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Prediction of ternary excess molar enthalpies for *n*-butylamine + 1,4-dioxane + acetonitrile from binary data alone

Isamu Nagata * and Marek Rogalski

Laboratoire de Thermodynamique Chimique et Appliquée, U.R.A. C.N.R.S. 1108, Ecole Nationale Supérieure des Industries Chimiques, Institut National Polytechnique de Lorraine, 1, rue Grandville-BP n° 451, 54001 Nancy Cedex (France)

Kazuhiro Tamura

Department of Chemistry and Chemical Engineering, Division of Physical Sciences, Kanazawa University, 40–20, Kodatsuno 2-chome, Kanazawa 920 (Japan)

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Abstract

A chemical association model based on mole fraction statistics is used to predict the ternary excess molar enthalpies of the *n*-butylamine + 1,4-dioxane + acetonitrile system using only binary parameters derived from excess molar enthalpy data for its three constituent binary systems. The model assumes that the self-association of *n*-butylamine and acetonitrile, the solvation between unlike molecules and the binary non-specific molecular interactions between the components are given by the NRTL equation.

LIST OF SYMBOLS

A, B, C	*n*-butylamine, 1,4-dioxane and acetonitrile
a_{IJ}	binary energy parameter for the I–J pair
C_{IJ}, D_{IJ}	constants of eqn. (22) for the I–J pair
G_{IJ}	coefficient as defined by $\exp(-\alpha_{IJ}\tau_{IJ})$
H^E	excess molar enthalpy
h_{A_2}	enthalpy of formation of *n*-butylamine dimer
h_A	enthalpy of hydrogen-bond formation in *n*-butylamine *i*mer
h_{A_iB}	enthalpy of formation of chemical complex A_iB between *n*-butylamine *i*mer and 1,4-dioxane

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* Corresponding author at the Department of Chemistry and Chemical Engineering, Division of Physical Sciences, Kanazawa University, 40–20, Kodatsuno 2-chome, Kanazawa 920, Japan.

$h_{A_iC_j}$	enthalpy of formation of chemical complex A_iC_j between *n*-butylamine *i*mer and acetonitrile *j*mer
h_{BC}	enthalpy of formation of chemical complex BC between 1,4-dioxane and acetonitrile
h_{C_2}	enthalpy of formation for head-to-head dimerization of acetonitrile
h_C	enthalpy of formation for head-to-tail chain association of acetonitrile
K_{A_2}	equilibrium constant of dimer formation of *n*-butylamine
K_A	equilibrium constant of open chain *i*mer formation of *n*-butylamine, $i > 2$
K_{A_iB}	equilibrium constant of formation of chemical complex A_iB between *n*-butylamine *i*mer and 1,4-dioxane
$K_{A_iC_j}$	equilibrium constant of formation of chemical complex A_iC_j between *n*-butylamine *i*mer and acetonitrile *j*mer
K_{BC}	equilibrium constant of formation of chemical complex BC between 1,4-dioxane and acetonitrile
K_{C_2}	equilibrium constant of head-to-head dimerization of acetonitrile
K_C	equilibrium constant of head-to-tail chain association of acetonitrile
R	universal gas constant
S	stoichiometric sum
S_A^*, S_C^*	stoichiometric sums for pure *n*-butylamine and acetonitrile
T	absolute temperature
x_I	liquid-phase mole fraction of component I
z	coefficient as defined by $K_A x_{A_1}$

Greek letters

α_{IJ}	non-randomness parameter of NRTL equation for I–J pair, here taken as 0.3
τ_{IJ}	coefficient as defined by a_{IJ}/T

Subscripts

A, B, C	*n*-butylamine, 1,4-dioxane and acetonitrile
A_1, A_i	*n*-butylamine monomer and *i*mer
A_iB	complex formation between *n*-butylamine *i*mer and 1,4-dioxane
A_iC_j	complex formation between *n*-butylamine *i*mer and acetonitrile *j*mer
BC	complex formation between 1,4-dioxane and acetonitrile
C_1, C_i	acetonitrile monomer and *i*mer
cal	calculated
chem	chemical

exp	experimental
I, J	components
phys	physical

Superscripts

E	excess
*	pure liquid

INTRODUCTION

The phase equilibrium and excess molar enthalpy properties of binary and ternary mixtures containing acetonitrile or an amine and non-associating components have been successfully reproduced using a chemical association model based on mole fraction statistics [1–9]. The model assumptions are that acetonitrile and the amine self-associate, and form chemical complexes with active non-associating components, and that the non-specific interactions between unlike molecules are expressed by the NRTL equation [10]. The model has not been applied for binary and ternary mixtures involving both acetonitrile and an aliphatic amine, because no experimental data on phase equilibrium or excess molar enthalpy were available to us. Recently, experimental excess molar enthalpy results were published for the ternary *n*-butylamine + 1,4-dioxane + acetonitrile system and its three component binary systems [11–14]. These data seem to be useful for testing the chemical association model cited above.

ASSOCIATION MODEL

To predict the ternary excess molar enthalpies for the *n*-butylamine(A) + 1,4-dioxane(B) + acetonitrile(C) system at 25°C, we must obtain the binary parameters of our association model in the correlation of binary excess molar enthalpies for the three component systems at 25°C. As stated previously, we take into consideration the self-association of *n*-butylamine(A) and acetonitrile(C), the solvation between unlike molecules in the chemical part of the association model, and the non-specific molecular interactions between components in the physical part of the model. Four association constants for *n*-butylamine(A) and acetonitrile(C) are defined by

$$K_{A_2} = x_{A_2}/x_{A_1}^2 \quad \text{for } A_1 + A_1 = A_2 \tag{1}$$

$$K_A = x_{A_{i+1}}/x_{A_i}x_{A_1} \quad \text{for } A_i + A_1 = A_{i+1} \quad (i > 1) \tag{2}$$

$$K_{C_2} = x_{C_2}/x_{C_1}^2 \quad \text{for } C_1 + C_1 = C_2 \tag{3}$$

$$K_C = x_{C_{i+1}}/x_{C_i}x_{C_1} \quad \text{for } C_i + C_1 = C_{i+1} \quad (i \geq 1) \tag{4}$$

The temperature dependences of the equilibrium constants are given by the van't Hoff relation

$$\partial \ln K_{A_2}/\partial(1/T) = -h_{A_2}/R \tag{5}$$

$$\partial \ln K_A/\partial(1/T) = -h_A/R \tag{6}$$

$$\partial \ln K_{C_2}/\partial(1/T) = -h_{C_2}/R \tag{7}$$

$$\partial \ln K_C/\partial(1/T) = -h_C/R \tag{8}$$

Before proceeding to the ternary expression of the excess molar enthalpy H^E, we describe briefly the basic equations of H^E for three component binary systems.

Binary systems

n-*Butylamine(A) + 1,4-dioxane(B)*

The solvation constant for the formation of chemical complexes A_iB is given by

$$K_{A_iB} = x_{A_iB}/x_{A_i}x_{B_1} \quad \text{for } A_i + B_1 = A_iB \quad (i \geq 1) \tag{9}$$

The nominal mole fractions of both components are expressed in terms of the monomer mole fractions of the components

$$x_A = (1 + K_{A_iB}x_{B_1})[x_{A_1} + K_{A_2}x_{A_1}^2(2-z)/(1-z)^2]/S \tag{10}$$

$$x_B = \{x_{B_1} + K_{A_iB}x_{B_1}[x_{A_1} + K_{A_2}x_{A_1}^2/(1-z)]\}/S \tag{11}$$

where $z = K_A x_{A_1}$ and the stoichiometric sum S is given by

$$S = (1 + K_{A_iB}x_{B_1})[x_{A_1} + K_{A_2}x_{A_1}^2(2-z)/(1-z)^2] + K_{A_iB}x_{B_1}[x_{A_1} + K_{A_2}x_{A_1}^2/(1-z)] + x_{B_1} \tag{12}$$

The mole fractions of all chemical species present in the mixture must satisfy the following equation

$$\sum_{i=1}^{\infty} x_{A_i} + \sum_{i=1}^{\infty} x_{A_iB} + x_{B_1} = (1 + K_{A_iB}x_{B_1})[x_{A_1} + K_{A_2}x_{A_1}^2/(1-z)] + x_{B_1} = 1 \tag{13}$$

The monomer mole fractions x_{A_1} and x_{B_1} are solved from eqns. (10)–(13).

The excess molar enthalpy of the mixture H^E consists of two contributory terms: chemical and physical

$$H^E = H^E_{\text{chem}} + H^E_{\text{phys}} \tag{14}$$

$$H^E_{\text{chem}} = \{(1 + K_{A_iB}x_{B_1})[h_{A_2}K_{A_2}x_{A_1}^2/(1-z) + h_A K_{A_2}K_A x_{A_1}^3/(1-z)^2] + h_{A_iB}K_{A_iB}x_{B_1}[x_{A_1} + K_{A_2}x_{A_1}^2/(1-z)]\}/S - x_A[h_{A_2}K_{A_2}x_{A_1}^{*2}/(1-z^*) + h_A K_{A_2}K_A x_{A_1}^{*3}/(1-z^*)^2]/S_A^* \tag{15}$$

For the pure amine state eqns. (12) and (13) reduce to

$$S_A^* = x_{A_1}^* + K_{A_2}x_{A_1}^{*2}(2-z^*)/(1-z^*)^2 \tag{16}$$

$$x^*_{A_1} + K_{A_2} x^{*2}_{A_1}/(1 - z^*) = 1 \tag{17}$$

Equation (17) provides the value of $x^*_{A_1}$.

$$H^E_{\text{phys}} = R x_A x_B \left\{ \frac{\tau'_{BA} G_{BA}}{x_A + x_B G_{BA}} + \frac{\tau'_{AB} G_{AB}}{x_B + x_A G_{AB}} - \alpha_{AB} \left[\frac{x_A \tau_{BA} G_{BA} \tau'_{BA}}{(x_A + x_B G_{BA})^2} + \frac{x_B \tau_{AB} G_{AB} \tau'_{AB}}{(x_B + x_A G_{AB})^2} \right] \right\} \tag{18}$$

where

$$\tau_{BA} = a_{BA}/T \qquad \tau_{AB} = a_{AB}/T \tag{19}$$

$$G_{BA} = \exp(-\alpha_{BA}\tau_{BA}) \qquad G_{AB} = \exp(-\alpha_{AB}\tau_{AB}) \tag{20}$$

$$\tau'_{BA} = \partial\tau_{BA}/\partial(1/T) \qquad \tau'_{AB} = \partial\tau_{AB}/\partial(1/T) \tag{21}$$

We assume the linear temperature dependence of the energy parameters

$$a_{BA} = C_{BA} + D_{BA}(T - 273.15) \quad a_{AB} = C_{AB} + D_{AB}(T - 273.15) \tag{22}$$

Each of the non-randomness parameters ($\alpha_{IJ} = \alpha_{JI}$) is taken as 0.3.

n-*Butylamine(A) + acetonitrile(C)*

We introduce a solvation constant between *n*-butylamine(A) and acetonitrile(C).

$$K_{A_iC_j} = x_{A_iC_j}/x_{A_i}x_{C_j} \quad \text{for } A_i + C_j = A_iC_j \quad (i \geq 1, j \geq 1) \tag{23}$$

The nominal mole fractions of the components are related to the monomer mole fractions of the components

$$x_A = [1 + K_{A_iC_j} x_{C_1}/(1 - K_C x_{C_1})][x_{A_1} + K_{A_2} x^2_{A_1}(2 - z)/(1 - z)^2]/S \tag{24}$$

$$x_C = \{[x_{A_1} + K_{A_2} x^2_{A_1}/(1 - z)] K_{A_iC_j} x_{C_1}/(1 - K_C x_{C_1})^2 + x_{C_1}/(1 - K_C x_{C_1})^2 + 2K_{C_2} x^2_{C_1}\}/S \tag{25}$$

where the stoichiometric sum S is

$$S = [1 + K_{A_iC_j} x_{C_1}/(1 - K_C x_{C_1})][x_{A_1} + K_{A_2} x^2_{A_1}(2 - z)/(1 - z)^2] + [x_{A_1} + K_{A_2} x^2_{A_1}/(1 - z)] K_{A_iC_j} x_{C_1}/(1 - K_C x_{C_1})^2 + x_{C_1}/(1 - K_C x_{C_1})^2 + 2K_{C_2} x^2_{C_1} \tag{26}$$

The sum of the mole fractions of all species present in the mixture must be unity

$$[1 + K_{A_iC_j} x_{C_1}/(1 - K_C x_{C_1})][x_{A_1} + K_{A_2} x^2_{A_1}/(1 - z)] + x_{C_1}/(1 - K_C x_{C_1}) + K_{C_2} x^2_{C_1} = 1 \tag{27}$$

The monomer mole fractions are solved simultaneously from eqns. (24)–(27). For the pure acetonitrile state we obtain

$$K_{C_2} x^{*2}_{C_1} + x^*_{C_1}/(1 - K_C x^*_{C_1}) = 1 \tag{28}$$

The value of $x^*_{C_1}$ is obtained from eqn. (28). The chemical contribution term is

$$\begin{aligned} H^E_{chem} = {} & ([1 + K_{A_iC_j} x_{C_1}/(1 - K_C x_{C_1})][h_{A_2} K_{A_2} x^2_{A_1}/(1 - z) + h_A K_{A_2} K_A x^3_{A_1}/(1 - z)^2] \\ & + \{1 + K_{A_iC_j}[x_{A_1} + K_{A_2} x^2_{A_1}/(1 - z)]\} h_C K_C x^2_{C_1}/(1 - K_C x_{C_1})^2 + h_{C_2} K_{C_2} x^2_{C_1} \\ & + [x_{A_1} + K_{A_2} x^2_{A_1}/(1 - z)] h_{A_iC_j} K_{A_iC_j} x_{C_1}/(1 - K_C x_{C_1}))/S \\ & - x_A[h_{A_2} K_{A_2} x^{*2}_{A_1}/(1 - z^*) + h_A K_{A_2} K_A x^{*3}_{A_1}/(1 - z^*)^2]/S^*_A \\ & - x_C[h_{C_2} K_{C_2} x^{*2}_{C_1} + h_C K_C x^{*2}_{C_1}/(1 - K_C x^*_{C_1})^2]/S^*_C \end{aligned} \tag{29}$$

where the value of S for the pure acetonitrile state S^*_C is

$$S^*_C = 2K_{C_2} x^{*2}_{C_1} + x^*_{C_1}/(1 - K_C x^*_{C_1})^2 \tag{30}$$

1,4-Dioxane(B) + acetonitrile(C)

Complex formation between 1,4-dioxane and acetonitrile is assumed according to the following solvation constant

$$K_{BC} = x_{BC}/x_{B_1} x_{C_1} \quad \text{for } B_1 + C_1 = BC \tag{31}$$

The stoichiometric mole fractions x_B and x_C are expressed in terms of the mole fractions of the chemical species

$$x_B = (K_{BC} x_{B_1} x_{C_1} + x_{B_1})/S \tag{32}$$

$$x_C = \{2K_{C_2} x^2_{C_1} + x_{C_1}/(1 - K_C x_{C_1})^2 + K_{BC} x_{B_1} x_{C_1}\}/S \tag{33}$$

where the sum S is given by

$$S = 2K_{C_2} x^2_{C_1} + x_{C_1}/(1 - K_C x_{C_1})^2 + 2K_{BC} x_{B_1} x_{C_1} + x_{B_1} \tag{34}$$

The mole fraction of each chemical species present in the mixture must satisfy the relationship

$$\begin{aligned} & x_{C_2} + \sum_{i=1}^{\infty} x_{C_i} + x_{BC} + x_{B_1} \\ & = K_{C_2} x^2_{C_1} + x_{C_1}/(1 - K_C x_{C_1}) + K_{BC} x_{B_1} x_{C_1} + x_{B_1} = 1 \end{aligned} \tag{35}$$

The monomer mole fractions of the components x_{B_1} and x_{C_1} are simultaneously solved from eqns. (32), (34) and (35). The chemical term H^E_{chem} is defined as

$$\begin{aligned} H^E_{chem} = {} & [h_C K_C x^2_{C_1}/(1 - K_C x_{C_1})^2 + h_{C_2} K_{C_2} x^2_{C_1} + h_{BC} x_{B_1} x_{C_1}]/S \\ & - x_C[h_{C_2} K_{C_2} x^{*2}_{C_1} + h_C K_C x^{*2}_{C_1}/(1 - K_C x^*_{C_1})^2]/S^*_C \end{aligned} \tag{36}$$

Ternary system

The equations for the mole fractions of the three components of the ternary system are

$$x_A = \{[1 + K_{A,B}x_{B_1} + K_{A,C_l}x_{C_1}/(1 - K_Cx_{C_1})] \times [x_{A_1} + K_{A_2}x_{A_1}^2(2 - z)/(1 - z)^2]\}/S \tag{37}$$

$$x_B = \{K_{A,B}x_{B_1}[x_{A_1} + K_{A_2}x_{A_1}^2/(1 - z)] + K_{BC}x_{B_1}x_{C_1} + x_{B_1}\}/S \tag{38}$$

$$x_C = \{[x_{A_1} + K_{A_2}x_{A_1}^2/(1 - z)]K_{A,C_l}x_{C_1}/(1 - K_Cx_{C_1})^2 + x_{C_1}/(1 - K_Cx_{C_1})^2 + 2K_{C_2}x_{C_1}^2 + K_{BC}x_{B_1}x_{C_1}\}/S \tag{39}$$

where the stoichiometric sum S is

$$S = [1 + K_{A,B}x_{B_1} + K_{A,C_l}x_{C_1}/(1 - K_Cx_{C_1})][x_{A_1} + K_{A_2}x_{A_1}^2(2 - z)/(1 - z)^2] + K_{A,B}x_{B_1}[x_{A_1} + K_{A_2}x_{A_1}^2/(1 - z)] + 2K_{BC}x_{B_1}x_{C_1} + x_{B_1} + [x_{A_1} + K_{A_2}x_{A_1}^2/(1 - z)]K_{A,C_l}x_{C_1}/(1 - K_Cx_{C_1})^2 + x_{C_1}/(1 - K_Cx_{C_1})^2 + 2K_{C_2}x_{C_1}^2 \tag{40}$$

The sum of the mole fractions of chemical species present in the mixture must be unity.

$$\{1 + K_{A,B}x_{B_1} + K_{A,C_l}x_{C_1}/(1 - K_Cx_{C_1})\} \cdot [x_{A_1} + K_{A_2}x_{A_1}^2/(1 - z)] + x_{B_1} + K_{BC}x_{B_1}x_{C_1} + x_{C_1}/(1 - K_Cx_{C_1}) + K_{C_2}x_{C_1}^2 = 1 \tag{41}$$

The ternary excess molar enthalpy H^E is

$$\begin{aligned} H^E = {} & ([1 + K_{A,B}x_{B_1} + K_{A,C_l}x_{C_1}/(1 - K_Cx_{C_1})][h_{A_2}K_{A_2}x_{A_1}^2/(1 - z) \\ & + h_AK_{A_2}K_Ax_{A_1}^3/(1 - z)^2] + h_{C_2}K_{C_2}x_{C_1}^2 \\ & + \{1 + K_{A,C_l}[x_{A_1} + K_{A_2}x_{A_1}^2/(1 - z)]\}h_CK_Cx_{C_1}^2/(1 - K_Cx_{C_1})^2 \\ & + [x_{A_1} + K_{A_2}x_{A_1}^2/(1 - z)][h_{A,B}K_{A,B}x_{B_1} + h_{A,C_l}K_{A,C_l}x_{C_1}/(1 - K_Cx_{C_1})] \\ & + h_{BC}x_{B_1}x_{C_1})/S - x_A[h_{A_2}K_{A_2}x_{A_1}^{*2}/(1 - z^*) + h_AK_{A_2}K_Ax_{A_1}^{*3}/(1 - z^*)^2]/S_A^* \\ & - x_C[h_{C_2}K_{C_2}x_{C_1}^{*2} + h_CK_Cx_{C_1}^{*2}/(1 - K_Cx_{C_1}^*)^2]/S_C^* \\ & + R\sum_{I=A}^{C} x_I \left[\frac{\sum_{J=A}^{C} x_J \dfrac{\partial(\tau_{JI}G_{JI})}{\partial(1/T)}}{\sum_{K=A}^{C} G_{KI}x_K} + \frac{\sum_{J=A}^{C} \tau_{JI}G_{JI}x_J \sum_{K=A}^{C} x_J \dfrac{\partial(\tau_{JI}G_{JI})}{\partial(1/T)}}{\left(\sum_{K=A}^{C} G_{KI}x_K\right)^2} \right] \end{aligned} \tag{42}$$

CALCULATED RESULTS

The association parameters for n-butylamine and acetonitrile were taken from previous papers [1,5]: for n-butylamine, $K_{A_2} = 0.6$ and $K_A = 1.2$ at 60°C, and $h_{A_2} = -9\,\mathrm{kJ\,mol^{-1}}$ and $h_A = -9\,\mathrm{kJ\,mol^{-1}}$; for acetonitrile, $K_{C_2} = 8.35$ and $K_C = 2.1$ at 45°C, and $h_{C_2} = -8.9\,\mathrm{kJ\,mol^{-1}}$ and $h_C = -6.7\,\mathrm{kJ\,mol^{-1}}$. Table 1 gives the values of the solvation constants and enthalpies of complex formation. The temperature dependences of the equilibrium constants were fixed by the van't Hoff relationship. All h values were assumed to be independent of temperature. Table 2 shows the binary results of excess molar enthalpy data reduction. Figure 1 presents a

TABLE 1

Solvation constants at 25°C and enthalpies of complex formation

Mixture	K	$-h/(\mathrm{kJ\ mol^{-1}})$
n-Butylamine(A) + 1,4-dioxane(B) [a]	1.5	7.1
n-Butylamine(A) + acetonitrile(C) [b]	3.6	14.0
1,4-Dioxane(B) + acetonitrile(C) [c]	3.5	7.3

[a] *i*:1 complex formation is assumed. [b] *i*:*j* complex formation is assumed. [c] 1:1 complex formation is assumed.

TABLE 2

Binary parameters and arithmetic mean deviation for the three systems at 25°C

Mixture (A + B)	No. of data points	C_{AB}/K	D_{AB}	C_{BA}/K	D_{BA}	Abs. arith. mean dev./ ($\mathrm{J\ mol^{-1}}$)	Ref.
n-Butylamine + 1,4-dioxane	9 [a]	674.05	2.5600	515.98	3.1825	5.9	12
n-Butylamine + acetonitrile	9	433.82	−1.8930	−378.68	−0.4369	7.9	13
1,4-Dioxane + acetonitrile	9	582.02	2.6803	380.71	0.5914	2.8	14

[a] Smoothed experimental data, which were obtained at equally spaced mole fractions from the Redlich–Kister equation whose constants are given in ref. 12.

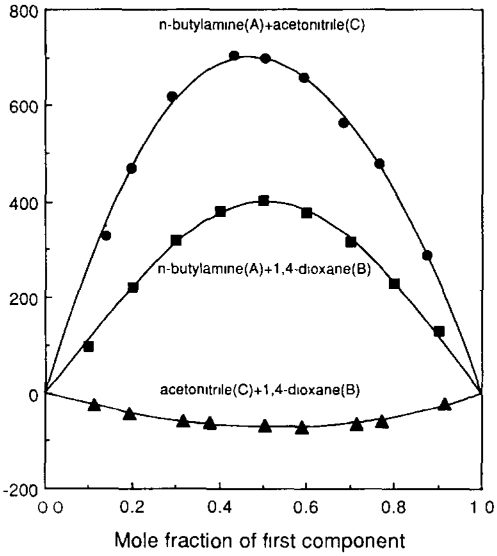

Fig. 1. Excess molar enthalpies H^E of binary mixtures at 25°C. Experimental data: ■, *n*-butylamine + 1,4-dioxane [12]; ●, *n*-butylamine + acetonitrile [13]; ▲, acetonitrile + 1,4-dioxane [14]. Results calculated from the associated model, ——.

TABLE 3

Ternary excess molar enthalpies of *n*-butylamine(A) + 1,4-dioxane(B) + acetonitrile(C) at 25°C

x_A	x_B	x_C	H^E_{exp}/ (J mol^{-1})	H^E_{cal}/ (J mol^{-1})	$\delta H^{E\,a}$/ (J mol^{-1})
$x'_A/x'_B = 0.5165$; $x'_A = 0.3406$					
0.1090	0.2110	0.6800	200	219.7	−19.7
0.1234	0.2390	0.6376	225	243.5	−18.5
0.1394	0.2699	0.5907	250	267.5	−17.5
0.1487	0.2878	0.5635	275	280.1	−5.1
0.1661	0.3218	0.5121	280	300.8	−20.8
0.2007	0.3885	0.4108	320	330.5	−10.5
0.2180	0.4220	0.3600	325	339.6	−14.6
0.2459	0.4750	0.2791	330	346.9	−16.9
0.3250	0.5750	0.1000	350	354.4	−4.4
$x'_A/x'_B = 0.9940$; $x'_A = 0.4985$					
0.0497	0.0500	0.5403	95	118.5	−23.5
0.0797	0.0802	0.8401	180	184.5	4.5
0.1196	0.1204	0.7600	245	263.2	−18.2
0.1225	0.1223	0.7552	260	268.8	−8.8
0.1785	0.1795	0.6420	350	356.4	−6.4
0.2052	0.2064	0.5884	395	388.5	6.5
0.2469	0.2494	0.5037	435	425.1	9.9
0.2827	0.2845	0.4328	440	444.6	−4.6
0.3700	0.3722	0.2578	450	448.0	2.0
0.4387	0.4413	0.1200	420	420.5	−0.5
$x'_A/x'_B = 1.4844$; $x'_A = 0.5975$					
0.0567	0.0383	0.9050	120	140.7	−20.7
0.1256	0.0846	0.7898	270	287.2	−17.2
0.2087	0.1406	0.6507	430	415.7	14.3
0.2241	0.1509	0.6250	440	433.2	6.8
0.3107	0.2093	0.4800	500	494.6	5.4
0.3577	0.2410	0.4013	505	503.5	1.5
0.4005	0.2699	0.3296	515	498.3	16.7
0.4272	0.2878	0.2850	500	489.6	10.4
0.5224	0.3519	0.1257	440	432.7	7.3
$x'_B/x'_C = 0.5254$; $x'_B = 0.3444$					
0.0920	0.3127	0.5953	150	166.6	−16.6
0.1400	0.2962	0.5638	250	263.2	−13.2
0.2386	0.2623	0.4991	400	412.0	−12.0
0.3989	0.2070	0.3941	535	530.0	5.0
0.4271	0.2015	0.3714	545	534.6	10.4
0.5340	0.1605	0.3055	550	531.6	18.4
0.6450	0.1248	0.2302	490	476.0	14.0
0.8701	0.0451	0.0848	250	234.9	15.1
$x'_B/x'_C = 1.0872$; $x'_B = 0.5209$					
0.0300	0.5002	0.4698	−60	5.7	−65.7
0.1030	0.4672	0.4298	145	164.7	−19.7
0.2990	0.3451	0.3559	420	432.5	−12.5
0.4986	0.2597	0.2417	500	487.0	13.0
0.6717	0.1710	0.1573	440	412.0	28.0
0.8903	0.0571	0.0526	190	180.5	9.5
$x'_A/x'_C = 0.4956$; $x'_A = 0.3314$					
0.1102	0.6674	0.2224	140	140.7	−0.7
0.1852	0.4412	0.3736	270	296.5	−26.5
0.2233	0.3262	0.4505	350	375.1	−25.1
0.2508	0.2431	0.5061	420	431.3	−11.3
0.2948	0.1103	0.5949	500	530.4	−30.4
$x'_A/x'_C = 0.9970$; $x'_A = 0.4992$					
0.2688	0.4617	0.2695	350	368.7	−18.7
0.2994	0.4083	0.2923	400	407.9	−7.9
0.3269	0.3452	0.3279	440	446.7	−6.6
0.3667	0.2656	0.3677	500	494.7	5.3
0.4202	0.1584	0.4214	580	560.1	19.9
0.4640[b]	0.0700	0.4660	653	626.1	26.9

[a] $\delta H^E = H^E_{exp} - H^E_{cal}$. [b] Mole fraction of *n*-butylamine is corrected according to $x'_A/x'_C = 0.9970$.

graphical comparison of the experimental results and calculated values for the constituent three binary systems of the ternary mixture. The ternary excess molar enthalpies of the *n*-butylamine + 1,4-dioxane + acetonitrile mixture were predicted using the binary parameters alone. Table 3 gives the ternary detailed calculated results. The absolute arithmetic mean deviation and standard deviation of the ternary excess molar enthalpies were 14.1 J mol^{-1} and 19.8 J mol^{-1}, respectively. De Ruiz Holgado et al. [11] fitted their binary and ternary excess molar enthalpy data using four empirical polynomials [15–18] and they obtained the standard deviations between the calculated and experimental excess molar enthalpy values using only binary parameters: 81 J mol^{-1} by the method of Tsao and Smith [15]; 71 J mol^{-1} by Kohler's equation [16]; 72 J mol^{-1} by the method of Radojkovič et al. [17]; 72 J mol^{-1} by the equation of Jacob and Fitzner [18]. These values for the deviations seem to be too large in comparison with the present deviation of 19.8 J mol^{-1} derived from our association model.

We conclude that the model used in this work represents well the excess molar enthalpies for binary and ternary mixtures containing an amine, acetonitrile and one active non-associating component using binary parameters alone.

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REFERENCES

1 I. Nagata and K. Tamura, Thermochim. Acta, 44 (1981) 157–169.
2 I. Nagata, K. Tamura and S. Tokuriki, Thermochim. Acta, 47 (1981) 315–331.
3 I. Nagata and K. Tamura, Thermochim. Acta, 86 (1985) 85–99.
4 I. Nagata and K. Tamura, Thermochim. Acta, 98 (1986) 147–158.
5 I. Nagata and K. Tamura, Thermochim. Acta, 101 (1986) 305–323.
6 I. Nagata and K. Tamura, Thermochim. Acta, 124 (1988) 53–63.
7 I. Nagata and K. Tamura, Thermochim. Acta, 140 (1989) 109–120.
8 I. Nagata and K. Tamura, Thermochim. Acta, 154 (1989) 333–344.
9 I. Nagata and K. Tamura, Thermochim. Acta, 162 (1990) 355–366.
10 H. Renon and J.M. Prausnitz, AIChE J., 14 (1968) 135–144.
11 M.E. de Ruiz Holgado, C.R. de Schaefer, F. Davolio and M. Katz, Thermochim. Acta, 196 (1992) 169–175.
12 I.I. Acevedo, M.A. Postigo and M. Katz, J. Solution Chem., 17 (1988) 977–986.
13 F. Davolio, C.R. de Schaefer, J.A. Salas and M. Katz, Lat. Am. Res. Appl., 20 (1990) 161–166.
14 F. Davolio, G.C. Pedrosa, N.L. Hernandez and M. Katz, unpublished data, 1992.

15 C.C. Tsao and J.M. Smith, Chem. Eng. Prog. Symp. Ser., 49 (1953) 107–117.
16 F. Kohler, Monatsh. Chem., 91 (1960) 738–740.
17 N. Radojkovič, A. Tasič, D. Grozdenič, B. Diordevič and M. Malič, J. Chem. Thermodyn., 9 (1977) 349–356.
18 K.J. Jacob and K. Fitzner, Thermochim. Acta, 18 (1977) 197–206.