ELSEVIER
Thermochimica Acta 255 (1995) 23-32
thermochimica
acta

Correlation of ternary excess molar enthalpies for mixtures containing an alkanol and two active non-associated components using a mole-fraction association model

Isamu Nagata

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

Received 29 July 1994; accepted 6 November 1994

Abstract

Excess molar enthalpies are reported for methanol + toluene + cyclohexane, measured with an isothermal dilution calorimeter at 25°C. The experimental results have been correlated with a mole-fraction association model having binary and ternary parameters. The workability of the proposed model has been confirmed satisfactorily for many ternary alcohol mixtures.

Keywords: Association model; Binary system; Excess enthalpy; Molecular complexation; Ternary system

List of symbols

a_{JI}	binary interaction parameter for J–I pair
C_{JI}, D_{JI}	parameters of Eq. (13)
G_{JI}	$\exp(-\alpha_{JI}\tau_{JI})$
g^E	excess Gibbs free energy
H^E	excess enthalpy
h_2	enthalpy of hydrogen bond formation for open dimer
h	enthalpy of hydrogen bond formation for $i$mer, $i > 3$
h_{AB}, h_{AC}	enthalpies of formation for chemical complexes A_iB and A_iC
K_2^0	equilibrium constant for open dimer formation

0040-6031/95/$09.50
SSDI 0040-6031(94)02176-7

K_3^0	equilibrium constant for open-chain trimer formation
K^0	equilibrium constant for open-chain *i*mer formation, $i > 3$
K_{cy}^0	equilibrium constant for cyclization of open-chain, *i*mer, $i > 4$
K_{AB}^0, K_{AC}^0	equilibrium constants for chemical complexes A_iB and A_iC
R	universal gas constant
S	stoichiometric sum
T	absolute temperature
x_I	liquid-phase mole fraction of component I
x'_{JI}	modified local mole-fraction as defined by Eq. (15)
x'_{JKI}	modified local mole-fraction as defined by Eq. (16)
z	coefficient as defined by $K^0 x_{A_1}$

Greek letters

α_{JI}	non-randomness parameter of NRTL equation for J–I pair
θ	constant related to K_{cy}^0
τ_{JI}	binary parameter as defined by a_{JI}/T
τ_{JKI}	ternary parameter
τ'_{JKI}	$\partial\tau_{JKI}/\partial(1/T)$

Subscripts

A, B, C	alkanol and unassociated components
A_1, A_i	alkanol monomer and *i*mer
AB, AC	complex formation between alkanol open *i*mer and component B or C
chem	chemical
I, J, K	components
phys	physical

Superscripts

E	excess
*	pure alkanol

1. Introduction

Experimental ternary excess enthalpy results have been frequently smoothed by means of empirical polynomial equations such as the Redlich–Kister type of equations. For weakly non-ideal mixtures these polynomials with only binary parameters can predict well the ternary excess enthalpy values. However, it is necessary to introduce many ternary parameters in these polynomials for the good representation of ternary excess enthalpy data for strongly non-ideal mixtures. We have published experimental ternary excess enthalpy data for many alkanol mixtures and compared those data with calculated results obtained from polynomials having binary and ternary parameters and from an association model with only binary parameters based on mole-fraction statistics [1–3]. In this paper we will show that for partially miscible ternary mixtures containing methanol and a saturated hydrocarbon, polynomials are not suitable for data smoothing and the association model with additional ternary parameters gives smaller deviations between experimental and calculated results than those obtained with only binary parameters.

2. Experimental

All chemicals used in this work were received from Wako Pure Chemical Industries Ltd. Cyclohexane and toluene (guaranteed reagent grade) were used directly. Methanol (first grade) was fractionated on a glass-packed column after drying over a calcium oxide. The densities of the chemicals, measured with an Anton-Paar densimeter at 25°C, agreed well with literature values [4] as shown in Table 1. An isothermal dilution calorimeter was used to measure excess enthalpies H^E for methanol + toluene + cyclohexane at 25°C as described previously [5]. The experimental error of the measured value was $\pm 0.005 \cdot H^E$.

3. Results and analysis

Table 2 gives the ternary experimental H^E values of methanol + toluene + cyclohexane at 25°C. The Redlich–Kister-type polynomial equations were unable to reproduce the present experimental ternary data having a partially miscible region. The ternary experimental H^E data were analysed with an association model based on mole-fraction statistics. Fig. 1 plots contours of the ternary H^E values calculated from the association model described here. Ternary liquid–liquid equilibria for the present system were taken from Ref. [6].

Stokes [7] proposed a model to reproduce quantitatively the activity coefficients, excess enthalpies and IR spectroscopic behaviour of diluted solutions of ethanol in cyclohexne ($x_A < 0.2$) in terms of the association of both open-chain and cyclic hydrogen-bonded groups plus a term for the Hildebrand interaction. To represent well the vapour–liquid equilibrium, liquid–liquid equilibrium, and excess enthalpy data over the whole concentration range, as well as the spectroscopic results in a

Table 1
Densities of pure components at 25°C

Component	Density/(g cm^{-3})	
	Obs.	Lit. [4]
Methanol	0.78662	0.78664
Toluene	0.86230	0.86231
Cyclohexane	0.77390	0.77389

Table 2
Experimental ternary excess molar enthalpies H^E for methanol(1) + toluene(2) + cyclohexane(3) at 25°C [a]

x_1	x_2	H^E/ (J mol^{-1})	x_1	x_2	H^E/ (J mol^{-1})	x_1	x_2	H^E/ (J mol^{-1})
$x'_2 = 0.2503$			$x'_2 = 0.4998$			$x'_2 = 0.7500$		
0.8676	0.0331	399.6	0.8860	0.0570	313.5	0.8902	0.0823	249.1
0.8242	0.0440	485.1	0.8728	0.0636	342.7	0.8593	0.1055	309.0
0.7734	0.0567	566.3	0.8215	0.0892	446.3	0.8146	0.1390	390.4
0.7122	0.0720	644.1	0.7656	0.1172	545.1	0.7651	0.1761	473.3
0.6661	0.0836	692.4	0.7244	0.1377	610.8	0.7144	0.2142	552.3
0.6192	0.0953	733.6	0.6727	0.1636	683.9	0.6639	0.2521	624.2
0.5785	0.1055	764.8	0.6259	0.1870	743.5	0.6162	0.2878	686.7
0.5384	0.1155	792.0	0.5794	0.2102	797.9	0.5656	0.3258	747.8
0.4939	0.1267	818.9	0.5282	0.2358	852.3	0.5128	0.3654	805.7
0.4511	0.1374	841.3	0.4795	0.2601	899.0	0.4581	0.4064	859.4
0.4034	0.1493	862.5	0.4349	0.2824	937.5	0.4027	0.4840	906.5
0.3605	0.1601	877.8	0.3886	0.3055	972.6	0.3569	0.4823	939-6
0.3142	0.1717	890.4	0.3399	0.3299	1005.3	0.3034	0.5224	970.6
0.2666	0.1836	897.6	0.2912	0.3542	1031.3	0.2516	0.5613	991.0
0.2179	0.1958	898.4	0.2437	0.3779	1048.9	0.2001	0.5999	999.5
0.1607	0.2101	889.1	0.1833	0.4081	1058.6	0.1535	0.6349	990.9
0.1046	0.2241	859.9	0.1063	0.4467	1036.5	0.0987	0.6760	953.2
0.0507	0.2376	793.6	0.0428	0.4784	946.3	0.0435	0.7174	838.6
0.0185	0.2357	698.2						

[a] Ternary mixtures were obtained by mixing pure methanol with $\{x'_2$ toluene + $(1 - x'_2)$cyclohexane$\}$.

diluted range of alkanol solutions, we [1–3] have replaced the Hildebrand interaction term with the NRTL equation [8]. In a ternary mixture including an alkanol (A) and two non-associated components (B and C), the model involves three association constants for open-chain formation, one association constant for cyclization, and two enthalpies of hydrogen-bond formation: K_2^0 and h_2 for $A_1 + A_1 = A_2$; K_3^0 and $h_3 = (2h - h_2)$ for $A_2 + A_1 = A_3$; K^0 and h for $A_i + A_1 = A_{i+1}$ $(i \geq 3)$; $K_{cy}^0 = \theta / i$, and h for $A_i(\text{open}) = A_i(\text{cyclic})$, where θ is independent of i and $i > 4$. The values of $K_2^0 K_3^0 / K^{02}$ must be independent of temperature according to the model. Two solvation constants and two enthalpies of complex formation are K_{AB}^0 and h_{AB} for $A_i + B = A_iB$, $i \geq 1$, and K_{AC}^0 and h_{AC} for $A_i + C = A_iC$, $i \geq 1$. The equilibrium constants are defined in terms of the mole fractions of chemical species. The van't Hoff equation fixes the temperature dependence of the equilibrium constants.

The ternary expression of H^E is given as the sum of two contribution terms: chemical and physical

$$H^E = H_{\text{chem}}^E + H_{\text{phys}}^E \tag{1}$$

$$H_{\text{chem}}^E = \{(1 + K_{AB}^0 x_{B_1} + K_{AC}^0 x_{C_1})[h_2 K_2^0 x_{A_1}^2 + h K_2^0 K_3^0 x_{A_1}^3 (2 - z)/(1 - z)^2]$$
$$+ h K_2^0 K_3^0 K^{02} \theta x_{A_1}^5 / (1 - z)$$

$$+(h_{AB}K^0_{AB}x_{B_1}+h_{AC}K^0_{AC}x_{C_1})[x_{A_1}+K^0_2x^2_{A_1}+K^0_2K^0_3x^3_{A_1}/(1-z)]\}/S$$
$$-x_A[h_2K^0_2x^{*2}_{A_1}+hK^0_2K^0_3x^{*2}_{A_1}(2-z^*)/(1-z^*)^2$$
$$+hK^0_2K^0_3K^{02}\theta x^{*5}_{A_1}/(1-z^*)]/S^* \tag{2}$$

where $z=K^0x_{A_1}$ and the stoichiometric sum S is expressed by

$$S=(1+K^0_{AB}x_{B_1}+K^0_{AC}x_{C_1})[x_{A_1}+2K^0_2x^2_{A_1}+K^0_2K^0_3x^3_{A_1}(3-2z)/(1-z)^2]$$
$$+K^0_2K^0_3K^{02}\theta x^5_{A_1}/(1-z)+(K^0_{AB}x_{B_1}+K^0_{AC}x_{C_1})[x_{A_1}+K^0_2x^2_{A_1}$$
$$+K^0_2K^0_3x^3_{A_1}/(1-z)]+x_{B_1}+x_{C_1} \tag{3}$$

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

$$(1+K^0_{AB}x_{B_1}+K^0_{AC}x_{C_1})[x_{A_1}+K^0_2x^2_{A_1}+K^0_2K^0_3x^3_{A_1}/(1-z)]$$
$$-(K^0_2K^0_3\theta/K^{03})[\ln(1-z)+z+z^2/2+z^3/3+z^4/4]+x_{B_1}+x_{C_1}=1 \tag{4}$$

The nominal mole fractions of the components, x_A, x_B and x_C, are given in terms of the monomeric mole fractions of the components, x_{A_1}, x_{B_1} and x_{C_1}, and the equilibrium constants

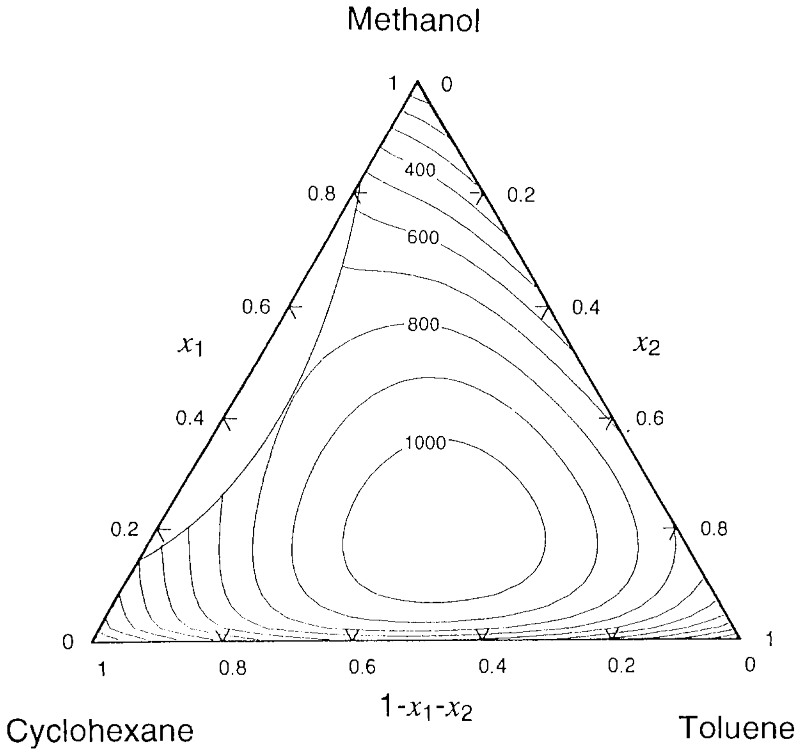

Fig. 1. Curves of constant excess molar enthalpies for methanol(1) + toluene(2) + cyclohexane(3) at 25°C: ——, calculated from the association model with binary and ternary parameters.

Table 3
Association constants at 25°C and enthalpies of hydrogen-bond formation for pure akanols

Component	K_2^0	K_3^0	K^0	K_{cy}^0	$-h_2/(\text{kJ mol}^{-1})$	$-h/(\text{kJ mol}^{-1})$	Ref.
Methanol	70	120	100	$90/i$	21.2	23.5	[1]
Ethanol	40	110	45	$85/i$	21.2	23.5	[2]
1-Propanol	35	90	40	$75/i$	21.2	23.5	[3]
2-Propanol	35	85	30	$70/i$	21.2	23.5	[3]

$$x_A = \{(1 + K_{AB}^0 x_{B_1} + K_{AC}^0 x_{C_1})[x_{A_1} + 2K_2^0 x_{A_1}^2 + K_2^0 K_3^0 x_{A_1}^3 (3-2z)/(1-z)^2] + K_2^0 K_3^0 K^{02} \theta x_{A_1}^5/(1-z)\}/S \quad (5)$$

$$x_B = \{x_{B_1} + K_{AB}^0 x_{B_1}[x_{A_1} + K_2^0 x_{A_1}^2 + K_2^0 K_3^0 x_{A_1}^3/(1-z)]\}/S \quad (6)$$

$$x_C = \{x_{C_1} + K_{AC}^0 x_{C_1}[x_{A_1} + K_2^0 x_{A_1}^2 + K_2^0 K_3^0 x_{A_1}^3/(1-z)]\}/S \quad (7)$$

Eqs. (3)–(7) are solved simultaneously to obtain x_{A_1}, x_{B_1} and x_{C_1}.

At pure alcohol state, $z^* = K^0 x_{A_1}^*$, $x_{A_1}^*$ and S^* are derived from Eqs. (8) and (9)

$$x_{A_1}^* + K_2^0 x_{A_1}^{*2} + K_2^0 K_3^0 x_{A_1}^{*3}/(1-z^*) - (K_2^0 K_3^0 \theta/K^{03})[\ln(1-z^*) + z^* + z^{*2}/2 + z^{*3}/3 + a^{*4}/4] = 1 \quad (8)$$

$$S^* = x_{A_1}^* + 2K_2^0 x_{A_1}^{*2} + K_2^0 K_3^0 x_{A_1}^{*3}(3-2z^*)/(1-z^*)^2 + K_2^0 K_3^0 K^{02} \theta x_{A_1}^{*5}/(1-z^*) \quad (9)$$

The physical contribution term is obtained by application of the Gibbs–Helmholtz equation to the NRTL equation for the excess Gibbs free energy [8]

$$H_{\text{phys}}^{\text{E}} = R \sum_I x_I \left(\frac{\sum_J x_j \dfrac{\partial(\tau_{JI} G_{JI})}{\partial(1/T)}}{\sum_K G_{KI} x_K} - \frac{\sum_J \tau_{JI} G_{JI} x_J \sum_K x_K \dfrac{\partial G_{KI}}{\partial(1/T)}}{\left(\sum_K G_{KI} x_K\right)^2} \right) \quad (10)$$

where τ_{JI} and G_{JI} are defined by

$$\tau_{JI} = a_{JI}/T \quad (11)$$

$$G_{JI} = \exp(-\alpha_{JI} \tau_{JI}) \quad (12)$$

and the non-randomness parameter α_{JI} is set as 0.3 for each binary mixture. The energy parameters a_{JI} are assumed to vary linearly with temperature

$$a_{JI} = C_{JI} + D_{JI}(T - 273.15) \quad (13)$$

The parameters C_{JI} and D_{JI} were obtained by minimizing the sum-of-squares of the deviation between experimental and calculated values by means of the Nelder–Mead simplex method [9].

Table 3 gives the association parameters of pure alkanols [1–3]. The values of h_2 and h are identical to those given by Stokes [7] and those of the association constants were obtained by fitting the model to binary experimental vapour–liquid equilibrium, and excess enthalpy and spectroscopic results for alkanol + saturated hydrocarbon mixtures. Table 4 shows the equilibrium constants evaluated from binary mixture properties (vapour–liquid equilibrium and/or excess enthalpy data) and enthalpies of complex formation, which were estimated approximately by taking the difference between the value of the enthalpy of dilution of ethanol in saturated hydrocarbons [10] and that of ethanol in active solvents at 25°C. The values of h_2, h and h_{AB} were assumed to be temperature-independent. The original ternary NRTL equation for the excess Gibbs free energy g^E was modified to include ternary parameters [11]

$$\begin{aligned} g^E/RT &= \sum_I x_I\left(\sum_J x'_{JI}\tau_{JI} + (1/2)\sum_J\sum_K x'_{JKI}\tau_{JKI}\right) \\ &= x_1(x'_{21}\tau_{21} + x'_{31}\tau_{31} + x'_{231}\tau_{231}) \\ &\quad + x_2(x'_{12}\tau_{12} + x'_{32}\tau_{32} + x'_{132}\tau_{132}) \\ &\quad + x_3(x'_{13}\tau_{13} + x'_{23}\tau_{23} + x'_{123}\tau_{123}) \end{aligned} \tag{14}$$

where $\tau_{IJ} \neq \tau_{JI} \neq 0$, $\tau_{JI} = 0$, the ternary parameters are $\tau_{JKI} \neq \tau_{KJI} \neq 0$, and $\tau_{JII} = \tau_{JJI} = \tau_{IJI} = 0$. When the ternary terms vanish, Eq. (14) reduces to the original NRTL equation. The modified local mole-fractions are defined as

$$x'_{JI} = \frac{x_J G_{JI}}{\sum_K x_K G_{KI} + (1/2)\sum_K\sum_J x_J x_K G_{JI} G_{KI}} \tag{15}$$

Table 4
Equilibrium constants and enthalpies of complex formation

System (A + B)	K^0_{AB}	$-h_{AB}/(\mathrm{kJ\ mol^{-1}})$	Temp./°C	Ref.
Methanol + acetone	15.0	21.0	50	[1]
Ethanol + acetone	23.0	21.0	25	[13]
1-Propanol + acetone	22.0	21.0	25	[14]
2-Propanol + acetone	20.0	21.0	25	[15]
Methanol + 2-butanone	25.0	18.0	25	[16]
Ethanol + 2-butanone	20.0	18.0	25	[16]
1-Propanol + 2-butanone	20.0	18.0	25	[17]
2-Propanol + 2-butanone	18.0	18.0	25	[17]
Methanol + MTBE [a]	20.0	21.0	25	[18]
Ethanol + MTBE	15.0	21.0	25	[19]
Methanol + benzene	3.0	8.2	55	[1]
Ethanol + benzene	3.6	8.2	25	[2]
1-Propanol + benzene	3.2	8.2	25	[14]
2-Propanol + benzene	2.8	8.2	25	[15]
Methanol + toluene	4.0	8.2	25	[1]

[a] Methyl *tert*-butyl ether.

Table 5
Binary parameters and absolute arithmetic-mean deviations at 25°C

System (A + B)	C_{BA}/K	C_{AB}/K	D_{BA}	D_{AB}	AAM [a]/ (J mol^{-1})	Ref. I [b]	Ref. II [c]
Methanol + acetone	−1070.58	338.58	−3.8742	0.5540	5.8	[12]	[12]
Ethanol + acetone	680.91	−409.78	−2.7906	−1.8535	3.0	[13]	[13]
1-Propanol + acetone	−1169.62	−295.35	−4.5201	−1.7821	16.7	[14]	[14]
2-Propanol + acetone	−923.77	−186.51	−3.7414	−1.6471	3.1	[15]	[15]
Methanol + 2-butanone	−1152.91	−1359.96	−4.1659	−4.8881	5.8	[20]	[16]
Ethanol + 2-butanone	554.76	314.58	2.1213	1.0086	11.9	[20]	[16]
1-Propanol + 2-butanone	−1144.78	320.31	−4.2734	−0.9837	6.5	[17]	[17]
2-Propanol + 2-butanone	−1041.62	56.57	−3.9450	−0.2372	4.6	[20]	[17]
Methanol + MTBE [d]	−448.42	409.70	−1.8118	−2.4867	8.7	[21]	[27]
Ethanol + MTBE	694.63	1.054	1.9576	0.2459	7.2	[19]	[19]
Methanol + benzene	−1084.29	843.71	−3.8301	3.5643	4.4	[22]	[12]
Ethanol + benzene	14.55	840.34	0.5554	4.5576	1.7	[22]	[13]
1-Propanol + benzene	−1135.43	594.67	−3.8897	2.0141	7.9	[22]	[14]
2-Propanol + benzene	−1097.98	485.01	3.6946	0.7566	7.0	[22]	[15]
Methanol + cyclohexane	−34.72	252.57	0.6775	−1.2864	8.5	[23]	[30]
Methanol + *n*-heptane	−98.20	384.44	−1.0367	0.8498	15.9	[24]	[30]
Methanol + toluene	285.66	499.40	0.8575	2.9187	8.6	[22]	This work
Acetone + benzene	596.46	513.11	1.7141	1.6470	1.1	[25]	[12]
2-Butanone + benzene	763.34	−227.61	2.4471	−0.6926	0.2	[26]	[16]
MTBE + benzene	2410.26	−458.56	8.8899	−1.8072	7.2	[27]	[27]
Benzene + cyclohexane	−46.62	−586.90	−1.4246	−2.1826	2.2	[5]	]30]
Benzene + *n*-heptane	−74.48	487.48	−1.3514	0.9370	2.4	[28]	[30]
Toluene + cyclohexane	135.59	−124.39	−1.5701	−0.2147	3.3	[29]	This work

[a] Absolute arithmetic-mean deviation between experimental and calculated values. [b] Data. [c] Parameter.
[d] Methyl *tert*-butyl ether.

$$x'_{JKI} = \frac{(1/2)\sum_K \sum_J x_J x_K G_{JI} G_{KI}}{\sum_K x_K G_{KI} + (1/2)\sum_K \sum_J x_J x_K G_{JI} G_{KI}} \tag{16}$$

The physical contribution term of the model H^E_{phys} is expressed by

$$\begin{aligned} H^E_{\text{phys}} &= \frac{\partial (g^E_{\text{phys}}/T)}{\partial (1/T)} \\ &= R \sum_I x_I \left(\sum_J \frac{\partial (x'_{JI} \tau_{JI})}{\partial (1/T)} + (1/2) \sum_K \sum_J \frac{\partial (x'_{JKI} \tau_{JKI})}{\partial (1/T)} \right) \end{aligned} \tag{17}$$

Table 5 summarizes the calculated results obtained from the association model for binary systems making up 13 ternary systems at 25°C together with references for the experimental data and parameters of all systems. Table 6 shows the absolute arithmetic-mean deviations obtained from polynomials and the association model, the number of ternary parameters of polynomials, and $\tau'_{231} = \partial\tau_{231}/\partial(1/T)$, $\tau'_{132} = \partial\tau_{132}/\partial(1/T)$, and $\tau'_{123} = \partial\tau_{123}/\partial(1/T)$. The deviations based on polynomials and the association model having only binary parameters were taken from previous

Table 6
Ternary calculated results obtained from polynomials and the association model at 25°C

System (1 + 2 + 3)	Ternary parameters		Abs. arith. mean devs./(J mol^{-1})			Ref.
			I[a]	II[b]	III[c]	
Methanol	$\tau_{231} = 9.6988$	$\tau'_{231} = -82.2796$	3.05	9.55	4.77	[16]
+ 2-butanone	$\tau_{132} = -13.8117$	$\tau'_{132} = -117.142$	(7)[d]			
+ benzene	$\tau_{123} = 17.8276$	$\tau'_{132} = -1038.15$				
Ethanol	$\tau_{231} = 29.2203$	$\tau'_{231} = -1276.67$	3.07	11.67	4.48	[16]
+ 2-butanone	$\tau_{132} = 4.0970$	$\tau'_{132} = -1436.07$	(9)			
+ benzene	$\tau_{123} = 24.8812$	$\tau'_{123} = -819.660$				
1-Propanol	$\tau_{231} = 21.3361$	$\tau'_{231} = -557.969$	4.20	12.21	6.33	[17]
+ 2-butanone	$\tau_{132} = 232.083$	$\tau'_{132} = -334.351$	(7)			
+ benzene	$\tau_{123} = -141.082$	$\tau'_{123} = 5916.20$				
2-Propanol	$\tau_{231} = 5.5584$	$\tau'_{231} = -61.4639$	9.00	11.15	7.79	[17]
+ 2-butanone	$\tau_{132} = 16.8077$	$\tau'_{132} = -340.278$	(7)			
+ benzene	$\tau_{123} = -10.3699$	$\tau'_{123} = 102.754$				
Methanol	$\tau_{231} = -60.9830$	$\tau'_{231} = 918.999$	10.21	23.51	13.22	[27]
+ MTBE	$\tau_{132} = -85.8527$	$\tau'_{132} = 4035.65$	(4)			
+ benzene	$\tau_{123} = 60.8527$	$\tau'_{123} = -5565.14$				
Ethanol	$\tau_{231} = -9.7634$	$\tau'_{231} = 462.780$	19.38	31.20	13.87	[19]
+ MTBE	$\tau_{132} = 2.6190$	$\tau'_{132} = 986.567$	(3)			
+ benzene	$\tau_{123} = 3.8784$	$\tau'_{123} = -916.057$				
Methanol	$\tau_{231} = 10.1125$	$\tau'_{231} = -123.035$	5.37	9.27	4.67	[12]
+ acetone	$\tau_{132} = 2.0114$	$\tau'_{132} = 85.9607$	(7)			
+ benzene	$\tau_{123} = 6.3132$	$\tau'_{123} = 122.589$				
Ethanol	$\tau_{231} = 10.9774$	$\tau'_{231} = -107.791$	6.19	14.88	5.25	[13]
+ acetone	$\tau_{132} = -5.8060$	$\tau'_{132} = 3.0451$	(7)			
+ benzene	$\tau_{123} = -4.7888$	$\tau'_{123} = 4.7039$				
1-Propanol	$\tau_{231} = 6.5120$	$\tau'_{231} = -75.4089$	6.87	14.82	9.49	[14]
+ acetone	$\tau_{132} = 12.1965$	$\tau'_{132} = 20.5808$	(7)			
+ benzene	$\tau_{123} = -83.0303$	$\tau'_{123} = -5.6554$				
2-Propanol	$\tau_{231} = 0.9781$	$\tau'_{231} = 90.1471$	9.1	16.75	8.64	[15]
+ acetone	$\tau_{132} = -5.5844$	$\tau'_{132} = 20.2216$	(7)			
+ benzene	$\tau_{123} = 10.1117$	$\tau'_{123} = 5.7057$				
Methanol	$\tau_{231} = -8.3392$	$\tau'_{231} = -890.490$		23.21	6.46	This work
+ toluene	$\tau_{132} = -4.8700$	$\tau'_{132} = 2831.87$				
+ cyclohexane	$\tau_{123} = -5.8942$	$\tau'_{123} = -1432.56$				
Methanol	$\tau_{231} = 28.2627$	$\tau'_{231} = -1378.54$		22.80	13.30	[30]
+ benzene	$\tau_{132} = 0.8448$	$\tau'_{132} = -3210.50$				
+ cyclohexane	$\tau_{123} = -10.0752$	$\tau'_{123} = 109.733$				
Methanol	$\tau_{231} = 53.8667$	$\tau'_{231} = -374.655$		23.25	10.98	[30]
+ benzene	$\tau_{132} = 19.4340$	$\tau'_{132} = 14565.0$				
+ *n*-heptane	$\tau_{123} = 66.9036$	$\tau'_{123} = -1229.69$				

[a] Polynomial equation with binary and ternary parameters. [b] Association model with only binary parameters. [c] Association model with binary and ternary parameters. [d] Number of ternary parameters.

papers [12–17,19,27,30]. To obtain the ternary parameters, a fitting program was used to minimize the sum-of-squares of deviation in excess enthalpy for all data points. In the ternary correlation of H^E results for completely miscible systems, polynomial equations, containing three to nine ternary parameters, were used and did not work for three partially miscible systems. For both systems the association model does a good job using six additional ternary parameters. For completely miscible ternary systems, polynomials gave the average deviation of 6.80 J mol^{-1} and the association model 7.85 J mol^{-1}. This means that the present method is good in the correlation of ternary H^E data for solutions containing an alkanol and two active non-associated components.

Acknowledgements

The author thanks Mrs K. Yazawa and Y. Enomoto for their help.

References

[1] I. Nagata and K. Tamura, Thermochim. Acta, 57 (1982) 331–349.
[2] I. Nagata and K. Tamura, Thermochim. Acta, 77 (1984) 281–298.
[3] I. Nagata and K. Tamura, Thermochim. Acta, 87 (1985) 129–140.
[4] J.A. Riddick and W.B. Bunger, Organic Solvents, Wiley-Interscience, New York, 3rd edn., 1970.
[5] I. Nagata and K. Kazuma, J. Chem. Eng. Data, 22 (1977) 79–84.
[6] I. Nagata, Fluid Phase Equilibria, 18 (1984) 83–92.
[7] R.H. Stokes, J. Chem. Soc. Faraday Trans. 1, 73 (1977) 1140–1148.
[8] H. Renon and J.M. Prausnitz, AIChE J., 14 (1968) 135–144.
[9] J.A. Nelder and R. Mead, Comput. J., 7 (1965) 308–313.
[10] R.H. Stokes and C. Burfitt, J. Chem. Thermodyn., 5 (1973) 623–631.
[11] I. Nagata and J. Nakajima, Fluid Phase Equilibria, 70 (1991) 275–292.
[12] I. Nagata, Thermochim. Acta, 236 (1994) 23–30.
[13] I. Nagata and A. Książczak, J. Chem. Thermodyn., 26 (1994) 165–169.
[14] I. Nagata and K. Takeuchi, Thermochim. Acta, 240 (1994) 103–110.
[15] I. Nagata, J. Chem. Thermodyn., 26 (1994) 691–695.
[16] I. Nagata and K. Tamura, J. Chem. Thermodyn., 22 (1990) 279–283.
[17] K. Tamura and I. Nagata, J. Chem. Thermodyn., 23 (1991) 359–364.
[18] I. Nagata, J. Chem. Thermodyn., 26 (1994) 779–783.
[19] I. Nagata, J. Chem. Thermodyn., 26 (1994) 1137–1142.
[20] I. Nagata, T. Ohta and S. Nakagawa, J. Chem. Eng. Jpn., 9 (1976) 276–281.
[21] E. Tusel-Langer, J.M. Garcia Alonso, M.A. Villamanan Olfos and R.N. Lichtenthaler, J. Solution Chem., 20 (1991) 153–163.
[22] R.V. Mrazek aknd H.C. Van Ness, AIChE J., 7 (1961) 190–195.
[23] H. Touhara, M. Ikeda, K. Nakanishi and N. Watanabe, J. Chem. Thermodyn., 7 (1975) 887–893.
[24] C.G. Savini, D.R. Winterhalter and H.C. Van Ness, J. Chem. Eng. Data, 10 (1965) 171–172.
[25] Y. Akamatsu, H. Ogawa and S. Murakami, Thermochim. Acta, 113 (1987) 141–150.
[26] O. Kiyohara, G.C. Benson and J.-P.E. Grolier, J. Chem. Thermodyn., 9 (1977) 315–323.
[27] I. Nagata, J. Chem. Thermodyn., 26 (1994) 779–783.
[28] E. Münsch, Thermochim. Acta, 22 (1978) 237–255.
[29] K.Y. Hsu and H.L. Clever, J. Chem. Thermodyn., 7 (1975) 435–442.
[30] I. Nagata, J. Chem. Thermodyn., 26 (1994) 1293–1296.