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INVESTIGATION OF EXCESS ENTHALPIES OF SELECTED BINARY AND TERNARY SOLUTIONS AND MIXTURES

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The excess enthalpies were investigated for 12 binary and 4 ternary systems, including mixtures and solutions of electrolytes and non-electrolytes. The excess enthalpies of mixtures and integral heats of solutions were measured with an isoperibol calorimeter at 35 °C. Heats of fusion and heat capacities as functions of temperature were measured with a Perkin Elmer Corp., DSC–2. Integral heats, heats of fusion and heat capacities allow investigations of excess enthalpies of solutions. For modelling of the experimental results, the modified Redlich-Kister equation was used with good success.

Excess enthalpies are of increasing importance for theoretical studies, technical developments and applications. The excess enthalpies of liquid mixtures can be measured in a direct way. For solutions, this is not possible. The excess enthalpy of a binary solution is given by the equation

$$\Delta^E \bar{h}_{ik} = x_k (\Delta^L \bar{h}_{ik} - \bar{h}^{SL}_{ok}) \tag{1}$$

with the integral heat of solution $\Delta^L \bar{h}_{ik}$ and the heat of fusion $\bar{h}^{SL}_{ok}$ of the solute component at the measuring temperature.

For measurements of heats of fusion and heat capacities as functions of temperature in the solid and liquid states, we used a PERKIN-ELMER Corp., DSC-2. The experimental results are to be found in [1–3]. For measurements of integral heats of solutions and excess enthalpies, we constructed a calorimeter [4].

For ternary systems, we have to distinguish between systems which consist of one solid component (index 3) dissolved in a mixture of two solvents (indices 1 and 2), determined by

$$\Delta^E \bar{h}_{3(12)} = x_3 (\Delta^L \bar{h}_{3(12)} - \bar{h}^{SL}_{03}) \tag{2}$$

and systems which consist of two solid components (indices 2 and 3) simultaneously dissolved in one solvent (index 1), determinated by

$$\Delta^E \bar{h}_{23(1)} = x_2 (\Delta^L \bar{h}_{23(1)} - \bar{h}^{SL}_{02}) + x_3 (\Delta^L \bar{h}_{23(1)} - \bar{h}^{SL}_{03}) \tag{3}$$

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Experimental

The following systems were included in our investigations:

(I) CH_3OH/H_2O; (II) C_2H_5OH/H_2O; (III) $n\text{-}C_3H_7OH/H_2O$;
(IV) CH_3COCH_3/H_2O; (V) $CH_3COCH_3/n\text{-}C_3H_7OH$; (VI) $H_2O/CO(NH_2)_2$;
(VII) H_2O/CH_3CONH_2; (VIII) $n\text{-}C_3H_7OH/CO(NH_2)_2$;
(IX) $n\text{-}C_3H_7OH/CH_3CONH_2$; (X) H_2O/KNO_3; (XI) H_2O/NH_4NO_3;
(XII) CH_3OH/NH_4NO_3; (XIII) $n\text{-}C_3H_7OH/H_2O/CH_3COCH_3$;
(XIV) $n\text{-}C_3H_7OH/H_2O/CH_3CONH_2$; (XV) $n\text{-}C_3H_7OH/H_2O/CO(NH_2)_2$;
(XVI) $CH_3OH/H_2O/NH_4NO_3$.

The used substances were dried and purified carefully. Water contents and purities were checked via gas chromatography, melting points, IR-spectroscopy and refractive indices.

The solubilities of the solid components in the used solvents were determined experimentally at several temperatures in earlier work [5, 6].

The measurements were carried out at 35° and in the whole concentration range. In the case of the ternary systems, we measured along several lines of constant relative mole fractions [7], given by

$$I_1' = x_1/(x_1 + x_2) \qquad (4)$$

The errors in heat capacities and heats of fusion amount to ± 2%. The measured heats of solutions and excess enthalpies have errors between 1 and 20%.

A publication on our experimental integral heats or mixing enthalpies of binary and ternary solutions is in preparation.

Results

The excess enthalpies of binary systems as mole fraction functions were correlated via the Redlich-Kister equation:

$$\Delta^E \bar{h}_{jk} = x_1 x_2 \sum_{i=o}^{m} (B_i)_{jk} (x_2 - x_1)^i \qquad (5)$$

Table 1 Constants of Eq. (5) and mean deviations in kJ/mol

System	B_0	B_1	B_2	B_3	B_4	*MD*
I	–2.968	1.570	1.609	–	–	0.011
II	–1.200	1.758	–1.674	2.956	–2.257	0.018
III	0.532	1.721	–0.909	2.411	–2.859	0.013
IV	–0.195	3.735	1.122	2.969	–4.724	0.012
V	5.878	–0.020	1.689	–0.272	–1.888	0.019
VI	–6.374	–3.968	2.421	–	–	0.004
VII	–7.271	–6.074	–1.769	–	–	0.012
VIII	124.924	83.098	–38.777	269.023	270.730	0.001
IX	3.023	47.353	149.906	199.007	96.491	0.008
X	13.160	–15.422	46.038	–	–	0.007
XI	13.349	–22.689	30.880	–	–	0.019
XII	6.839	–17.703	21.563	–	–	0.003

The constants of Eq. (5) are collected in Table 1, together with the mean deviations MD.

For the ternary systems, the excess enthalpies were correlated via Eq. (6):

$$\Delta^E\bar{h}'_{123} = \Delta^E\bar{h}'_{12} + \Delta^E\bar{h}'_{13} + \Delta^E\bar{h}'_{23} + x'_1 \cdot x'_2 \cdot x'_3$$

$$[B + C \cdot x'_1 + C_2 \cdot x'_2 + \ldots] \qquad (6)$$

Table 2 lists the constants of Eq. (6) and the mean deviations between the experimental and calculated values.

Table 2 Constants of Eq. (6) and mean deviation in kJ/mol

System	B	C_1	C_2	C_3	$\Delta\Delta^E\bar{h}'_{123}$
XIII	2.456	–4.867	0.000	–	0.021
XIV	6.943	3.709	8.047	–	0.030
XV	–1.739	222.603	167.215	–	0.010
XVI	–270.893	–437.935	316.684	1784.160	0.015
				C_6 =	–1142.496

Discussion

With Eqs (1), (2) and (3), we determined the excess enthalpies. For this, it must be taken into consideration that the heat of fusion is a function of temperature:

$$\frac{\partial \bar{h}^{SL}_{ok}}{\partial T} = \Delta \bar{c}_{p,ok} \tag{7}$$

This relation leads to three approximations:

Approximation 1:

$$\Delta \bar{c}^{SL}_{p,ok} = \bar{c}'_{p,ok} - \bar{c}_{p.ok} = 0 \tag{8}$$

$$(\bar{c}'_{p,ok} = b'_o + b'_1 T + b'_2 T^2 \text{ for the liquid state;}$$

$$\bar{c}_{p,ok} = b_o + b_1 T + b_2 T^2 \text{ for the solid state)}$$

$$\Delta^E \bar{h}_{ik} = x_k \, [\Delta^L \bar{h}_{ik} - \bar{h}^{SL}_{ok} \, (T^{SL}_{ok})] \tag{9}$$

Approximation 2:

$$\Delta \bar{c}^{SL}_{p,ok} = \text{const} \tag{10}$$

$$\Delta^E \bar{h}_{ik} = x_k \, [\Delta^L \bar{h}_{ik} - \bar{h}^{SL}_{ok} \, (T^{SL}_{ok}) - \Delta \bar{c}^{SL}_{p,ok} \, (T - T^{SL}_{ok})] \tag{11}$$

Approximation 3:

$$\Delta \bar{c}^{SL}_{p,ok} = f(T)$$

$$\begin{aligned}\Delta^E \bar{h}_{ik} = x_k \cdot \Delta^L \bar{h}_{ik} - x_k \Big\{ & \bar{h}^{SL}_{ok} \, (T^{SL}_{ok}) + (T - T^{SL}_{ok}) \, (b'_o - b_o) + \\ & + [T^2 - (T^{SL}_{ok})^2] \, (\frac{b'_1 - b_1}{2}) + [T^3 - (T^{SL}_{ok})^3] (\frac{b'_2 - b_2}{3}) \Big\}\end{aligned} \tag{12}$$

Figure 1 presents the different results obtained through the use of these three approximations for the water/urea system as one example.

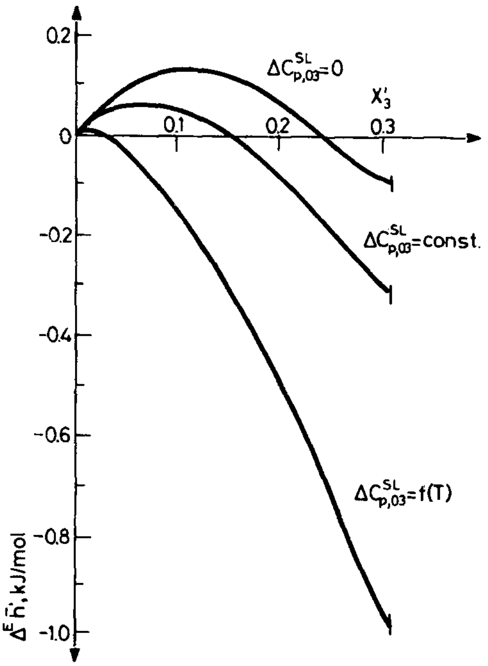

Fig. 1 Excess enthalpies of $H_2O/CO(NH_2)_2$ – system at 35 °C

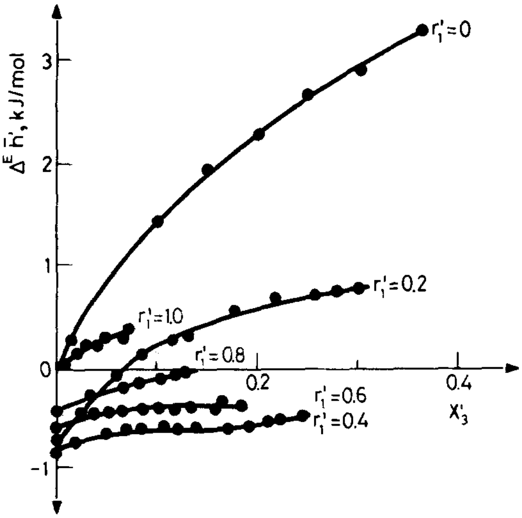

Fig. 2 Excess enthalpies of $CH_3OH/H_2O/NH_4NO_3$ – system at 35 °C

The excess enthalpies of electrolyte solutions are all positive values. For solutions of urea, acetamide and acetone, and in mixtures of water with the three aliphatic alcohols and acetone, we found a relation between the excess enthalpies and the structures of the components. The results for the methanol/water/NH_4NO_3 system are given in Fig. 2. The calculated values are in good agreement with our experimental data.

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Zusammenfassung — Für 12 binäre und ternäre Systeme, darunter Mischungen und Lösungen von Elektrolyten und Nichtelektrolyten, wurden die Exzessenthalpien untersucht. Die Exzessenthalpien der Mischungen und die integralen Lösungsenthalpien wurden mit einem isoperibolen Kalorimeter bei 35 °C gemessen. Die Schmelzwärmen und spezifischen Wärmekapazitäten in Abhängigkeit von der Temperatur wurden mit einem DSC 2 der Fa. Perkin-Elmer bestimmt. Die integralen Wärmen, Schmelzwärmen und Wärmekapazitäten erlauben, die Exzessenthalpien der Lösungen zu untersuchen. Die Versuchsergebnisse lassen sich erfolgreich mit modifizierten Redlich-Kister-Gleichungen modellieren.

РЕЗЮМЕ — Исследованы избыточные энтальпии для 12 двойных и 4 тройных систем, включая растворы и смеси электролитов и неэлектролитов. С помощью изопериболического калориметра измерены при 35° избыточные энтальпии смесей и интегральные теплоты растворов. Посредством ДСК—2 фирмы Перкин-Эльмер были измерены теплоты плавления и теплоемкости в зависимости от температуры. Интегральная теплота, теплота плавления и теплоемкость могут быть использованы для исследования избыточной энтальпии растворов. Для моделирования экспериментальных результатов с хорошим приближением было использовано модифицированное уравнение Ридлиха-Кистера.