*Thermochimica Acta*, 196 (1992) 169–175
Elsevier Science Publishers B.V., Amsterdam

# Excess molar enthalpies for the *n*-butylamine–1,4-dioxane–ethanenitrile system at 298.15 K

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(Received 28 May 1991)

## Abstract

Heat of mixing data for the ternary liquid system *n*-butylamine–1,4-dioxane–ethanenitrile at 298.15 K are reported along with data for the constituent binary systems. Different expressions published in the literature were used to predict excess enthalpies from the corresponding binary data. The empirical correlation of Tanaka and Tamura gave the best prediction for this system.

## INTRODUCTION

Data of excess molar enthalpies $H^E$ are known for a number of binary liquid mixtures of non-electrolytes, and such data can be found in several articles. However, experimental data on excess molar enthalpies of mixtures of more than two components are quite rare in the literature. It is therefore interesting to estimate excess molar enthalpies of mixtures of three components from binary data.

In previous papers [1,2], we have published experimental data of excess molar enthalpies at 298.15 K for the binary systems *n*-butylamine–1,4-dioxane and *n*-butylamine–ethanenitrile. The 1,4-dioxane–ethanenitrile system has not been published [3]. In this study, we determined the excess molar enthalpies at 298.15 K for the *n*-butylamine–1,4-dioxane–ethanenitrile (BA–D–EN) ternary system, in order to consider some methods for empirical correlations, assuming interactions in a ternary mixture are closely dependent on the interactions of the constituents in binary mixtures.

## EXPERIMENTAL

The methods used in our laboratory have been described previously [1,2]. Densities were determined with an AP digital densimeter, model DMA 45.

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All weighings were made on an H315 Mettler balance. The adiabatic calorimeter described by Loiseleur et al. [4] was used with some modifications to determine enthalpy changes. The estimated error was $\pm 0.1$ kg m$^{-3}$ in densities and $\pm 5$ J mol$^{-1}$ in enthalpies. *n*-Butylamine (Riedel de Haen puriss.) was dried over potassium hydroxide pellets for three days, refluxed for two hours, distilled and the middle fraction was collected [5]. Ethanenitrile (Carlo Erba puriss.) was distilled over phosphorous pentoxide and 1,4-dioxane (Fluka, puriss.) was distilled over sodium at reduced pressure. In all cases, the middle fractions were collected. Mixtures were prepared by weighing the correct amounts of the pure components. Caution was taken to prevent evaporation. Each experimental run was performed by adding the third component to a binary mixture of the other two. A ternary system was regarded as a pseudo-binary system made up of one binary mixture and the third component. One mole of the ternary mixtures was prepared by mixing $(1-x_3)$ of the initial binary mixture and $x_3$ of component 3. The ternary excess molar enthalpy $H_{123}^{\mathrm{E}}$ at $x_1$, $x_2$ and $x_3$ is given by

$$H_{123}^{\mathrm{E}} = \Delta H_{\mathrm{m}} + (1-x_3) H_{12}^{\mathrm{E}} \tag{1}$$

where $\Delta H_{\mathrm{m}}$ is the observed molar excess enthalpy for the pseudo-binary mixture and $H_{12}^{\mathrm{E}}$ is the binary excess molar enthalpy of the *n*-butylamine(1) and 1,4-dioxane(2). The same procedure was followed with *n*-butylamine(1)–ethanenitrile(3) and 1,4-dioxane(2)–ethanenitrile(3).

## RESULTS AND DISCUSSION

The values of $H_{ij}^{\mathrm{E}}$ for binary mixtures can be calculated from the experimental data (the mole fraction being known) by using a Redlich–Kister polynomial expression

$$H_{ij}^{\mathrm{E}} = x_i x_j \sum_{k=0}^{n} a_k (x_i - x_j)^k \tag{2}$$

where $a_k$ are polynomial coefficients. The method of least squares was used to determine the values of the coefficients. In each case the optimum number of coefficients was ascertained from an examination of the variation of the standard error estimate with $n$

$$\sigma = \left[ \sum \left( H_{ij}^{\mathrm{E}}(\mathrm{obs}) - H_{ij}^{\mathrm{E}}(\mathrm{cal}) \right)^2 / (n_{\mathrm{obs}} - n) \right]^{1/2} \tag{3}$$

The values adopted for the coefficients and the standard error of the estimates associated with the use of eqn. (3) are summarized in Table 1.

Figure 1 shows the experimental values of $H_{ij}^{\mathrm{E}}$ for the three binary systems. The continuous curves were calculated from eqn. (2) using these values for the coefficients. Table 2 shows the experimental values of $H_{123}^{\mathrm{E}}$

TABLE 1

Coefficients $a_k$ from eqn. (2) and standard deviations for the binary systems at 298.15 K

| System | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $a_5$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| BA(1)-D(2) | 1604 | −25 | −530 | −45 | 716 | - | 3 |
| D(2)-EN(3) | 221 | −18 | 240 | −86 | 0.51 | 0.014 | 0.7 |
| BA(1)-EN(3) | 2800 | −600 | 300 | 1000 | −800 | - | 7 |

for the BA(1)–D(2)–EN(3) system at 298.15 K. Figure 2 shows curves of constant excess molar enthalpies for the ternary system.

If interaction in a ternary system *i–j–k* is assumed to be closely dependent on the interaction of the constituent mixtures *i–j*, *j–k* and *i–k*, it should be possible to evaluate excess molar enthalpies for ternary mixtures of non-electrolytes when the corresponding enthalpies for the binary systems are known.

Tsao and Smith [6] proposed an equation for predicting the excess enthalpy of a ternary system

$$H^E_{123} = \left(\frac{x_2}{1-x_1}\right)H^E_{12} + \left(\frac{x_3}{1-x_1}\right)H^E_{13} + (1-x_1)H^E_{23} \tag{4}$$

in which $H^E_{ij}$ refers to the excess enthalpy for the binary mixtures at compositions $x_i^{\ominus}$ and $x_j^{\ominus}$, such that $x_i^{\ominus} = x_i$ for the 1–2 and 1–3 binary systems and $x_2^{\ominus} = x_2/(x_2+x_3)$ for the 2–3 binary system. This equation is asymmetrical and needs some specification to identify component 1.

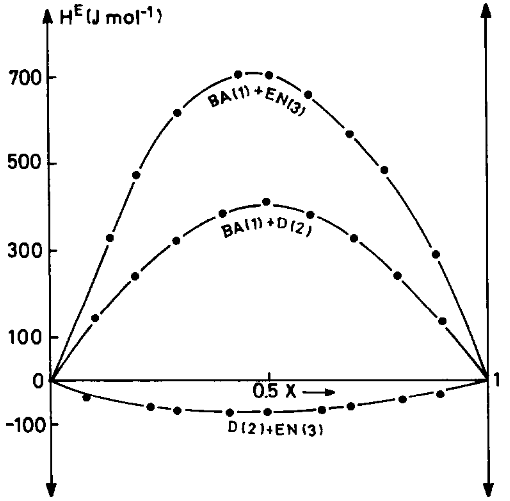

Fig. 1. Excess molar enthalpies for binary systems at 298.15 K. Experimental results, ●; continuous curves were calculated from eqn. (2).

TABLE 2

Experimental excess molar enthalpies for the *n*-butylamine(1)–1,4-dioxane(2)–ethanenitrile(3) system at 298.15 K

| $x_1$ | $x_2$ | $\Delta H_m$ (J mol$^{-1}$) | $H^E_{123}$ (J mol$^{-1}$) |
|---|---|---|---|
| $x'_2/x'_2 = 0.5165$; $x'_1 = 0.3406$; $H^E_{12} = 373$ J mol$^{-1}$ | | | |
| 0.1090 | 0.2110 | 81 | 200 |
| 0.1234 | 0.2390 | 90 | 225 |
| 0.1394 | 0.2699 | 97 | 250 |
| 0.1487 | 0.2878 | 112 | 275 |
| 0.1661 | 0.3218 | 98 | 280 |
| 0.2007 | 0.3885 | 100 | 320 |
| 0.2180 | 0.4220 | 86 | 325 |
| 0.2459 | 0.4750 | 61 | 330 |
| 0.3250 | 0.5750 | 14 | 350 |
| $x'_1/x'_2 = 0.9940$; $x'_1 = 0.4985$; $H^E_{12} = 401$ J mol$^{-1}$ | | | |
| 0.0497 | 0.0500 | 55 | 95 |
| 0.0797 | 0.0802 | 116 | 180 |
| 0.1196 | 0.1204 | 149 | 245 |
| 0.1225 | 0.1223 | 162 | 260 |
| 0.1785 | 0.1795 | 206 | 350 |
| 0.2052 | 0.2064 | 230 | 395 |
| 0.2469 | 0.2494 | 236 | 435 |
| 0.2827 | 0.2845 | 213 | 440 |
| 0.3700 | 0.3722 | 152 | 450 |
| 0.4387 | 0.4413 | 67 | 420 |
| $x'_1/x'_2 = 1.4844$; $x'_1 = 0.5975$; $H^E_{12} = 382$ J mol$^{-1}$ | | | |
| 0.0567 | 0.0383 | 84 | 120 |
| 0.1256 | 0.0846 | 190 | 270 |
| 0.2087 | 0.1406 | 297 | 430 |
| 0.2241 | 0.1509 | 297 | 440 |
| 0.3107 | 0.2093 | 301 | 500 |
| 0.3577 | 0.2410 | 276 | 505 |
| 0.4005 | 0.2699 | 259 | 515 |
| 0.4272 | 0.2878 | 227 | 500 |
| 0.5224 | 0.3519 | 106 | 440 |
| $x'_2/x'_3 = 0.5254$; $x'_2 = 0.3444$; $H^E_{23} = -63$ J mol$^{-1}$ | | | |
| 0.0920 | 0.3127 | 207 | 150 |
| 0.1400 | 0.2962 | 304 | 250 |
| 0.2386 | 0.2623 | 448 | 400 |
| 0.3989 | 0.2070 | 572 | 535 |
| 0.4271 | 0.2015 | 581 | 545 |
| 0.5340 | 0.1605 | 579 | 550 |
| 0.6450 | 0.1248 | 512 | 490 |
| 0.8701 | 0.0451 | 258 | 250 |
| $x'_2/x'_3 = 1.0872$; $x'_2 = 0.5209$; $H^E_{23} = -68$ J mol$^{-1}$ | | | |
| 0.0300 | 0.5002 | −28 | −60 |
| 0.1030 | 0.4672 | 206 | 145 |
| 0.2990 | 0.3451 | 468 | 420 |
| 0.4986 | 0.2597 | 534 | 500 |
| 0.6717 | 0.1710 | 462 | 440 |
| 0.8903 | 0.0571 | 198 | 190 |

TABLE 2 (continued)

| $x_1$ | $x_2$ | $\Delta H_m$ (J mol$^{-1}$) | $H^E_{123}$ (J mol$^{-1}$) |
|---|---|---|---|
| $x'_1/x'_3 = 0.4956$; $x'_1 = 0.3314$; $H^E_{13} = 667$ J mol$^{-1}$ | | | |
| 0.1102 | 0.6674 | −82 | 140 |
| 0.1852 | 0.4412 | −103 | 270 |
| 0.2233 | 0.3262 | −99 | 350 |
| 0.2508 | 0.2431 | −85 | 420 |
| 0.2948 | 0.1103 | −93 | 500 |
| $x'_1/x'_3 = 0.9970$; $x'_1 = 0.4992$; $H^E_{13} = 700$ J mol$^{-1}$ | | | |
| 0.2688 | 0.4617 | −27 | 350 |
| 0.2994 | 0.4083 | −14 | 400 |
| 0.3269 | 0.3452 | −58 | 440 |
| 0.3667 | 0.2656 | −14 | 500 |
| 0.4202 | 0.1584 | −9 | 580 |
| 0.2640 | 0.0700 | 2 | 653 |

Kohler [7] proposed an equation for a ternary system of the following form:

$$H^E_{123} = (x_1 + x_2)^2 H^E_{12} + (x_1 + x_3)^2 H^E_{13} + (x_2 + x_3)^2 H^E_{23} \tag{5}$$

Kohler's equation is symmetrical in that all three binary systems are treated identically. In this equation, $H^E_{ij}$ refers to the excess molar enthalpies of $x_i^{\ominus}$, $x_j^{\ominus}$ where $x_i^{\ominus} = 1 - x_j^{\ominus} = x_i/(x_i + x_j)$.

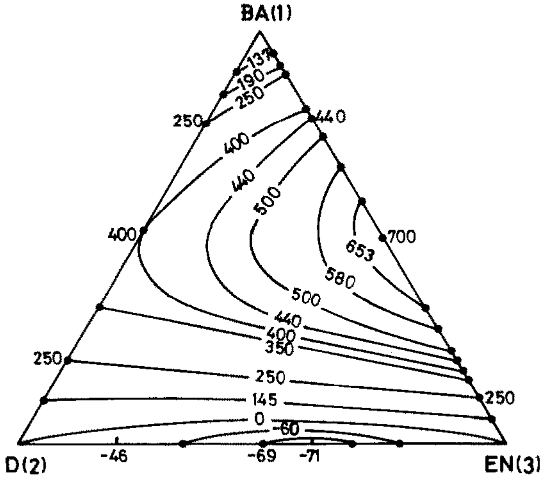

Fig. 2. Lines of constant excess molar enthalpies for the *n*-butylamine(1)–1,4-dioxane(2)–ethanenitrile(3) system at 298.15 K.

Radojkovič et al. [8] considered an expression proposed by Redlich and Kister of the form

$$H^{\mathrm{E}}_{123} = H^{\mathrm{E}}_{12*} + H^{\mathrm{E}}_{13*} + H^{\mathrm{E}}_{23*} \tag{6}$$

where $H^{\mathrm{E}}_{12*}$, $H^{\mathrm{E}}_{13*}$ and $H^{\mathrm{E}}_{23*}$ represent the excess molar enthalpies with $x_1$, $x_2$ and $x_3$ mole fractions of the ternary systems calculated from eqn. (2) using the coefficients of Table 1.

Jacob and Fitzner [9] suggested an equation for estimating properties of a ternary mixture of the form

$$H^{\mathrm{E}}_{123} = \frac{x_1 x_2 H^{\mathrm{E}}_{12}}{(x_1 + x_3/2)(x_2 + x_3/2)} + \frac{x_1 x_3 H^{\mathrm{E}}_{13}}{(x_1 + x_2/2)(x_3 + x_2/2)} + \frac{x_2 x_3 H^{\mathrm{E}}_{23}}{(x_2 + x_1/2)(x_3 + x_1/2)} \tag{7}$$

so that the binary system at compositions $x_i^{\ominus}$, $x_j^{\ominus}$ is $x_i - x_j = x_i^{\ominus} - x_j^{\ominus}$.

Cibulka [10] proposed the equation

$$H^{\mathrm{E}}_{123} = H^{\mathrm{E}}_{12*} + H^{\mathrm{E}}_{23*} + H^{\mathrm{E}}_{13*} + x_1 x_2 x_3 (A + B x_1 + C x_2) \tag{8}$$

where $A$, $B$ and $C$ are parameters characteristic of the mixtures evaluated by fitting this equation by the least-squares method with a standard deviation defined as in eqn. (3). The parameters obtained are $A = -5529$, $B = 8694$ and $C = 1623$.

Singh et al. [11] proposed an equation of the following form

$$H^{\mathrm{E}}_{123} = H^{\mathrm{E}}_{12*} + H^{\mathrm{E}}_{23*} + H^{\mathrm{E}}_{13*} + x_1 x_2 x_3 \left[A + B x_1 (x_2 - x_3) + C x_1^2 (x_2 - x_3)^2\right] \tag{9}$$

The parameters obtained are $A = -2389$, $B = 2169$ and $C = 13298$.

These two equations are modifications of the equation of Radojkovič et al. [8]. Nagata and Tamura [12] proposed the equation

$$H^{\mathrm{E}}_{123} = H^{\mathrm{E}}_{12*} + H^{\mathrm{E}}_{23*} + H^{\mathrm{E}}_{13*} + x_1 x_2 x_3 \Delta_{123} \tag{10}$$

where

$$\frac{\Delta_{123}}{RT} = \sum_{j=1}^{6} b_j (1 - 2x_3)^{j-1} \tag{11}$$

Equation (10) was used by Van Ness and his coworkers [13,14] in correlating their excess molar enthalpy results. The coefficients of eqn. (11) together with the standard deviations are: $b_1 = -1.2363$, $b_2 = 1.4147$, $b_3 = 0.1029$, $b_4 = -2.4868$, $b_5 = 0.5290$, $b_6 = 3.7180$ and $\sigma = 0.34$.

Table 3 shows the standard deviations calculated by using all the above-mentioned equations for excess molar enthalpies. Equation (10) shows the best agreement with the experimental data. Obviously, the

TABLE 3

Standard deviations for the *n*-butylamine(1)–1,4-dioxane(2)–ethanenitrile(3) system at 298.15 K

| Equation | $\sigma(H^{E}_{123})$ (J mol$^{-1}$) | Equation | $\sigma(H^{E}_{123})$ (J mol$^{-1}$) |
|---|---|---|---|
| 4 | 81 | 8 | 27 |
| 5 | 71 | 9 | 37 |
| 6 | 72 | 10 | 0.34 |
| 7 | 72 | | |

models using ternary parameters are superior to the predictive ones (not containing ternary parameters).

## ACKNOWLEDGMENTS

We are grateful to Ing. Mario R. Cesca for aid in computer programming. The present work was financed by a CONICET (PID) and CIUNT research grant.

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