Thermochimica Acta, 47 (1981) 315—331
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

EXCESS ENTHALPIES AND COMPLEX FORMATION OF ACETONITRILE WITH ACETONE, CHLOROFORM, AND BENZENE

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(Received 4 March 1981)

ABSTRACT

Excess enthalpies of binary systems of acetonitrile—acetone, chloroform—acetone and chloroform—benzene, and ternary systems of acetonitrile—chloroform—acetone and acetonitrile—chloroform—benzene are reported at 25°C. The results are analyzed with thermodynamic association theory for complex ternary liquid mixtures. The theory involves two types of self-association of acetonitrile, formation of binary complexes for component pairs of a ternary system, and a nonspecific interaction term expressed by the NRTL equation between various chemical species.

Notation

C_l, D_l	constants in eqn. (48)
G_{ij}	coefficient as defined by $\exp(-\alpha_{ij}\tau_{ij})$
g^E	excess Gibbs free energy
g_{ij}	binary interaction parameter
h_2	enthalpy of formation of a bond for head-to-head dimerization of acetonitrile
h_A	enthalpy of formation of a bond for chain association of acetonitrile
h_{AB}, h_{AC}	enthalpies of formation of chemical complexes A_1B_1 and A_1C_1
h_{BC}	enthalpy of formation of chemical complex B_1C_1
h_{B_2C}	enthalpy of formation of chemical complex B_2C_1
h_f	total enthalpy of chemical complex formation
h^E	excess enthalpy
K_2	chemical equilibrium constant of head-to-head dimerization of acetonitrile
K_A	chemical equilibrium constant of chain association of acetonitrile
K_{AB}, K_{AC}	chemical equilibrium constants of formation of chemical complexes A_1B_1 and A_1C_1
K_{BC}	chemical equilibrium constant of formation of chemical complex B_1C_1
K_{B_2C}	chemical equilibrium constant of formation of chemical complex B_2C_1
n	number of moles of a particular species
R	gas constant
S	stoichiometric sum
T	absolute temperature
x_i	liquid phase mole fraction of component i
α_{ij}	nonrandomness parameter of NRTL equation
γ_i	activity coefficient of component i
τ_{ji}	coefficient as defined by $(g_{ji} - g_{ii})/RT$

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Subscripts

A	acetonitrile
A_1, A_i	acetonitrile monomer and i-mer
A_1B_1	1 : 1 complex between acetonitrile and component B
A_1C_1	1 : 1 complex between acetonitrile and component C
B, C	unassociated components
B_1C_1	1 : 1 complex between components B and C
B_2C_1	2 : 1 complex between components B and C
chem	chemical
f	complex formation
i, j, k	components
phys	physical
1, 2, 3	acetonitrile and nonassociating components

Superscripts

E	excess
*	pure acetonitrile
′	head-to-head dimer

INTRODUCTION

Recently Nagata and Tamura [1] presented thermodynamic association theory for ternary liquid mixtures containing acetonitrile and nonassociating components such as carbon tetrachloride, benzene and *n*-heptane. The theory involves two types of self-association of acetonitrile and formation of binary complexes between acetonitrile and aromatic hydrocarbons (benzene, toluene etc.) to predict well vapor—liquid and liquid—liquid equilibria and excess enthalpies for the ternary mixtures from only binary parameters. The theory neglected binary complex formation between nonassociating components.

In this work the theory will be extended to include complex ternary systems where there is complex formation for three constituent binaries. Nuclear magnetic resonance studies revealed that chloroform forms 1 : 1 molecular complexes with acetonitrile and benzene [2,3]. The thermodynamic properties of the chloroform—acetone system were well described by the ideal association model of the type $A + B + AB + AB_2$ (B = chloroform) [4,5], which McGlashan and Rastogi [6] derived for the dioxane—chloroform system. Ternary excess Gibbs free energies for the acetonitrile—acetone—methyl acetate system at 50°C were reported [7]. We report excess enthalpies of the acetonitrile—acetone, chloroform—acetone, chloroform—benzene, acetonitrile—chloroform—acetone, and acetonitrile—chloroform—benzene systems at 25°C and analyze the observed results with the thermodynamic association theory.

TABLE 1

Densities and refractive indices of compounds at 25°C

Compound	Density (g cm^{-3})		Refractive index	
	Exptl.	Ref. 8	Exptl.	Ref. 8
Acetone	0.7848	0.7844	1.3556	1.3560
Acetonitrile	0.7767	0.7766	1.3417	1.3416
Benzene	0.8737	0.8737	1.4978	1.4979
Chloroform	1.4797	1.4799	1.4429	1.4429

EXPERIMENTAL

Materials

Reagent grade acetonitrile and spectrograde carbon tetrachloride were directly used. C.P. benzene was purified by repeated recrystallization. C.P. chloroform was shaken with concentrated sulfuric acid to remove alcohol, then washed with dilute sodium hydroxide and then with distilled water. The chloroform was treated with dry potassium carbonate and fractionally distilled. Densities and refractive indices for the compounds for experimental work are compared with the literature values [8] in Table 1.

TABLE 2

Excess enthalpies of binary systems at 25°C

x_1	$-h^E$ (J mole^{-1})	x_1	$-h^E$ (J mole^{-1})	x_1	$-h^E$ (J mole^{-1})	x_1	$-h^E$ (J mole^{-1})
Acetonitrile(1)—acetone(2)							
0.0281	14.1	0.3012	97.8	0.6094	99.1	0.8582	47.1
0.0646	30.5	0.3548	104.2	0.6573	92.4	0.8974	35.2
0.1150	50.4	0.4303	108.5	0.7078	83.1	0.9453	19.0
0.1830	72.3	0.4966	107.9	0.7639	71.6	0.9808	6.8
0.2332	85.1	0.5517	105.1	0.8105	60.2		
Chloroform(1)—acetone(2)							
0.0156	78.2	0.2887	1327.8	0.5129	1903.8	0.7751	1475.8
0.0453	226.9	0.3421	1517.1	0.5605	1929.5	0.8243	1228.1
0.0912	451.2	0.3940	1676.2	0.6188	1899.8	0.8727	940.3
0.1355	662.6	0.4256	1756.3	0.6749	1811.2	0.9238	588.2
0.1851	891.5	0.4679	1840.5	0.7294	1657.9	0.9782	174.6
0.2352	1108.6						
Chloroform(1)—benzene(2)							
0.0452	55.4	0.3590	357.1	0.6729	385.2	0.8870	185.1
0.0873	106.2	0.4122	383.7	0.7236	354.7	0.9105	151.9
0.1701	197.4	0.4902	407.4	0.7675	321.4	0.9319	116.4
0.2061	234.2	0.5584	415.2	0.8144	276.0	0.9547	79.5
0.2455	275.2	0.5620	413.8	0.8642	216.8	0.9770	40.6
0.3030	321.2	0.6191	404.7				

TABLE 3

Excess enthalpies of the acetonitrile(1)—chloroform(2)—acetone(3) system [a] at 25° C

$x'_2 = 0.2509$			$x'_2 = 0.4997$			$x'_2 = 0.7493$		
x_1	x_2	$-h^E$ (J mole^{-1})	x_1	x_2	$-h^E$ (J mole^{-1})	x_1	x_2	$-h^E$ (J mole^{-1})
0.0364	0.2418	1116.8	0.0291	0.4851	1612.6	0.0263	0.7296	1566.9
0.0626	0.2352	1075.0	0.0606	0.4694	1730.6	0.0639	0.7014	1537.9
0.1093	0.2235	1002.2	0.0949	0.4523	1643.5	0.1263	0.6546	1476.5
0.1554	0.2119	934.2	0.1343	0.4326	1544.7	0.1839	0.6114	1406.2
0.2202	0.1957	839.0	0.1839	0.4078	1423.1	0.2592	0.5550	1297.2
0.2804	0.1805	753.5	0.2451	0.3772	1279.1	0.3393	0.4950	1165.0
0.3173	0.1713	702.7	0.3113	0.3441	1129.0	0.3717	0.4707	1108.1
0.3610	0.1603	643.9	0.3813	0.3091	976.2	0.4131	0.4398	1032.0
0.4144	0.1469	573.6	0.4503	0.2747	833.0	0.4498	0.4122	963.3
0.4619	0.1350	513.5	0.5009	0.2494	732.8	0.5082	0.3685	851.2
0.5092	0.1231	455.5	0.5636	0.2180	615.1	0.5587	0.3307	753.4
0.5509	0.1127	406.2	0.6230	0.1882	509.4	0.6066	0.2948	660.0
0.6089	0.0981	340.7	0.6411	0.1793	479.5	0.6499	0.2623	576.7
0.6598	0.0854	286.9	0.6913	0.1542	398.1	0.6775	0.2414	525.9
0.7071	0.0735	239.2	0.7323	0.1337	334.8	0.7127	0.2151	461.0
0.7495	0.0629	198.4	0.7647	0.1176	286.6	0.7502	0.1870	392.6
0.7758	0.0562	173.5	0.7982	0.1009	238.9	0.7827	0.1627	334.3
0.8097	0.0477	143.5	0.8217	0.0891	206.6	0.8034	0.1472	298.2
0.8213	0.0448	133.5	0.8420	0.0790	179.8	0.8286	0.1284	255.4
						0.8502	0.1122	220.0

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

Experimental apparatus and results

The continuous dilution calorimeter described previously [9] was used to obtain excess enthalpies for binary and ternary mixtures. Table 2 lists binary excess enthalpy data for the acetonitrile—acetone, chloroform—acetone, and chloroform—benzene systems at 25°C. Tables 3 and 4 present ternary excess enthalpy data for the acetonitrile—chloroform—acetone and acetonitrile—chloroform—benzene systems at 25° C, respectively. Excess enthalpy data for other component binary systems for these two ternary systems have been measured at 25°C in our laboratory: acetonitrile—chloroform [10]; acetonitrile—benzene [11].

THEORY

Binary systems

In the acetonitrile (A = component 1)—nonassociating component (B = component 2) system, we assume two self-association reactions for acetoni-

TABLE 4

Excess enthalpies of the acetonitrile(1)—chloroform(2)—benzene(3) system [a] at 25°C

$x'_1 = 0.2505$			$x'_1 = 0.5003$			$x'_1 = 0.7489$		
x_1	x_2	$-h^E$ (J $mole^{-1}$)	x_1	x_2	$-h^E$ (J $mole^{-1}$)	x_1	x_2	$-h^E$ (J $mole^{-1}$)
0.2428	0.0310	−221.5	0.4841	0.0324	−353.1	0.7304	0.0247	−333.2
0.2318	0.0748	−127.0	0.4689	0.0627	−268.8	0.7111	0.0504	−261.4
0.2219	0.1144	−42.1	0.4541	0.0922	−188.5	0.6873	0.0823	−174.3
0.2109	0.1584	46.2	0.4365	0.1276	−94.4	0.6683	0.1077	−105.3
0.2030	0.1897	106.9	0.4171	0.1663	6.4	0.6406	0.1447	−5.3
0.1923	0.2325	178.2	0.3978	0.2048	99.4	0.6135	0.1808	88.6
0.1840	0.2658	234.2	0.3748	0.2509	202.9	0.5859	0.2177	180.8
0.1750	0.3015	289.3	0.3539	0.2926	289.1	0.5576	0.2555	270.3
0.1658	0.3381	340.3	0.3335	0.3333	365.7	0.5308	0.2912	350.5
0.1571	0.3728	382.8	0.3132	0.3739	434.2	0.5048	0.3259	423.4
0.1440	0.4252	435.7	0.2925	0.4153	493.7	0.4804	0.3585	486.9
0.1312	0.4764	474.1	0.2717	0.4570	542.8	0.4465	0.4038	564.7
0.1202	0.5204	496.4	0.2505	0.4993	580.4	0.4150	0.4459	624.9
0.1086	0.5665	509.5	0.2413	0.5176	592.6	0.3904	0.4788	661.7
0.0972	0.6120	510.5	0.2328	0.5346	602.4	0.3859	0.4847	670.3
0.0870	0.6527	500.9	0.2262	0.5479	609.0	0.3670	0.5100	691.9
0.0739	0.7049	473.0	0.2109	0.5784	619.0	0.3414	0.5441	715.9
0.0635	0.7466	438.8	0.1902	0.6199	621.0	0.3034	0.5948	734.5
0.0557	0.7778	406.4	0.1690	0.6621	608.3	0.2669	0.6436	730.5
0.0494	0.8029	375.5	0.1421	0.7160	571.9	0.2314	0.6910	704.3
			0.1224	0.7554	530.0	0.2018	0.7306	665.3
			0.1091	0.7820	494.8	0.1799	0.7598	627.4

[a] Ternary mixtures were obtained by mixing pure chloroform with $\{x'_1$acetonitrile + $(1-x'_1)$benzene$\}$.

trile molecules as suggested in previous papers [1,12]: head-to-head dimerization and head-to-tail chain association. Chemical equilibrium constants for these two reactions are defined in terms of mole fractions of chemical species in the solution.

$$A_1 + A_1 = A'_2, \qquad K_2 = x'_{A_2}/x^2_{A_1} \tag{1}$$

$$A_1 + A_i = A_{i+1}, \qquad K_A = x_{A_{i+1}}/x_{A_i}x_{A_1} \tag{2}$$

Acetonitrile and nonassociating component molecules are assumed to form a 1 : 1 complex as defined by

$$A_1 + B = A_1B, \qquad K_{AB} = x_{A_1B}/x_{A_1}x_{B_1} \tag{3}$$

Solution nonideality is described by the sum of chemical and physical contributions. The excess Gibbs free energy and the activity coefficients are given by

$$g^E = g^E_{chem} + g^E_{phys} \tag{4}$$

where g^{E}_{chem} based on the mole fraction model is [13]

$$g^{E}_{\text{chem}}/RT = x_1 \ln(x_{A_1}/x^{*}_{A_1}x_1) + x_2 \ln(x_{B_1}/x_2) \tag{5}$$

and g^{E}_{phys} is expressed by the NRTL equation [14].

$$g^{E}_{\text{phys}}/RT = x_1 x_2[\tau_{21}G_{21}/(x_1 + x_2 G_{21}) + \tau_{12}G_{12}/(x_2 + x_1 G_{12})] \tag{6}$$

where

$$\tau_{12} = (g_{12} - g_{22})/RT, \qquad \tau_{21} = (g_{21} - g_{11})/RT \tag{7}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}), \qquad G_{21} = \exp(-\alpha_{21}\tau_{21}) \tag{8}$$

Then, the activity coefficients are given by

$$(\ln\gamma_1)_{\text{chem}} = \ln(x_{A_1}/x^{*}_{A_1}x_1) \tag{9}$$

$$(\ln\gamma_2)_{\text{chem}} = \ln(x_{B_1}/x_2) \tag{10}$$

$$(\ln\gamma_1)_{\text{phys}} = x_2^2[\tau_{21}G_{21}^2/(x_1 + x_2 G_{21})^2 + \tau_{12}G_{12}/(x_2 + x_1 G_{12})^2] \tag{11}$$

$$(\ln\gamma_2)_{\text{phys}} = x_1^2[\tau_{12}G_{12}^2/(x_2 + x_1 G_{12})^2 + \tau_{21}G_{21}/(x_1 + x_2 G_{21})^2] \tag{12}$$

The monomer mole fractions, x_{A_1} and x_{B_1}, are numerically solved from the following equations [eqn. (13) or eqn. (14) and eqn. (16)].

$$x_1 = n_A/(n_A + n_B) = (2n'_{A_2} + \sum_{i=1}^{\infty} i n_{A_i} + n_{A_1B_1})/(2n'_{A_2} + \sum_{i=1}^{\infty} i n_{A_i} + 2n_{A_1B_1} + n_{B_1})$$

$$= [2K_2 x_{A_1}^2 + x_{A_1}/(1 - K_A x_{A_1})^2 + K_{AB} x_{A_1} x_{B_1}]/S \tag{13}$$

$$x_2 = n_B/(n_A + n_B) = (n_{A_1B_1} + n_{B_1})/(2n'_{A_2} + \sum_{i=1}^{\infty} i n_{A_i} + 2n_{A_1B_1} + n_{B_1})$$

$$= (K_{AB} x_{A_1} x_{B_1} + x_{B_1})/S \tag{14}$$

where the stoichiometric sum S is given by

$$S = 2K_2 x_{A_1}^2 + x_{A_1}/(1 - K_A x_{A_1})^2 + 2K_{AB} x_{A_1} x_{B_1} + x_{B_1} \tag{15}$$

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

$$x'_{A_2} + \sum_{i=1}^{\infty} x_{A_i} + x_{A_1B_1} + x_{B_1} = K_2 x_{A_1}^2 + x_{A_1}/(1 - K_A x_{A_1})$$

$$+ K_{AB} x_{A_1} x_{B_1} + x_{B_1} = 1 \tag{16}$$

The monomer mole fraction acetonitrile $x^{*}_{A_1}$ in the pure state is obtained from

$$K_2 x^{*2}_{A_1} + x^{*}_{A_1}/(1 - K_A x^{*}_{A_1}) = 1 \tag{17}$$

The excess enthalpy is also expressed by the sum of chemical and physical terms.

$$h^{E} = h^{E}_{\text{chem}} + h^{E}_{\text{phys}} \tag{18}$$

The definition of excess enthalpy gives

$$h_{\text{chem}}^{E} = h_f - x_1 h_f^* \tag{19}$$

The total amount of enthalpy of all chemical species is

$$\begin{aligned} h_f &= [h_2 n'_{A_2} + h_A \sum_{i=1}^{\infty} (i-1) n_{A_i} + h_{AB} n_{A_1B_1}]/(n_A + n_B) \\ &= [h_2 K_2 x_{A_1}^2 + h_A K_A x_{A_1}^2/(1 - K_A x_{A_1})^2 + h_{AB} K_{AB} x_{A_1} x_{B_1}]/S \end{aligned} \tag{20}$$

At the pure liquid condition h_f reduces to h_f^*.

$$h_f^* = [h_2 K_2 x_{A_1}^{*2} + h_A K_A x_{A_1}^{*2}/(1 - K_A x_{A_1}^*)^2]/S^* \tag{21}$$

$$S^* = 2K_2 x_{A_1}^{*2} + x_{A_1}^*/(1 - K_A x_{A_1}^*)^2 \tag{22}$$

h_{phys}^E is obtained by applying the Gibbs—Helmholtz equation to g_{phys}^E.

$$\begin{aligned} h_{\text{phys}}^E &= \frac{\partial (g_{\text{phys}}^E/T)}{\partial (1/T)} = R x_1 x_2 \left(\frac{\tau'_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau'_{12} G_{12}}{x_2 + x_1 G_{12}} \right. \\ &\quad \left. - \alpha_{12} \left[\frac{x_1 \tau_{21} G_{21} \tau'_{21}}{(x_1 + x_2 G_{21})^2} + \frac{x_2 \tau_{12} G_{12} \tau'_{12}}{(x_2 + x_1 G_{12})^2} \right] \right) \end{aligned} \tag{23}$$

where $\tau'_{21} = \partial \tau_{21}/\partial (1/T)$ and $\tau'_{12} = \partial \tau_{12}/\partial (1/T)$.

We assume the energy parameters to be linearly dependent on temperature.

$$g_{21} - g_{11} = C_1 + D_1(T - 273.15), \quad g_{12} - g_{22} = C_2 + D_2(T - 273.15) \tag{24}$$

For the chloroform (B = component 1)—acetone (C = component 2) system the ideal associated solution model of the type $B + C + BC + B_2C$ is verified [4,5].

Two complex-forming reactions are shown as follows.

$$B + C = B_1C_1, \quad K_{BC} = x_{B_1C_1}/x_{B_1} x_{C_1} \tag{25}$$

$$2B + C = B_2C_1, \quad K_{B_2C} = x_{B_2C_1}/x_{B_1}^2 x_{C_1} \tag{26}$$

The excess Gibbs free energy is given by

$$\begin{aligned} g^E/RT &= x_1 \ln(x_{B_1}/x_1) + x_2 \ln(x_{C_1}/x_2) \\ &= x_1 \ln \frac{x_{B_1}}{x_1} + x_2 \ln \frac{1 - x_{B_1}}{(1 + K_{BC} x_{B_1} + K_{B_2C} x_{B_1}^2) x_2} \end{aligned} \tag{27}$$

The true mole fractions of the species B, BC, B_2C, and C are interrelated by the following equations.

$$x_1 = \frac{x_{B_1} + x_{B_1C_1} + 2x_{B_2C_1}}{x_{B_1} + 2x_{B_1C_1} + 3x_{B_2C_1} + x_{C_1}} = \frac{(1 + K_{BC}) x_{B_1} + K_{B_2C} x_{B_1}^2 (2 - x_{B_1})}{1 + K_{BC} x_{B_1}(2 - x_{B_1}) + K_{B_2C} x_{B_1}^2 (3 - 2x_{B_1})} \tag{28}$$

$$x_{B_1} + x_{B_1C_1} + x_{B_2C_1} + x_{C_1} = x_{B_1} + K_{BC} x_{B_1} x_{C_1} + K_{B_2C} x_{B_1}^2 x_{C_1} + x_{C_1} = 1 \tag{29}$$

For a given x_1, the monomer mole fractions, x_{B_1} and x_{C_1} are obtained from eqns. (28) and (29).

The excess enthalpy is expressed by

$$h^E = (h_{BC} n_{B_1C_1} + h_{B_2C} n_{B_2C_1})/(n_B + n_C) = x_{B_1} x_{C_1} (h_{BC} K_{BC} + h_{B_2C} K_{B_2C} x_{B_1})/S \tag{30}$$

where the stoichiometric sum S is

$$S = x_{B_1} + 2x_{B_1C_1} + 3x_{B_2C_1} + x_{C_1} = x_{B_1} + 2K_{BC} x_{B_1} x_{C_1} + 3K_{B_2C} x_{B_1}^2 x_{C_1} + x_{C_1} \tag{31}$$

h_{BC} and h_{B_2C} are the enthalpies of formation of BC and B_2C complexes, respectively. According to the assumption for this system, g^E_{phys} and h^E_{phys} vanish.

In the chloroform—benzene system, we will consider the B + C + BC type of association except for a physical interaction term.

Ternary systems

In the acetonitrile (A = component 1)—chloroform (B = component 2)—acetone (C = component 3) system, we assume that acetonitrile self-associates according to eqns. (1) and (2) and forms binary complexes with chloroform and acetone (AB and AC), and chloroform and acetone molecules form two kinds of complexes BC and B_2C. g^E_{chem} and g^E_{phys} for the system are given as follows.

$$g^E_{chem} = RT[x_1 \ln(x_{A_1}/x^*_{A_1} x_1) + x_2 \ln(x_{B_1}/x_2) + x_3 \ln(x_{C_1}/x_3)] \tag{32}$$

$$g^E_{phys} = RT \sum_{i=1}^{3} x_i \frac{\sum_{j=1}^{3} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{3} G_{ki} x_k} \tag{33}$$

where

$$\tau_{ji} = (g_{ji} - g_{ii})/RT \tag{34}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{35}$$

The mole numbers of acetonitrile, chloroform, and acetone are related to the sum of mole numbers of chemical species.

$$n_A = 2n'_{A_2} + \sum_{i=1}^{\infty} i n_{A_i} + n_{A_1B_1} + n_{A_1C_1} \tag{36}$$

$$n_B = n_{A_1B_1} + n_{B_1C_1} + 2n_{B_2C_1} + n_{B_1} \tag{37}$$

$$n_C = n_{A_1C_1} + n_{B_1C_1} + n_{B_2C_1} + n_{C_1} \tag{38}$$

The nominal mole fractions are given by

$$x_1 = n_A/(n_A + n_B + n_C) = [2K_2 x_{A_1}^2 + x_{A_1}/(1 - K_A x_{A_1})^2 + K_{AB} x_{A_1} x_{B_1} + K_{AC} x_{A_1} x_{C_1}]/S \tag{39}$$

$$x_2 = n_B/(n_A + n_B + n_C) = [K_{AB}x_{A_1}x_{B_1} + K_{BC}x_{B_1}x_{C_1} + 2K_{B_2C}x^2_{B_1}x_{C_1} + x_{B_1}]/S \tag{40}$$

$$x_3 = n_C/(n_A + n_B + n_C) = [K_{AC}x_{A_1}x_{C_1} + K_{BC}x_{B_1}x_{C_1} + K_{B_2C}x^2_{B_1}x_{C_1} + x_{C_1}]/S \tag{41}$$

where the stoichiometric sum S is expressed by

$$S = 2K_2x^2_{A_1} + x_{A_1}/(1 - K_Ax_{A_1})^2 + 2K_{AB}x_{A_1}x_{B_1} + 2K_{AC}x_{A_1}x_{C_1}$$
$$+ 2K_{BC}x_{B_1}x_{C_1} + 3K_{B_2C}x^2_{B_1}x_{C_1} + x_{B_1} + x_{C_1} \ . \tag{42}$$

The sum of mole fractions of all chemical species should be unity.

$$x'_{A_2} + \sum_{i=1}^{\infty} x_{A_i} + x_{A_1B_1} + x_{A_1C_1} + x_{B_1C_1} + x_{B_2C_1} + x_{B_1} + x_{C_1}$$
$$= K_2x^2_{A_1} + x_{A_1}/(1 - K_Ax_{A_1}) + K_{AB}x_{A_1}x_{B_1} + K_{AC}x_{A_1}x_{C_1} + K_{BC}x_{B_1}x_{C_1}$$
$$+ K_{B_2C}x^2_{B_1}x_{C_1} + x_{B_1} + x_{C_1} = 1. \tag{43}$$

The monomer mole fractions are obtained by solving simultaneously eqns. (39), (40) [or eqn. (41)], and (43).

The total enthalpy of complex formation obtained by mixing acetonitrile, chloroform, and acetone is given by

$$h_f = [h_2n'_{A_2} + h_A\sum_{i=1}^{\infty}(i-1)n_{A_i} + h_{AB}n_{A_1B_1} + h_{AC}n_{A_1C_1}$$
$$+ h_{BC}n_{B_1C_1} + h_{B_2C}n_{B_2C_1}]/(n_A + n_B + n_C) \tag{44}$$

$$h^*_f = [h_2n'^*_{A_2} + h_A\sum_{i=1}^{\infty}(i-1)n^*_{A_i}]/n^*_A \tag{45}$$

Then, h^E_{chem} is given by

$$h^E_{chem} = h_f - x_1h^*_f$$
$$= [h_2K_2x^2_{A_1} + h_AK_Ax^2_{A_1}/(1 - K_Ax_{A_1})^2 + h_{AB}K_{AB}x_{A_1}x_{B_1}$$
$$+ h_{AC}K_{AC}x_{A_1}x_{C_1} + h_{BC}K_{BC}x_{B_1}x_{C_1} + h_{B_2C}K_{B_2C}x^2_{B_1}x_{C_1}]/S$$
$$- x_1[h_2K_2x^{*2}_{A_1} + h_AK_Ax^{*2}_{A_1}/(1 - K_Ax^*_{A_1})^2]/S^* \tag{46}$$

where S and S^* are expressed by eqns. (42) and (22), respectively. h^E_{phys} is obtained by differentiation of g^E_{phys} with respect to temperature.

$$h^E_{phys} = R\sum_{i=1}^{3}x_i\left[\frac{\sum_{j=1}^{3}x_j\frac{\partial(\tau_{ji}G_{ji})}{\partial(1/T)}}{\sum_{k=1}^{3}G_{ki}x_k} - \frac{\sum_{j=1}^{3}\tau_{ji}G_{ji}x_j\sum_{k=1}^{3}x_k\frac{\partial G_{ki}}{\partial(1/T)}}{\left(\sum_{k=1}^{3}G_{ki}x_k\right)^2}\right] \tag{47}$$

The energy parameters are assumed to have a linear temperature dependence.

$$g_{ji} - g_{ii} = C_i + D_i(T - 273.15). \tag{48}$$

For the acetonitrile—chloroform—benzene system we put $K_{B_2C} = 0$, because chloroform and benzene molecules form only a 1 : 1 complex. In the acetonitrile—benzene—carbon tetrachloride system $K_{AC} = K_{B_2C} = 0$. In the acetonitrile—acetone—methyl acetate system $K_{B_2C} = K_{BC} = 0$.

ANALYSIS OF RESULTS AND DISCUSSION

The chemical equilibrium constants and enthalpies of complex formation due to self-association of acetonitrile are $K_2 = 8.35$, $K_A = 2.1$ at 45°C, $h_2 = -8.9$ kJ mole^{-1} and $h_A = -6.7$ kJ mole^{-1} [1,12]. The van't Hoff equation fixes the temperature dependence of the equilibrium constant. The enthalpy of complex formation is assumed independent of temperature.

The enthalpies of complex formation of the acetonitrile—nonassociating component systems were estimated by taking the difference between the value of h_A of acetonitrile and the limiting value of h^E/x_1x_2 for the acetonitrile—nonassociating systems at infinite dilution of acetonitrile: —5.2 kJ mole^{-1} for acetonitrile—benzene; —11.0 kJ mole^{-1} for acetonitrile—chloroform; —7.5 kJ mole^{-1} for acetonitrile—acetone. The enthalpy of complex formation between chloroform and benzene molecules was estimated as —4 kJ mole^{-1} from the difference between the limiting value of h^E/x_1x_2 for the chloroform—cyclohexane system [15] and that for the chloroform—benzene system at infinite dilution of chloroform.

Lin and Tsay [3] obtained the equilibrium constants of complex formation for the acetonitrile—chloroform and chloroform—benzene systems at 26°C and their values are used in this work, but that for the acetonitrile—chloroform system was extrapolated to 40°C. In a previous paper [1], we neglected complex formation in the benzene—carbon tetrachloride system. However, in the present work, we assume a 1 : 1 complex between benzene and carbon tetrachloride molecules in accordance with the analysis of McGlashan et al. [16] for this system and use the equilibrium constant and enthalpy of complex formation given by McGlashan et al. [16]. The equilibrium constants of the chloroform—acetone system at 25°C are the same as given by Kearns [4] and the enthalpies of complex formation were fitted to the experimental results by the method of least squares. Table 5 compares the enthalpies of complex formation with the literature values. Table 6 lists

TABLE 5

Enthalpies of formation of chloroform(A)—acetone(B) complexes at 25°C

$h_{A_1B_1}$ (kJ mole^{-1})	$h_{A_2B_1}$ (kJ mole^{-1})	Ref.
—10.1	—13.8	4
—10.3	—13.0	17
—10.1	—13.0	18
—10.3	—20.1	5
—10.5	—13.2	This work

TABLE 6

Equilibrium constants and enthalpies of complex formation between unlike molecules

System	t (°C)	K	h (kJ mole^{-1})
Acetonitrile—acetone	50	2.5	−7.5
Acetonitrile—benzene	45	0.2	−5.2
Acetonitrile—chloroform	40	2.8	−11.0
Acetonitrile—methyl acetate	50	2.3	
Benzene—carbon tetrachloride	25	0.215	−5.28
Chloroform—acetone			
1 : 1 complex	25	0.967	−10.5
2 : 1 complex	25	1.117	−13.2
Chloroform—benzene	26	0.36	−4.0

the equilibrium constants and enthalpies of complex formation for binary systems.

Calculated results of vapor—liquid equilibria and excess Gibbs free energies, and excess enthalpies for binary systems are presented in Tables 7 and 8, respectively. We have used the nonrandomness parameter $\alpha_{ji} (= \alpha_{ij}) = 0.3$ for

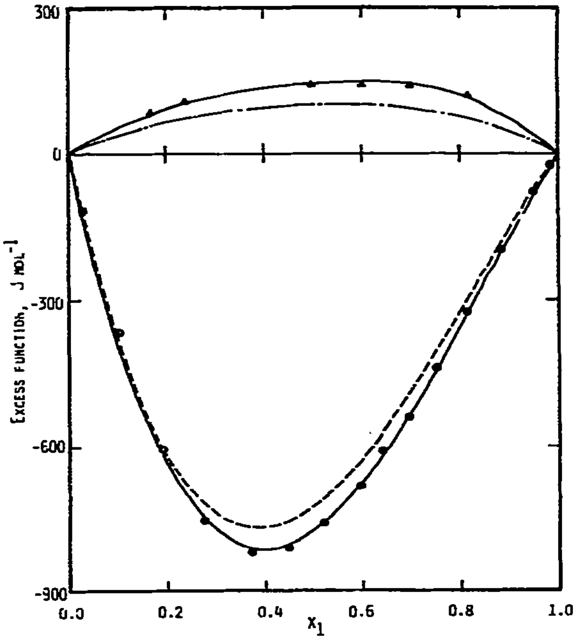


Fig. 1. Representation of excess functions for the acetonitrile(1)—chloroform (2) system. Experimental: ▲, g^E at 40°C [20]; ●, h^E at 25°C [10]. Calculated: ———; g^E_{chem}, · — · — ·; h^E_{chem}, - - - - - -.

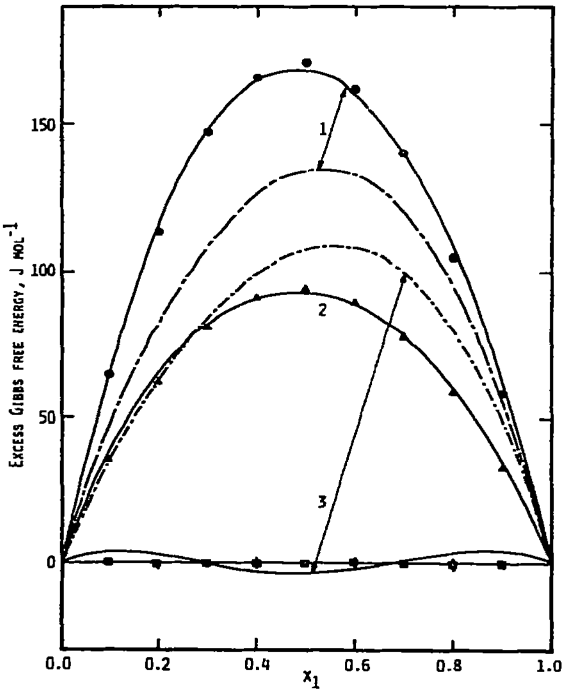


Fig. 2. Representation of excess Gibbs free energies for three systems at 50°C. Experimental [7]: 1, acetonitrile(1)—methyl acetate(2), ●; 2, acetone(1)—methyl acetate(2), ▲; 3, acetonitrile(1)—acetone(2), ■. Calculated: ———; g^E_{chem}, · — · — ·.

TABLE 7

Correlation of binary excess Gibbs free energies and vapor—liquid equilibria

System(1—2)	Temp. (°C)	No. of data points	Parameters (J mole^{-1})			Absolute arith. mean dev.			Ref.
			$g_{21}-g_{11}$	$g_{12}-g_{22}$	α_{12}	Δg^E (J mole^{-1})	Vapor mole fraction (×1000)	Press. (mm Hg)	
Acetone—methyl acetate	50	9	645.69	−243.61	0.3	0.2 [a]			7
Acetonitrile—acetone	50	9	3999.02	−3047.70	0.3	2.5 [a]			7
Acetonitrile—benzene [b]	45	11	−1561.17	3067.38	0.3		2.9	1.2	19
Acetonitrile—chloroform	40	6	−1526.07	2232.98	0.3	3.3			20
Acetonitrile—methyl acetate	50	9	2618.74	−1899.03	0.3	1.9 [a]			7
Acetonitrile—carbon tetrachloride [b]	45	13	1988.32	1135.48	0.3		4.8	1.7	21
Benzene—carbon tetrachloride	45	9	371.98	428.34	0.3	0.3 [c]			22

[a] Deviation from smoothed experimental g^E data, which were obtained at equally spaced mole fractions from the Margules equation whose constants were described in ref. 7.

[b] Calculated results were taken from ref. 1.

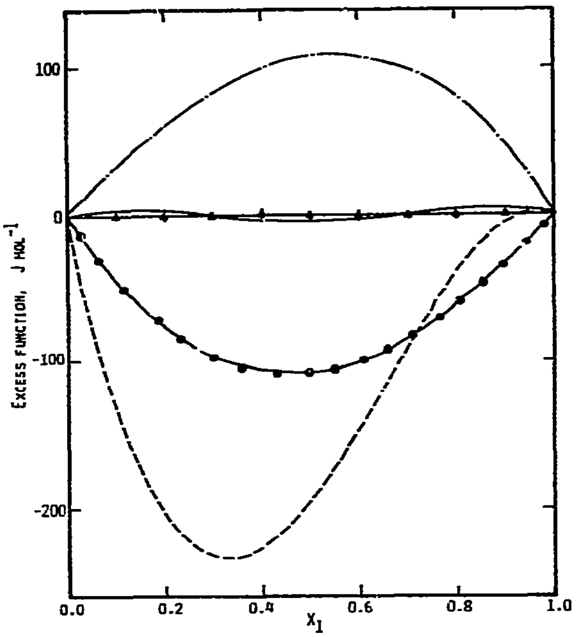
[c] Deviation from smoothed experimental g^E data, which were obtained at equally spaced mole fractions from the Redlich—Kister equation whose constants were described in ref. 22.

TABLE 8

Correlation of binary excess enthalpies

System(1–2)	Temp. (°C)	No. of data points	Parameters					Absolute arith. mean dev. (J mole^{-1})	Ref.
			C_1 (J mole^{-1})	C_2 (J mole^{-1})	D_1 (J mole^{-1} K^{-1})	D_2 (J mole^{-1} K^{-1})	α_{12}		
Acetonitrile–acetone	25	19	992.86	1013.59	8.6843	15.6340	0.3	1.2	This work
Acetonitrile–benzene	25	16	3320.51	−181.94	21.6210	−7.8097	0.3	1.3	11
	45	16	3519.78	785.04	19.3932	−3.3768	0.3	2.3	19
Acetonitrile–chloroform	25	15	3424.18	−3103.38	4.5703	−7.4791	0.3	6.8	10
Acetonitrile–carbon tetrachloride	25	15	8786.35	−199.35	25.7713	−6.8688	0.3	1.3	11
	45	9 [a]	4526.95	8287.08	0.5440	23.3628	0.3	3.2	23
Benzene–carbon tetrachloride	25	16	−138.97	4074.74	−5.7676	15.2612	0.3	0.3	11
	45	5	540.63	4320.64	−3.0901	15.2925	0.3	4.6	24
Chloroform–acetone	25	21	0	0	0	0	0.3	9.5	This work
Chloroform–benzene	25	22	377.52	1984.21	−0.3981	12.1007	0.3	1.6	This work

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



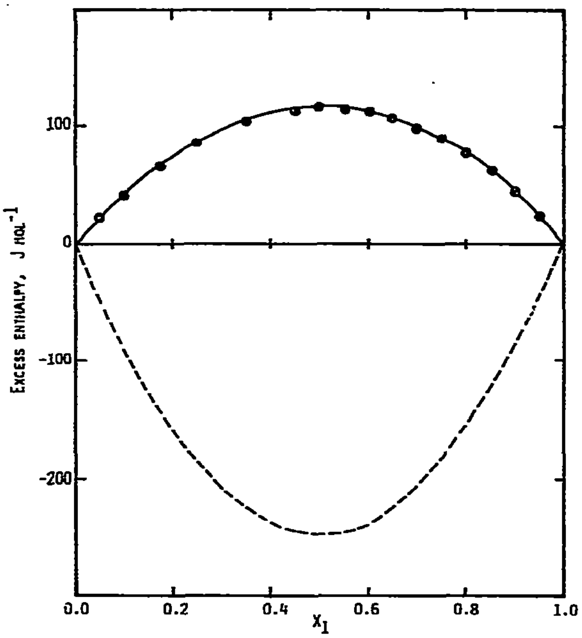


Fig. 3. Representation of excess functions for the acetonitrile(1)—acetone(2) system. Experimental: ▲, g^E at 50°C; ●, h^E at 25°C (this work). Calculated: ———; g^E_{chem}, — · — ·; h^E_{chem}, - - - - - -.

Fig. 4. Representation of excess enthalpies for the benzene(1)—carbon tetrachloride(2) system at 25°C. Experimental: ●, h^E (this work). Calculated: ———; h^E_{chem}, - - - - - -.

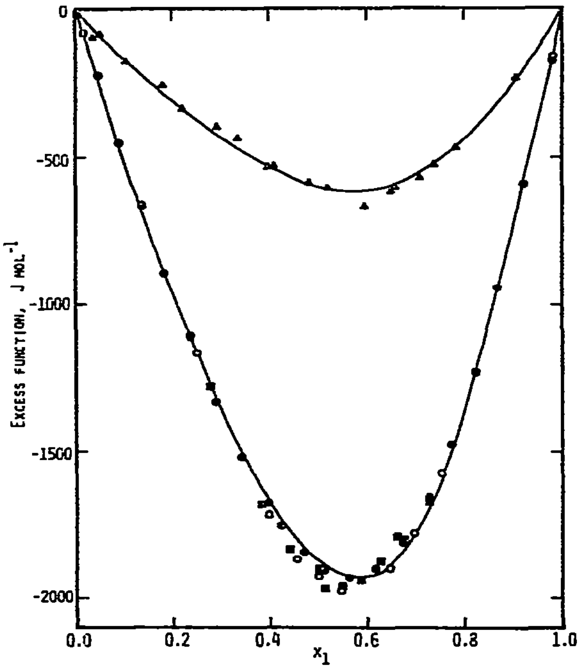


Fig. 5. Representation of excess functions for the chloroform(1)—acetone(2) system at 25°C. Experimental: △, g^E [4]; ▲, g^E [5]; ■, h^E [17]; ○, h^E [25]; ●, h^E (this work). Calculated: ———.

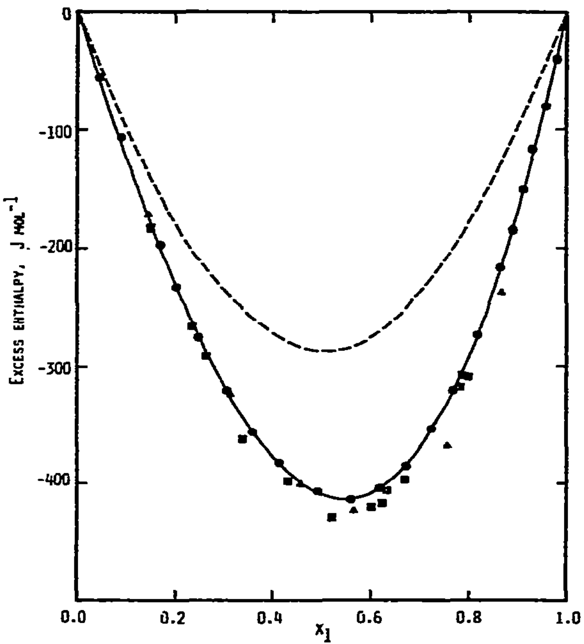


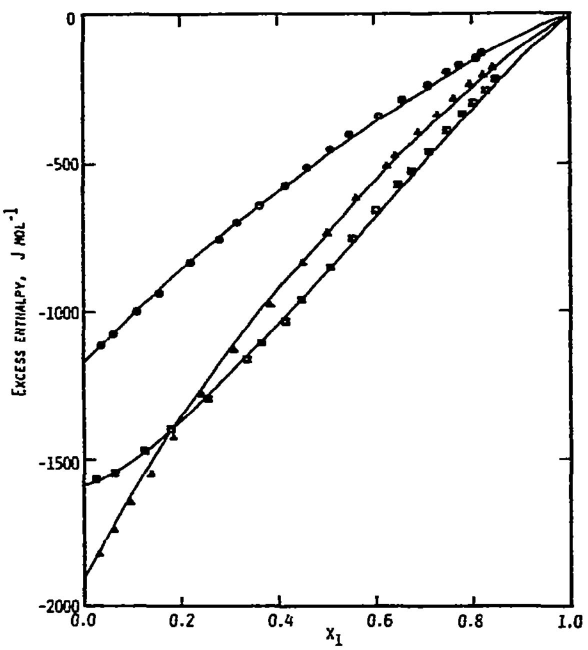
Fig. 6. Representation of excess enthalpies for the chloroform(1)—benzene(2) system at 25°C. Experimental: ▲, h^E [25]; ■, h^E [26]; ●, h^E (this work). Calculated: ———; h^E_{chem}, - - - - - -.

TABLE 9

Predicted results of ternary excess Gibbs free energies and excess enthalpies

System	Temp. (°C)	No. of data points	Data type	Absolute arith. mean dev. (J mole^{-1})	Root-mean square deviation (J mole^{-1})	Ref.
Acetonitrile—acetone—methyl acetate	50	36 [a]	g^E	5.8	6.6	7
Acetonitrile—benzene—carbon tetrachloride	25	54	h^E	19.8	24.0	11
	45	26	h^E	23.2	28.5	24
	45	62	g^E	16.7	20.4	22
Acetonitrile—chloroform—acetone	25	58	h^E	14.1	15.4	This work
Acetonitrile—chloroform—benzene	25	64	h^E	18.2	22.1	This work

[a] Smoothed experimental data, which were obtained at equally spaced mole fractions from a correlating equation whose constants were described in ref. 7.



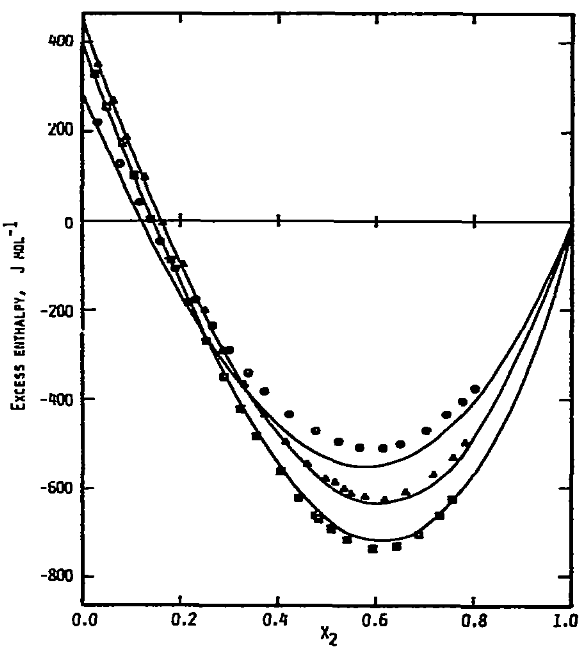


Fig. 7. Prediction of ternary excess enthalpies for the acetonitrile(1)—chloroform(2)—acetone(3) system at 25°C. Experimental (this work): ●, $x_2' = 0.2509$; ▲, $x_2' = 0.4997$; ■, $x_2' = 0.7493$. Calculated, ———. The ternary mixtures used in this work were obtained by mixing pure acetonitrile with $\{x_2'\text{chloroform} + (1 - x_2')\text{acetone}\}$.

Fig. 8. Prediction of ternary excess enthalpies for the acetonitrile(1)—chloroform(2)—benzene(3) system at 25°C. Experimental (this work): ●, $x_1' = 0.2505$; ▲, $x_1' = 0.5003$; ■, $x_1' = 0.7489$. Calculated, ———. The ternary mixtures used in this work were obtained by mixing pure chloroform with $\{x_1'\text{acetonitrile} + (1 - x_1')\text{benzene}\}$.

all binary systems studied here. The simplex method [27] was used to obtain C_i and D_i. Figures 1—6 show how well the association theory reproduces the binary experimental excess functions, illustrating the magnitude of the chemical contribution to the excess functions.

Prediction of the ternary excess functions was attempted for four systems; the results are shown in Table 9. Figures 7 and 8 compare experimental and predicted values for the excess enthalpies at 25°C for the three runs of the acetonitrile—chloroform—acetone and acetonitrile—chloroform—benzene systems, respectively. In conclusion, the association theory developed previously by Nagata and Tamura has been shown to be satisfactory for the prediction of excess functions of ternary liquid mixtures containing acetonitrile and nonassociating components from binary parameters alone.

REFERENCES

1 I. Nagata and K. Tamura, Thermochim. Acta, 44 (1981) 157.
2 P.J. Berkeley, Jr. and M.W. Hanna, J. Phys. Chem., 67 (1963) 846.
3 W.-C. Lin and S.-J. Tsay, J. Phys. Chem., 74 (1970) 1037.
4 E.R. Kearns, J. Phys. Chem., 65 (1961) 314.
5 A. Apelblat, A. Tamir and M. Wagner, Fluid Phase Equilibria, 4 (1980) 229.

6 M.L. McGlashan and R.P. Rastogi, Trans. Faraday Soc., 54 (1958) 496.
7 D.P. DiElsi, R.B. Patel, M.M. Abbott and H.C. Van Ness, J. Chem. Eng. Data, 23 (1978) 242.
8 J.A. Riddick and W.B. Bunger, Organic Solvents, Wiley-Interscience, New York, 3rd edn., 1970.
9 I. Nagata and K. Kazuma, J. Chem. Eng. Data, 22 (1977) 79.
10 I. Nagata and Y. Kawamura, Fluid Phase Equilibria, 3 (1979) 1.
11 I. Nagata, K. Tamura, Y. Kawamura and S. Tokuriki, J. Chem. Thermodyn., submitted for publication.
12 J.W. Lorimer and D.E. Jones, Can. J. Chem., 55 (1977) 2980.
13 I. Prigogine and R. Defay, Chemical Thermodynamics, Wiley, New York, 1954.
14 H. Renon and J.M. Prausnitz, AIChE J., 14 (1968) 135.
15 I. Nagata, Y. Kawamura, Y. Ogasawara and S. Tokuriki, J. Chem. Thermodyn., 12 (1980) 223.
16 M.L. McGlashan, D. Stubley and H. Watta, J. Chem. Soc. A, (1969) 673.
17 K.W. Morcom and D.N. Traverse, Trans. Faraday Soc., 61 (1965) 230.
18 T. Matsui, L.G. Hepler and D.V. Fenby, J. Phys. Chem., 77 (1973) 2397.
19 D.A. Palmer and B.D. Smith, J. Chem. Eng. Data, 17 (1972) 71.
20 A. Kreglewski, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 13 (1965) 723.
21 I. Brown and F. Smith, Aust. J. Chem., 7 (1954) 269.
22 H.A. Clarke and R.W. Missen, J. Chem. Eng. Data, 19 (1974) 343.
23 I. Brown and W. Fock, Aust. J. Chem., 9 (1956) 180.
24 T.R. Lien and R.W. Missen, J. Chem. Eng. Data, 19 (1974) 84.
25 H. Hirobe, J. Fac. Sci. Univ. Tokyo, 1 (1926) 155.
26 R.P. Rastogi, J. Nath and R.R. Misra, J. Chem. Thermodyn., 3 (1971) 307.
27 J.A. Nelder and R. Mead, Comput. J., 7 (1965) 308.