | 0.819 | 630 | 615 |
| 0.396 | 1104 | 1115 | 0.859 | 510 | 517 |

butanol–*n*-heptane and 1-hexanol–cyclohexanol–*n*-nonane), and the three binaries 2-butanol–*n*-heptane, 1-hexanol–cyclohexanol and cyclohexanol–*n*-nonane. For the two binary systems containing cyclohexanol we have not found excess enthalpies in the literature, and for the third system the $H^{E}$ data are given at temperatures differing from 298.15 K [3].

Table 2

Coefficients $A_i$ of Eq. (1) and standard deviations $\sigma(H^{E})$ in J mol$^{-1}$ for binary systems

| Binary system | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma(H^{E})$ |
|---|---|---|---|---|---|---|
| 2-Butanol–*n*-heptane | 3626.43 | −953.50 | 550.89 | −2064.26 | 2480.76 | 24.3 |
| 1-Hexanol–cyclohexanol | 696.25 | −163.81 | 181.55 | −285.61 | | 5.6 |
| Cyclohexanol–*n*-nonane | 4404.59 | −1073.37 | 570.88 | −706.80 | 2278.11 | 18.3 |
| 1-Butanol–2-butanol [a] | −399.80 | 46.34 | −6.68 | | | 0.4 |
| 1-Butanol–*n*-heptane [a] | 2270.13 | 979.24 | 648.17 | 1339.91 | 1028.91 | 10.2 |
| 1-Hexanol–*n*-nonane [a] | 2532.20 | −690.00 | 523.06 | −1937.05 | 1031.04 | 5.2 |

[a] Experimental data for the calculation of coefficients are taken from the literature: 1-butanol–2-butanol [3], 1-butanol–*n*-heptane [4], 1-hexanol–*n*-nonane [5].

Table 3

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

| $x_1$ | $x_2$ | $x_3$ | $H^E/(\mathrm{J\ mol}^{-1})$ | $x_1$ | $x_2$ | $x_3$ | $H^E/(\mathrm{mol}^{-1})$ |
|---|---|---|---|---|---|---|---|
| $r_{12} = 0.5$ [a] | | | | $r_{13} = 1.0$ [a] | | | |
| 0.158 | 0.308 | 0.534 | 746 | 0.178 | 0.644 | 0.178 | 311 |
| 0.275 | 0.536 | 0.189 | 279 | 0.357 | 0.286 | 0.357 | 506 |
| $r_{12} = 1.0$ [a] | | | | $r_{13} = 2.0$ [a] | | | |
| 0.099 | 0.099 | 0.802 | 714 | 0.268 | 0.600 | 0.132 | 220 |
| 0.202 | 0.202 | 0.596 | 736 | 0.494 | 0.263 | 0.243 | 360 |
| 0.347 | 0.347 | 0.306 | 473 | | | | |
| 0.467 | 0.467 | 0.066 | 33 | $r_{23} = 0.5$ [a] | | | |
| 0.482 | 0.482 | 0.036 | −31 | 0.315 | 0.226 | 0.459 | 644 |
| | | | | 0.366 | 0.209 | 0.425 | 599 |
| $r_{12} = 2.0$ [a] | | | | 0.767 | 0.077 | 0.156 | 203 |
| 0.092 | 0.046 | 0.862 | 562 | | | | |
| 0.391 | 0.195 | 0.414 | 652 | $r_{23} = 1.0$ [a] | | | |
| 0.524 | 0.262 | 0.214 | 265 | 0.343 | 0.330 | 0.327 | 470 |
| 0.608 | 0.304 | 0.088 | 76 | 0.687 | 0.157 | 0.156 | 170 |
| $r_{13} = 0.5$ [a] | | | | $r_{23} = 2.0$ [a] | | | |
| 0.114 | 0.656 | 0.230 | 502 | 0.342 | 0.442 | 0.216 | 357 |
| 0.215 | 0.341 | 0.434 | 688 | 0.411 | 0.396 | 0.193 | 290 |
| | | | | 0.841 | 0.107 | 0.052 | 35 |

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

Excess enthalpies of the other binary systems which are component binaries of the above ternary systems have been reported previously: those of 1-butanol–*n*-heptane by Oswald et al. [4], 1-butanol–2-butanol by Murakami and Benson [3] and 1-hexanol–*n*-nonane by Ortega [5].

The Redlich–Kister equation is used to correlate the binary experimental data and to predict those of ternary systems from binary data alone. The experimental data are compared also with the results predicted by a version of UNIFAC which we have named UNIFAC(3Q) [6].

## 2. Experimental

Measurements were made in a Calvet-type differential micro-calorimeter. The procedure has been described in our earlier papers [1,2].

*n*-Heptane and *n*-nonane ("puriss" grade) were supplied by Reakhim (Kharkov, Ukraine) and used without further purification. The alcohols, which were first grade chemicals, were purified by fractional distillation before use in the measurements. Analysis by GLC showed purity levels to be $> 99.8\%$ for both the *n*-alkanes and 99.5% for the alcohols. Densities measured at 293.15 K were in close agreement with the literature values: *n*-heptane 683.8 kg $\mathrm{m}^{-3}$, *n*-nonane 717.6 kg $\mathrm{m}^{-3}$,

Table 4
Excess enthalpies $H^E$ at 298.15 K for the system 1-hexanol(1)–cyclohexanol(2)–$n$-nonane(3)

| $x_1$ | $x_2$ | $x_3$ | $H^E/(\mathrm{J\ mol^{-1}})$ | $x_1$ | $x_2$ | $x_3$ | $H^E/(\mathrm{J\ mol^{-1}})$ |
|---|---|---|---|---|---|---|---|
| $r_{12} = 0.5$ [a] | | | | $r_{13} = 1.0$ [a] | | | |
| 0.086 | 0.172 | 0.742 | 893 | 0.152 | 0.696 | 0.152 | 530 |
| 0.125 | 0.249 | 0.626 | 972 | 0.196 | 0.608 | 0.196 | 623 |
| 0.222 | 0.446 | 0.332 | 765 | 0.313 | 0.374 | 0.313 | 737 |
| 0.278 | 0.557 | 0.165 | 525 | | | | |
| | | | | $r_{23} = 1.0$ | | | |
| $r_{12} = 1.0$ [a] | | | | 0.236 | 0.382 | 0.382 | 871 |
| 0.171 | 0.171 | 0.658 | 856 | 0.438 | 0.281 | 0.281 | 654 |
| 0.318 | 0.318 | 0.364 | 787 | | | | |
| 0.411 | 0.411 | 0.178 | 523 | $r_{23} = 2.0$ [a] | | | |
| | | | | 0.478 | 0.348 | 0.174 | 494 |
| $r_{12} = 2.0$ [a] | | | | 0.688 | 0.208 | 0.104 | 299 |
| 0.185 | 0.093 | 0.722 | 744 | | | | |
| 0.271 | 0.136 | 0.593 | 810 | | | | |
| 0.405 | 0.203 | 0.392 | 724 | | | | |
| 0.495 | 0.247 | 0.258 | 570 | | | | |

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

1-butanol 810.0 kg m$^{-3}$, 2-butanol 806.9 kg m$^{-3}$, 1-hexanol 818.7 kg m$^{-3}$ and cyclohexanol 962.5 kg m$^{-3}$.

## 3. Results

The experimental values of $H^E$ for the binary systems studied are compared in Table 1 with those obtained by smoothing them using the Redlich–Kister equation

$$H^E/\mathrm{J\ mol^{-1}} = x_1(1-x_1)\sum_{i=0}^{n} A_i(2x_1-1)^i \qquad (1)$$

where $x_1$ is the mole fraction of the first component. The Redlich–Kister coefficients $A_i$, with the standard deviations $\sigma(H^E)$, are given in Table 2. The standard deviation is defined by

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

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

The coefficients of Eq. (1) are presented in Table 2 also for three other systems which are component binaries of the ternary systems studied. We have checked some values of $H^E$ for these systems using our calorimeter and our substances, and have found good agreement with the literature data used.

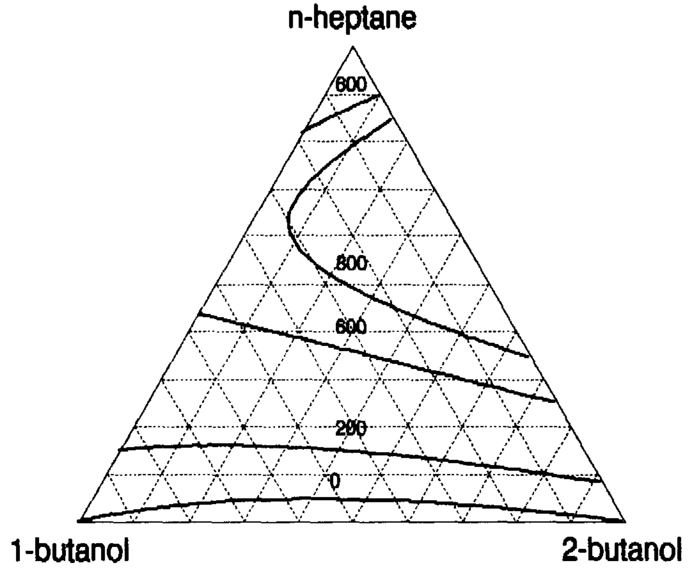

Fig. 1. Isoenthalpic curves of the excess enthalpy for the ternary system 1-butanol–2-butanol–*n*-heptane at 298.15 K calculated by UNIFAC(3Q).

Tables 3 and 4 present the ternary excess enthalpy data at 298.15 K for the systems 1-butanol–2-butanol–*n*-heptane and 1-hexanol–cyclohexanol–*n*-nonane, respectively.

## 4. Discussion

The positive excess enthalpies have been measured over the entire composition range of the system 1-hexanol–cyclohexanol–*n*-nonane and for most compositions of the system 1-butanol–2-butanol–*n*-heptane. For some compositions of the

Table 5
Mean percentage deviation $\delta(H^E)/\%$ between experimental ternary excess enthalpies and those predicted by Eq. (3) and UNIFAC(3Q)

| System | Predicted by Eq. (3) | Predicted by UNIFAC(3Q) |
|---|---|---|
| 1-Butanol–2-butanol–*n*-heptane | 29.8 | 30.5 (OH(prim))<br>11.6 (OH(prim) + OH(sec)) |
| 1-Hexanol–cyclohexanol–*n*-nonane | 12.7 | 31.3 (OH(prim))<br>15.8 (OH(prim) + OH(sec) + cOH)<br>6.5 (OH(prim) + OH(sec) + cOH) |

Table 6
The UNIFAC(3Q) group interaction parameters $a_{st}$[a] fitted to binary $H^E$ data, the number of sets/points used for correlation and mean percentage deviation $\delta(H^E)$

| Groups | | Parameters | | Number of sets/points | $\delta(H^E)$/% |
|---|---|---|---|---|---|
| s | t | $a_{st}$ | $a_{ts}$ | | |
| $CH_2$ | $cCH_2$ | −35.15 | 52.31 | 4/83 | 7.5 |
| | OH(prim) | 459.84 | −169.83 | 10/122 | 16.4 |
| | OH(sec) | 486.54 | −136.71 | 9/140 | 16.2 |
| | cOH | 328.41 | −127.27 | 5/58 | 7.8 |
| $cCH_2$ | OH(prim) | 375.81 | −154.29 | 4/60 | 9.7 |
| | OH(sec) | 375.58 | −125.86 | 3/66 | 9.7 |
| | cOH | 416.44 | −144.75 | 4/78 | 9.7 |
| OH(prim) | OH(sec) | −70.02 | 80.99 | 4/7 | 18.2 |
| | cOH | −16.89 | 4.57 | 1/13 | 3.5 |

[a] Determined using the trebled values of the surface area parameters of the original UNIFAC.

latter with a low content of *n*-heptane, the values of $H^E$ are negative, because the mixing of 1- and 2-butanol is an exothermic process [3].

In Fig. 1 the isoenthalpic curves are shown as a function of composition for the system 1-butanol–2-butanol–*n*-heptane. It can be seen that in the vicinity of the 1-butanol–2-butanol axis there is the isoenthalpic curve of $H^E = 0$, splitting the triangle diagram into two parts, positive and negative.

The $H^E$ data $H^E{}_{123}$ for the ternary systems 1-butanol (1)–2-butanol (2)–*n*-heptane (3) and 1-hexanol (1)–cyclohexanol (2)–*n*-nonane (3) were predicted by the Redlich–Kister binary contribution equations

$$H^E_{123} = H^E_{12} + H^E_{23} + H^E_{31} \tag{3}$$

where $H^E_{ik}$ are the binary contributions obtained on inserting mole fractions $x_i$ and $x_k$ of the ternary mixture into Eq. (1) using the coefficients given in Table 2.

The results are compared in Table 5 with those obtained by the UNIFAC version UNIFAC(3Q), taking into account the trebled values of the group surface area parameters $Q_s$ of the original UNIFAC model. The notation used for the main groups is shown in Table 6 together with the group interaction parameters corresponding to the trebled values of $Q_s$.

The group interaction parameters were determined using the simplex method, the Nelder–Mead procedure described by Fredenslund et al. [7, p. 79], and the minimization function

$$F = \sum_{i=1}^{k} \left( \frac{H^E_{\text{exp}} - H^E_{\text{calc}}}{H^E_{\text{exp}}} \right)_i^2 \tag{4}$$

where $k$ is the overall number of experimental points.

Most of the experimental data used for $a_{st}$ determination have been taken from $H^E$ data collections [3–5]. Only the interaction parameters of the groups OH(prim)/cOH were calculated from the measurement results obtained in this paper for the 1-hexanol–cyclohexanol system.

The different alcohol groups, OH(prim) in primary alcohols, OH(sec) in secondary ones, and cOH in cycloalkanols, were used to obtain more reliable results for the ternary systems studied. The values of the mean percentage deviation presented in Table 5 demonstrate the necessity and the validity of differentiation of these three types of hydroxyl group.

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