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Thermodynamics of associated solutions. Prediction and correlation of the ternary P–x data of systems including two alkanoic alcohols and one aliphatic hydrocarbon

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Abstract

The ability of the UNIQUAC associated-solution model is tested in the prediction and correlation of the two sets of experimental P–x data for methanol + 2-butanol + n-pentane and ethanol + i-butanol + n-heptane at 30°C by use of the binary parameters and additional ternary parameters.

LIST OF SYMBOLS

A, B, C	alcohols and saturated hydrocarbon
a_{IJ}	binary interaction energy parameter for I–J pair
C_{A_i}	molar concentration of $A_i$mer
F_1, F_2	objective functions as defined by eqns. (20) and (22)
g^E	excess molar Gibbs energy
h_A, h_B	enthalpies of hydrogen bond formation of alcohols A and B
h_{AB}	enthalpy of hydrogen bond formation between alcohols A and B
K_A, K_B	association constants of alcohols A and B
K_{AB}	multisolvation constant between $i$mers of alcohols A and B
P	total pressure
q_I	molecular geometric-area parameter of pure component I
R	universal gas constant
r_I	molecular geometric-volume parameter of pure component I
$\bar{S}_A$, $\bar{S}_B$	sums as defined by eqns. (11) and (12)
S_A, S_B	sums as defined by eqns. (13) and (14)
T	absolute temperature

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V	true molar volume of alcohol mixture
V_A^0, V_B^0	true molar volumes of pure alcohols A and B
x_I	liquid-phase mole fraction of component I
y	vapour-phase mole fraction
Z	lattice coordination number, here set as 10

Greek letters

γ_I	activity coefficient of component I
θ_I	area fraction of component I
σ_P, σ_T, σ_X	standard deviations in pressure, temperature and liquid-phase mole fraction
τ_{IJ}, τ_{IJK}	binary and ternary parameters
ϕ_I	segment fraction of component I
ϕ_{I_1}	monomeric segment fraction of component I
$\phi_{A_1}^0$, $\phi_{B_1}^0$	monomeric segment fractions of pure alcohols A and B

Subscripts

A, B, C	alcohols and saturated hydrocarbon
A_1, B_1, C_1	monomers of components A, B and C
A_i, B_i	*i*mers of alcohols A and B
A_iB_j	complex containing *i* molecules of alcohols A and *j* molecules of alcohol B
calc	calculated
exp	experimental
I, J, K	components I, J and K
i, *j*, *k*, *l*	*i*, *j*, *k* and *l*mers of alcohols or indices

INTRODUCTION

Any solution models must be tested by using a variety of good experimental binary and ternary physico-chemical properties. Alcohols are known to form hydrogen bonded *i*mers. The UNIQUAC associated-solution model which accounts for the association of alcohol molecules has been developed to analyse vapour–liquid and liquid–liquid equilibria and excess enthalpies of binary and ternary mixtures of one or two alcohols with non-associating components [1–12]. The model has not been applied for a study of vapour–liquid equilibrium for ternary systems in which two of the components are associating species and the other one is a saturated hydrocarbon because of the lack of such experimental data. Recently total pressure versus liquid-phase composition data were reported for *n*-pentane + methanol + 2-butanol and ethanol + *n*-heptane + *i*-butanol and each of their constituting binary systems at 30°C [13, 14]. These experimental data are useful for the testing of the UNIQUAC associated-solution model which takes into account the cross-association of the two alcohols.

DATA ANALYSIS

We summarize the UNIQUAC associated-solution model for a ternary mixture including two alcohols (A and B) and one saturated hydrocarbon (C). We assume that two alcohols associate linearly and the resulting pure polymers form copolymers by multisolvation, and that the equilibrium constants K_A, K_B and K_{AB} are independent of the degree of association and solvation.

$$K_A = \frac{C_{A_{i+1}}}{C_{A_i} C_{A_1} r_A} = \frac{\phi_{A_{i+1}}}{\phi_{A_i} \phi_{A_1}} \frac{i}{i+1} \qquad \text{for } A_i + A_1 = A_{i+1}$$

$$= K_A^* \exp\left[-\frac{h_A}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right] \tag{1}$$

$$K_B = \frac{C_{B_{i+1}}}{C_{B_i} C_{B_1} r_B} = \frac{\phi_{B_{i+1}}}{\phi_{B_i} \phi_{B_1}} \frac{1}{i+1} \qquad \text{for } B_i + B_1 = B_{i+1}$$

$$= K_B^* \exp\left[-\frac{h_B}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right] \tag{2}$$

$$K_{AB} = \frac{C_{A_iB_j}}{C_{A_i} C_{B_j} r_A r_B} = \frac{\phi_{A_iB_j}}{\phi_{A_i} \phi_{B_j}} \frac{r_{A_i} r_{B_j}}{r_{A_iB_j} r_A r_B} \qquad \text{for } A_i + B_j = A_iB_j$$

$$= \frac{C_{A_iB_jA_k}}{C_{A_iB_j} C_{A_k} r_A r_B} = \frac{\phi_{A_iB_jA_k}}{\phi_{A_iB_j} \phi_{A_k}} \frac{r_{A_iB_j} r_{A_k}}{r_{A_iB_jA_k} r_A r_B} \qquad \text{for } A_iB_j + A_k = A_iB_jA_k$$

$$= \frac{C_{A_iB_jA_kB_1}}{C_{A_iB_jA_k} C_{B_1} r_A r_B} = \frac{\phi_{A_iB_jA_kB_1}}{\phi_{A_iB_jA_k} \phi_{B_1}} \frac{r_{A_iB_jA_k} r_{B_1}}{r_{A_iB_jA_kB_1} r_A r_B} \qquad \text{for } A_iB_jA_k + B_1 = A_iB_jA_kB_1$$

$$= K_{AB}^* \exp\left[-\frac{h_{AB}}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right] \tag{3}$$

Similarly, B_iA_j, $B_iA_jB_k$, $B_iA_jB_kA_1, \ldots$, are formed. Here, C_{A_i}, C_{B_j} and $C_{A_iB_j}$ are the molar concentrations of A_i, B_j and A_iB_j; r_{A_i}, r_{B_j} and $r_{A_iB_j}$ are the molecular geometric-volume parameters of linear segments A_i, B_j and A_iB_j ($r_{A_i} = ir_A$, $r_{B_j} = jr_B$ and $r_{A_iB_j} = ir_A + jr_B$ are assumed) and h_A, h_B and h_{AB} are the molar enthalpies of hydrogen bonds in the pure polymers and copolymers.

The activity coefficients of the components A and C of the ternary mixture are given by

$$\ln \gamma_A = \ln\left(\frac{\phi_{A_1}}{\phi_{A_1}^0 x_A} \right) + \frac{r_A}{V_A^0} - \frac{r_A}{\mathrm{V}} - \left(\frac{Z}{2} \right) q_A \left(\ln \frac{\phi_A}{\theta_A} + 1 - \frac{\phi_A}{\theta_A} \right)$$

$$+ q_A \left[1 - \ln\left(\sum_J \theta_A \tau_{JA} \right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}} \right] \tag{4}$$

$$\ln \gamma_{\mathrm{C}} = \ln\left(\frac{\phi_{\mathrm{C}_1}}{x_{\mathrm{C}}}\right) + 1 - \frac{r_{\mathrm{C}}}{\mathrm{V}} - \left(\frac{Z}{2}\right) q_{\mathrm{C}}\left(\ln\frac{\phi_{\mathrm{C}}}{\theta_{\mathrm{C}}} + 1 - \frac{\phi_{\mathrm{C}}}{\theta_{\mathrm{C}}}\right) + q_{\mathrm{C}}\left[1 - \ln\left(\sum_{\mathrm{J}} \theta_{\mathrm{C}} \tau_{\mathrm{JC}}\right) - \sum_{\mathrm{J}} \frac{\theta_{\mathrm{J}} \tau_{\mathrm{CJ}}}{\sum_{\mathrm{K}} \theta_{\mathrm{K}} \tau_{\mathrm{KJ}}}\right] \tag{5}$$

where Z is the lattice coordination number, here set as 10, $\phi_{\mathrm{C}_1} = \phi_{\mathrm{C}}$, and the segment fraction ϕ, the surface fraction θ, and the binary adjustable parameter τ_{IJ} related to the energy parameter a_{IJ} for the I–J pair are given by

$$\phi_{\mathrm{I}} = r_{\mathrm{I}} x_{\mathrm{I}} \Big/ \sum_{\mathrm{J}} r_{\mathrm{J}} x_{\mathrm{J}} \tag{6}$$

$$\theta_{\mathrm{I}} = q_{\mathrm{I}} x_{\mathrm{I}} \Big/ \sum_{\mathrm{J}} q_{\mathrm{J}} x_{\mathrm{J}} \tag{7}$$

$$\tau_{\mathrm{IJ}} = \exp(-a_{\mathrm{IJ}}/T) \tag{8}$$

where q_{I} is the pure component molecular-area parameter. The method of Vera et al. [15] was used to calculate the values of r and q. The activity coefficient of the component B is derived by changing the subscript A to B in eqn. (4). The monomeric segment fractions ϕ_{A_1} and ϕ_{B_1} are solved from the mass balance equations

$$\phi_{\mathrm{A}} = \bar{S}_{\mathrm{A}} + \frac{r_{\mathrm{A}} K_{\mathrm{AB}} \bar{S}_{\mathrm{A}} S_{\mathrm{B}}}{(1 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^2 S_{\mathrm{A}} S_{\mathrm{B}})^2} \times [2 + r_{\mathrm{B}} K_{\mathrm{AB}} S_{\mathrm{A}}(2 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^2 S_{\mathrm{A}} S_{\mathrm{B}}) + r_{\mathrm{A}} K_{\mathrm{AB}} S_{\mathrm{B}}] \tag{9}$$

$$\phi_{\mathrm{B}} = \bar{S}_{\mathrm{B}} + \frac{r_{\mathrm{B}} K_{\mathrm{AB}} S_{\mathrm{A}} \bar{S}_{\mathrm{B}}}{(1 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^2 S_{\mathrm{A}} S_{\mathrm{B}})^2} \times [2 + r_{\mathrm{A}} K_{\mathrm{AB}} S_{\mathrm{B}}(2 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^2 S_{\mathrm{A}} S_{\mathrm{B}}) + r_{\mathrm{B}} K_{\mathrm{AB}} S_{\mathrm{A}}] \tag{10}$$

The sums $\bar{S}_{\mathrm{A}}$, $\bar{S}_{\mathrm{B}}$, S_{A} and S_{B} are defined by

$$\bar{S}_{\mathrm{A}} = \phi_{\mathrm{A}_1}/(1 - K_{\mathrm{A}} \phi_{\mathrm{A}_1})^2 \tag{11}$$

$$\bar{S}_{\mathrm{B}} = \phi_{\mathrm{B}_1}/(1 - K_{\mathrm{B}} \phi_{\mathrm{B}_1})^2 \tag{12}$$

$$S_{\mathrm{A}} = \phi_{\mathrm{A}_1}/(1 - K_{\mathrm{A}} \phi_{\mathrm{A}_1}) \tag{13}$$

$$S_{\mathrm{B}} = \phi_{\mathrm{B}_1}/(1 - K_{\mathrm{B}} \phi_{\mathrm{B}_1}) \tag{14}$$

The true molar volume of the ternary mixture V is expressed by

$$\frac{1}{\mathrm{V}} = \frac{S_{\mathrm{A}}}{r_{\mathrm{A}}} + \frac{S_{\mathrm{B}}}{r_{\mathrm{B}}} + \left(\frac{2}{r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}} + \frac{S_{\mathrm{A}}}{r_{\mathrm{A}}} + \frac{S_{\mathrm{B}}}{r_{\mathrm{B}}}\right) \frac{r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^2 S_{\mathrm{A}} S_{\mathrm{B}}}{(1 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^2 S_{\mathrm{A}} S_{\mathrm{B}})} + \frac{\phi_{\mathrm{C}_1}}{r_{\mathrm{C}}} \tag{15}$$

At the pure liquid states V_A^0, V_B^0, $\phi_{A_1}^2$ and $\phi_{B_1}^0$ reduce to

$$1/V_A^0 = (1 - K_A\phi_{A_1}^0)/r_A \tag{16}$$

$$1/V_B^0 = (1 - K_B\phi_{B_1}^0)/r_B \tag{17}$$

$$\phi_{A_1}^0 = [2K_A + 1 - (1 + 4K_A)^{0.5}]/2K_A^2 \tag{18}$$

$$\phi_{B_1}^0 = [2K_B + 1 - (1 + 4K_B)^{0.5}]/2K_B^2 \tag{19}$$

Two sets of the association parameters for pure alcohols are as follows: (I) the equilibrium constants K_A^* at 50°C were taken from Brandani [16] and $h_A = h_B = -23.2\ \mathrm{kJ\ mol^{-1}}$ was obtained from Stokes and Burfitt [17]; (II) the values of K_A^* and h_A were taken from Nagata [8]. The values of the association parameters and molecular structural constants of the pure components are shown in Table 1. The values of the solvation parameters between unlike molecules are: for methanol + 2-butanol, (I) $K_{AB}^* = 50$ at 50°C and $h_{AB} = -23.2\ \mathrm{kJ\ mol^{-1}}$, (II) $K_{AB}^* = 47.5$ and $h_{AB} = (h_A + h_B)/2 = -23.1\ \mathrm{kJ\ mol^{-1}}$; for ethanol + *i*-butanol, (I) $K_{AB}^* = 45$ and $h_{AB} = -23.2\ \mathrm{kJ\ mol^{-1}}$, (II) $K_{AB}^* = 40$ and $h_{AB} = (h_A + h_B)/2 = -23.3\ \mathrm{kJ\ mol^{-1}}$.

The energy parameters were sought using a computer program as described by Prausnitz et al. [18] and minimizing the objective function given by

$$F_1 = \sum_{i=1}^{N} \left[\frac{(P_{i,\mathrm{exp}} - P_{i,\mathrm{calc}})^2}{\sigma_P^2} + \frac{(T_{i,\mathrm{exp}} - T_{i,\mathrm{calc}})^2}{\sigma_T^2} + \frac{(x_{i,\mathrm{exp}} + x_{i,\mathrm{calc}})^2}{\sigma_x^2} \right] \tag{20}$$

The standard deviations in the measured values were taken as: for pressure, $\sigma_P = 1$ Torr; for temperature, $\sigma_T = 0.05$ K; for liquid-phase mole fraction, $\sigma_x = 0.001$. The virial equation of state neglecting all third virial coefficients was used to calculate vapour-phase nonidealities and the Poynting corrections were taken into account. Second virial coefficients were estimated with use of the correlation of Hayden and O'Connell [19],

TABLE 1

Association parameters and molecular structural constants for pure components

Component	K_A^*(50°C)		$-h_A$ (kJ mol^{-1})		r	q
	I[a]	II[b]	I[a]	I[b]		
Methanol	173.9	125.1	23.2	23.6	1.15	1.12
Ethanol	110.4	103.2	23.2	23.6	1.69	1.55
2-Butanol	31.1	57.5	23.2	22.6	2.77	2.42
i-Butanol	50.6	67.0	23.2	23.0	2.77	2.42
n-Pentane					3.06	2.65
n-Heptane					4.15	3.52

[a] I, K_A^* were obtained from Brandani [16] and h_A from Stokes and Burfitt [17].
[b] II, K_A^* and h_A were taken from Nagata [8].

TABLE 2

Liquid molar volumes for the pure components and second virial coefficients at 30°C

Pure component	Molar volume ($cm^3\ mol^{-1}$)	Second virial coefficient ($cm^3\ mol^{-1}$)
Methanol	39.35	−2474
Ethanol	58.13	−1973
2-Butanol	93.28	−4037
i-Butanol	93.92	−4845
n-Pentane	117.56	−1144
n-Heptane	148.33	−2814

Mixture	Cross second virial coefficient ($cm^3\ mol^{-1}$)
Methanol + 2-butanol	−2568
Methanol + *n*-pentane	−479
2-Butanol + *n*-pentane	−1034
Ethanol + i-butanol	−2740
Ethanol + *n*-heptane	−995
Isobutanol + *n*-heptane	−1569

and pure liquid molar volumes at 30°C were calculated from the modified Rackett equation [20].

The original residual term of the UNIQUAC model includes only the binary interaction parameters and was further modified to have the form suggested previously [21] in order to account for ternary interactions among unlike molecules.

$$\begin{aligned}\left(\frac{g^E}{RT}\right)_{\text{residual}} &= -q_A x_A \ln(\theta_A \tau_{AA} + \theta_B \tau_{BA} + \theta_C \tau_{CA} + \theta_B \theta_C \tau_{BCA}) \\ &\quad - q_B x_B \ln(\theta_A \tau_{AB} + \theta_B \tau_{BB} + \theta_C \tau_{CB} + \theta_A \theta_C \tau_{ACB}) \\ &\quad - q_C x_C \ln(\theta_A \tau_{AC} + \theta_B \tau_{BC} + \theta_C \tau_{CC} + \theta_A \theta_B \tau_{ABC}) \qquad (21)\end{aligned}$$

The ternary parameters τ_{BCA}, τ_{ACB} and τ_{ABC} in eqn. (21) must be evaluated from ternary data. Parameter estimation was performed by using a non-linear regression program based on a simplex method [22] and minimizing the objective function

$$F_2 = \sum_{i=1}^{N} \left(\frac{P_{i,\text{exp}} - P_{i,\text{calc}}}{P_{i,\text{exp}}}\right)^2 \qquad (22)$$

CALCULATED RESULTS

Binary systems

The pure component vapour pressures were taken from original sources [13, 14]. Table 3 gives the binary parameters and root-mean-square

TABLE 3

Calculated results for binary VLE data at 30°C

System (A + B)	No. of data points	Case [a]	K_{AB} at 50°C	Root-mean-square deviations			Parameters (K)	
				δP (kPa)	δT (K)	δx ($\times 10^3$)	a_{Ab}	a_{BA}
Methanol + 2-butanol	22	I	50	0.01	0.00	0.0	2.95	39.52
		II	47.5	0.17	0.00	0.1	99.31	−97.26
Methanol + *n*-pentane	22	I		0.51	0.01	1.6	94.25	14.03
		II		0.76	0.02	2.6	54.70	54.45
2-Butanol + *n*-pentane	26	I		0.29	0.00	1.1	206.65	−112.53
		II		0.64	0.00	2.0	265.35	−148.09
Ethanol + i-butanol	21	I	45	0.02	0.00	0.0	−44.91	155.61
		II	40	0.01	0.00	0.0	47.96	−22.91
Ethanol + *n*-heptane	22	I		0.03	0.00	0.1	65.51	−2.00
		II		0.04	0.00	0.1	56.51	6.72
i-Butanol + *n*-heptane	22	I		0.06	0.00	0.0	153.21	−89.38
		II		0.08	0.00	0.0	180.65	−109.11

[a] I, association constants were taken from Brandani [16] and $h_A = -23.2$ kJ mol^{-1} from Stokes and Burfitt [17]; II, association parameters were taken from Nagata [8].

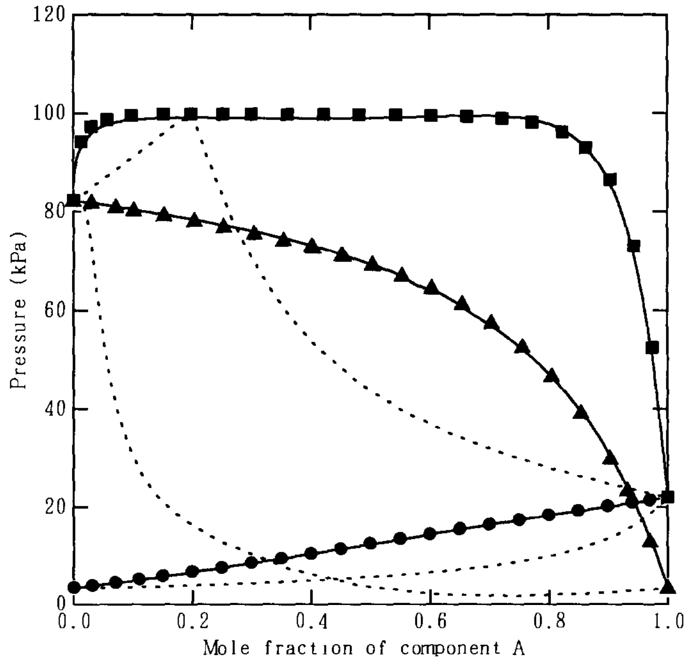

Fig. 1. P–x–y diagram for three binaries of methanol + 2-butanol + *n*-pentane at 30°C: ■, methanol(A) + *n*-pentane(B); ▲, 2-butanol(A) + *n*-pentane(B); ●, methanol(A) + 2-butanol(B). Solid curves are calculated P–x results, and broken curves are predicted P–y results. Both cases give nearly the same results.

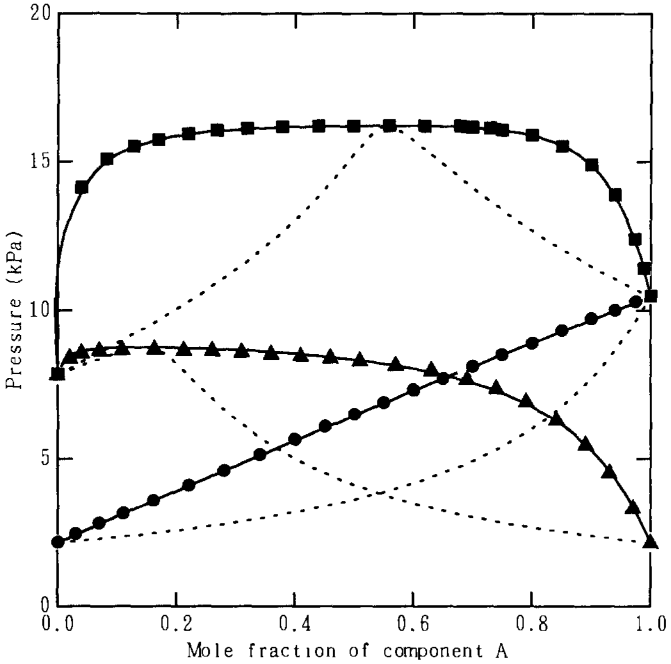

Fig. 2. P–x–y diagram for three binaries of ethanol + i-butanol + n-heptane at 30°C: ■, ethanol(A) + n-heptane(B); ▲, i-butanol(A) + n-heptane(B); ●, ethanol(A) + i-butanol(B). Solid curves are calculated P–x results, and broken curves are predicted P–y results. Both cases give nearly the same result.

TABLE 4

Calculated results for ternary VLE data at 30°C

System (A + B + C)	No. of data points	Case[a]	Abs. arith. mean dev.				Ternary parameters		
			Prediction[b]		Correlation[c]		τ_{BCA}	τ_{ACB}	τ_{ABC}
			δP (kPa)	$\delta P/P$ (%)	δP (kPa)	$\delta P/P$ (%)			
Methanol + 2-butanol + n-pentane	67	I	1.56	2.2	0.80	1.1	−0.9854	−0.0514	0.7376
		II	1.23	2.1	0.47	0.6	−0.2207	−0.5495	0.2629
Ethanol + i-butanol + n-heptane	78[d]	I	0.37	3.7	0.14	1.3	−1.1974	0.8616	0.3084
		II	0.19	1.9	0.09	0.8	−0.2152	0.3087	−0.2054

[a] I, association constants were taken from Brandani [16] and $h_A = -23.2$ kJ mol^{-1} from Stokes and Burfitt [17]; II, association parameters were taken from Nagata [8].

[b] Only binary parameters used.

[c] Binary parameters and ternary parameters used.

[d] Two experimental points were rejected because the computer could not solve the mass balance equations for these points.

TABLE 5

Calculated results of ternary VLE data for methanol(A) + 2-butanol(B) + *n*-pentane(C) at 30°C by use of binary and ternary parameters

x_A	x_B	P_{exp} (kPa)	δP [a] (kPa)		x_A	x_B	P_{exp} (kPa)	δP (kPa)	
			I [b]	II [c]				I	II
0.0063	0.0224	85.29	1.19	1.11	0.3069	0.2973	81.91	0.90	−0.18
0.0165	0.0539	85.21	1.24	0.81	0.3322	0.3216	79.87	0.56	−0.11
0.0265	0.0845	84.73	1.65	0.96	0.3327	0.3224	79.94	0.70	0.04
0.0391	0.1228	83.97	1.51	0.36	0.3585	0.3474	77.11	0.24	0.13
0.0522	0.1630	83.15	1.50	0.17	0.3841	0.3722	73.27	−0.23	0.26
0.0623	0.1937	82.42	1.44	0.01	0.4096	0.3971	67.83	−0.64	0.35
0.0766	0.2372	81.34	1.44	−0.09	0.4349	0.4215	60.22	−0.79	0.32
0.0889	0.2747	80.31	1.47	−0.11	0.4604	0.4462	49.13	−0.50	0.24
0.1013	0.3125	79.19	1.55	−0.02	0.4792	0.4646	37.66	−0.08	0.13
0.1136	0.3503	77.91	1.61	0.14	0.4936	0.4785	26.49	0.25	0.14
0.1259	0.3878	76.47	1.67	0.48	0.0202	0.0077	92.97	1.04	1.18
0.1382	0.4251	74.69	1.62	0.74	0.0429	0.0151	94.38	0.69	0.70
0.1385	0.4260	74.67	1.65	0.77	0.0736	0.0251	94.83	−0.05	−0.07
0.1508	0.4637	72.42	1.50	1.01	0.1123	0.0376	94.85	−0.02	−0.29
0.1631	0.5015	69.55	1.25	1.18	0.1515	0.0501	94.63	0.07	−0.38
0.1756	0.5402	65.82	0.97	1.31	0.1901	0.0626	94.38	0.25	−0.36
0.1879	0.5780	60.99	0.61	1.23	0.2284	0.0747	94.03	0.39	−0.40
0.2001	0.6155	54.76	0.35	1.01	0.2671	0.0872	93.70	0.73	−0.09
0.2100	0.6462	48.17	0.19	0.65	0.3053	0.0994	93.31	0.77	0.07
0.2194	0.6750	40.44	0.18	0.25	0.3433	0.1117	92.87	0.93	−0.41
0.2290	0.7046	30.52	0.27	−0.13	0.3818	0.1238	92.34	1.01	−0.45
0.2382	0.7328	18.68	0.38	−0.26	0.4195	0.1360	91.67	1.02	−0.51
0.0130	0.0145	89.13	1.06	1.30	0.4573	0.1480	90.77	0.90	−0.61
0.0293	0.0304	89.89	0.96	0.89	0.4951	0.1601	89.53	0.65	−0.71
0.0500	0.0505	89.91	0.88	0.44	0.5325	0.1720	87.78	0.28	−0.81
0.0764	0.0758	89.55	0.76	−0.04	0.5697	0.1840	85.17	−0.19	−0.90
0.1019	0.1004	89.06	0.72	0.03	0.6069	0.1960	81.22	−0.64	−0.93
0.1276	0.1250	88.50	0.73	0.01	0.5713	0.1846	85.03	−0.21	−0.90
0.1535	0.1499	87.89	0.80	0.01	0.6094	0.1970	80.86	−0.66	−0.93
0.1792	0.1747	87.25	0.92	−0.31	0.6471	0.2092	74.27	−0.93	−0.74
0.2050	0.1994	86.51	1.02	−0.36	0.6845	0.2214	63.59	−0.68	−0.58
0.2308	0.2242	85.67	1.12	−0.35	0.7136	0.2307	50.49	−0.10	−0.30
0.2562	0.2486	84.70	1.17	−0.30	0.7350	0.2377	36.34	0.27	−0.05
0.2816	0.2730	83.47	1.09	−0.25					

[a] Experimental value minus calculated one.

[b] Association constants were taken from Brandani [16] and $h_A = -23.2$ kJ mol^{-1} from Stokes and Burfitt [17].

[c] Association parameters were taken from Nagata [8].

TABLE 6

Calculated results of ternary VLE data for ethanol(A) + i-butanol(B) + *n*-heptane(C) at 30°C by use of the binary and ternary parameters

x_A	x_B	P_{exp} (kPa)	δP[a] (kPa)		x_A	x_B	P_{exp} (kPa)	δP (kPa)	
			I[b]	II[c]				I	II
0.0683	0.8573	5.32	0.16	0.18	0.2601	0.3679	11.48	0.38	0.02
0.1096	0.8193	5.64	0.03	0.10	0.3101	0.3431	11.91	0.36	0.00
0.1590	0.7738	6.04	−0.07	0.04	0.3597	0.3184	12.29	0.32	0.00
0.2097	0.7271	6.41	−0.14	−0.03	0.4092	0.2938	12.63	0.24	−0.01
0.2594	0.6814	6.79	−0.16	−0.05	0.4599	0.2686	12.95	0.23	−0.12
0.3104	0.6345	7.21	−0.13	−0.02	0.5095	0.2439	13.24	0.17	−0.06
0.3596	0.5892	7.52	−0.16	−0.07	0.5594	0.2191	13.44	0.15	−0.23
0.4100	0.5428	7.87	−0.15	−0.07	0.6097	0.1940	13.65	0.08	−0.10
0.4603	0.4965	8.21	−0.12	−0.06	0.6595	0.1693	13.79	0.07	−0.04
0.5095	0.4512	8.52	−0.10	−0.06	0.7097	0.1443	13.87	0.03	−0.01
0.5597	0.4050	8.81	−0.09	−0.06	0.7093	0.1446	13.87	0.04	−0.01
0.6098	0.3589	9.12	−0.04	−0.03	0.7585	0.1209	13.87	0.00	0.02
0.6604	0.3124	9.41	0.00	0.01	0.8095	0.0948	13.72	0.01	−0.05
0.0717	0.7300	7.56	0.38	0.32	0.8597	0.0699	13.39	0.01	0.01
0.1098	0.7000	7.89	0.28	0.20	0.9094	0.0452	12.83	0.02	0.03
0.1613	0.6595	8.35	0.07	0.13	0.9496	0.0252	12.04	0.04	0.04
0.2104	0.6209	8.73	−0.01	0.06	0.9748	0.0126	11.44	0.11	0.11
0.2602	0.5817	9.13	−0.01	0.03	0.0299	0.2403	9.55	0.17	0.02
0.3095	0.5430	9.51	−0.01	0.03	0.0690	0.2307	10.45	0.58	0.23
0.3598	0.5034	9.83	−0.07	0.00	0.1104	0.2204	11.21	0.46	0.11
0.4106	0.4634	10.15	−0.08	−0.04	0.1606	0.2080	12.01	0.40	0.07
0.4600	0.4246	10.47	−0.06	0.00	0.2088	0.1960	12.61	0.32	0.03
0.5106	0.3847	10.76	−0.03	0.00	0.2589	0.1837	13.13	0.20	−0.81
0.5602	0.3457	10.99	−0.01	0.00	0.3091	0.1712	13.55	−0.07	−0.60
0.6105	0.3062	11.20	0.01	0.00	0.3594	0.1588	13.91	0.07	−0.41
0.6604	0.2669	11.39	0.03	0.02	0.4100	0.1463	14.23	0.15	−0.24
0.7103	0.2277	11.51	0.05	0.04	0.4594	0.1340	14.47	0.13	−0.15
0.6601	0.2672	11.37	0.02	0.00	0.5091	0.1217	14.69	0.04	−0.06
0.7098	0.2282	11.49	0.04	0.03	0.5597	0.1091	14.87	0.06	−0.02
0.7701	0.1808	11.55	0.05	0.03	0.6095	0.0967	15.00	−0.20	−0.01
0.8297	0.1340	11.52	0.06	0.06	0.6598	0.0843	15.11	−0.13	−0.03
0.8801	0.0944	11.39	0.07	0.06	0.7097	0.0720	15.16	−0.08	−0.06
0.9287	0.0561	11.15	0.06	0.06	0.7099	0.0720	15.17	−0.07	−0.05
0.9702	0.0235	10.80	0.03	0.03	0.7596	0.0596	15.13	−0.04	−0.01
0.0297	0.4825	8.81	0.32	0.28	0.8099	0.0472	14.96	−0.28	−0.05
0.0696	0.4627	9.37	0.53	0.26	0.8597	0.0348	14.59	−0.09	−0.04
0.1093	0.4429	9.84	0.45	0.13	0.9102	0.0223	13.88	0.00	0.05
0.1603	0.4176	10.48	0.46	0.15	0.9497	0.0126	12.84	0.05	0.06
0.2089	0.3934	10.99	0.40	0.05	0.9802	0.0050	11.57	0.01	0.02

[a] Experimental value minus calculated one.

[b] Association constants were taken from Brandani [16] and $h_A = -23.2$ kJ mol^{-1} from Stokes and Burfitt [17].

[c] Association parameters were taken from Nagata [8].

deviations, and the experimental and calculated results are shown in Figs. 1 and 2.

Ternary systems

Table 4 summarizes the deviations between experimental and calculated pressures, together with the values of ternary parameters. Case (II) gives slightly better results than case (I). The results of prediction based on the binary parameters are similar to those for ternary mixtures including one alcohol and two non-associating components [3]. The detailed results derived from the binary and ternary parameters are shown in Tables 5 and 6. The use of the modified Margules equation for binary systems and the additional term containing nine or ten ternary parameters gives smaller deviations than the present results [13, 14]. The workability of solution models should be studied on their performance in fitting the models to various physico-chemical properties.

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