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Thermodynamics of alcohol solutions

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Abstract

An associated-solution model, based on the new local composition model (see Nagata et al. Thermochim. Acta, 224 (1993) 59–69), is presented. The association parameters of pure alcohols have been estimated using ethers as homomorphs of alcohols. The model shows a good performance in representing vapour–liquid equilibria, coexistence curves, and excess enthalpies for binary alcohol mixtures and in predicting ternary vapour–liquid and liquid–liquid equilibria and excess enthalpies for many alcohol mixtures from binary parameters.

Keywords: Associated solution; Binary system; Excess enthalpy; LLE; Molecular complexation; Ternary system; VLE

List of symbols

A, B, C	associated component and non-associated components
$A_{\mathrm{BA}}, B_{\mathrm{BA}}, C_{\mathrm{BA}}$	coefficients of Eq. (35)
$A_{\mathrm{AB}}, B_{\mathrm{AB}}, C_{\mathrm{AB}}$	coefficients of Eq. (36)
A_i	*i*mer of component A
$\mathrm{A}_i\mathrm{B}_1$	complex between component A *i*mer and component B monomer
$\mathrm{A}_i\mathrm{C}_1$	complex between component A *i*mer and component C monomer
a_{IJ}	binary interaction energy parameter for I–J pair
B^{F}	free contribution to second virial coefficient
C_{IJ}, D_{IJ}	coefficients of Eq. (31)

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F	objective function as defined by Eq. (11)
f_{AB}, f_{AC}	quantities defined by Eqs. (19) and (20)
g^E	excess molar Gibbs energy
$\Delta_r H_A$	enthalpy of hydrogen-bond formation of associated component A
$\Delta_r H_{AB}$	enthalpy of complex formation between associated component A and active non-associated component B
$\Delta_r H_{AC}$	enthalpy of complex formation between associated component A and active non-associated component C
H^E	excess molar enthalpy
H_f	total enthalpy of complex formation
H^0_{fA}	total enthalpy of hydrogen-bond formation of pure component A
K_A	self-association constant of associated component A
K_{AB}, K_{AC}	solvation constants between associated component A and active non-associated component B or C
n_I	number of moles of component I
n^*	effective number of carbon atoms in an ether molecule
P	total pressure
P^S_I	saturated vapour pressure of pure component I
R	universal gas constant
r_I	molecular geometric-size parameter of pure component I
r'_I	$r_I^{2/3}$
T	absolute temperature
V'	modified molar volume of associated mixture
$V^{0'}_A$	modified molar volume of pure associated component A
v^L_I	liquid molar volume of pure component I
x_I	liquid-phase mole fraction of component I
$x^0_{A_1}$	liquid-phase mole fraction of monomeric component A
y_I	vapour-phase mole fraction of component I
Z	lattice coordination number equal to 10

Greek letters

γ_I	activity coefficient of component I
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid-phase mole fraction and vapour-phase mole fraction
ρ'_{IJ}	$(r_J/r_I)^{2/3}$
τ_{IJ}	binary parameters as defined by $\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I given by Eq. (3)
Φ'_I	modified segment fraction of component I given by Eq. (2)
Φ'_{I_1}	modified monomeric segment fraction of component I
$\Phi^{0'}_{A_1}$	modified monomeric segment fraction of pure associated component A given by Eq. (8)
ϕ_I	fugacity coefficient of component I at P and T
ϕ^S_I	fugacity coefficient of pure component I at P^S_I and T
λ	molar latent heat of vaporization for alcohol

λ_h	molar latent heat of vaporization for homomorph (ether) of alcohol

Subscripts

A, B, C	alcohol and non-associated components
A_1, B_1, C_1	monomers of components A, B and C
A_i	*i*mer of alcohol A
A_iB_1	complex between alcohol A *i*mer and component B monomer
A_iC_1	complex between alcohol A *i*mer and component C monomer
calc	calculated
chem	chemical
exp	experimental
f	complex formation
phys	physical
I, *J*, *K*	components *I*, *J* and *K*

Superscripts

0	pure
*	reference state at 50°C
E	excess
F	free contribution
S	saturation
α, β	phases

1. Introduction

There are many solution models with which to treat the strongly non-ideal behaviours of solutions containing a self-associating alkanol. These models should describe accurately thermodynamic properties such as vapour–liquid equilibria, liquid–liquid equilibria, and excess enthalpies for various alkanol solutions over the whole concentration range [1]. An association model based on a continuous self-association concept has been published from this laboratory [2, 3] for the good description of the thermodynamic properties of alkanol mixtures. In the model the association constants of alkanols were obtained from mixture properties and was unable to show phase separation for non-associated mixtures. The association parameters should be estimated from pure-component properties as pointed out by Brandani [4] and a basic expression for the excess Gibbs free energy function g^E must be workable for partially miscible mixtures.

Recently a new local composition model for mixtures involving three or more components has proved its good performance in the representation of binary coexistence curves of liquid–liquid equilibrium over a wide temperature range and ternary and quaternary phase equilibria [5–7]. The new model gives g^E for systems containing any number of components as follows

$$\frac{g^E}{RT}=\sum_{I=1}^{n} x_I \ln\left(\frac{\Phi'_I}{x_I}\right)-\sum_{I=1}^{n} x_I \ln\left(\sum_{J=1}^{n}\Phi_J\tau_{JI}\right) \tag{1}$$

with

$$\Phi'_I=\frac{r_I^{2/3}x_I}{\sum_{J=1}^{n} r_J^{2/3}x_J} \tag{2}$$

$$\Phi_I=\frac{r_I x_I}{\sum_{J=1}^{n} r_J x_J} \tag{3}$$

$$\tau_{IJ}=\exp\left(-\frac{a_{IJ}}{T}\right) \tag{4}$$

where x_I is the nominal mole fraction of component I, Φ'_I and Φ_I are the modified- and nominal-segment fraction of component I, r_I is the molecular geometric-size parameter of pure component I, and a_{IJ} is the binary energy parameter for the I–J pair $a_{ii}=0$ and $a_{ij}=a_{ji}$.

In this paper we apply this new model to associated solutions involving one alcohol and non-associated components.

2. Determination of association parameters for pure alcohols

The alcohol associates to form linear polymers by successive chemical reactions. The self-association constant K_A is defined by

$$K_A=\frac{\Phi'_{A_{i+1}}}{\Phi'_{A_i}\Phi'_{A_1}} \quad \text{for } A_i + A_1 = A_{i+1}$$
$$=K_A^* \exp\left[-\frac{\Delta_r H_A}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \tag{5}$$

where K_A^* is the value of K_A at $T^*=323.15\,\mathrm{K}$ and $\Delta_r H_A$ is the molar enthalpy of hydrogen-bond formation. K_A is independent of the association degree.

Brandani [4] presented the key equation for calculation of the vapour pressure of a pure alcohol liquid P_A^S given below

$$P_A^S=\gamma_{A_1}^0 x_{A_1}^0 P_h^S \exp[(P_A^S-P_h^S)(v_A^L-B_A^F)/RT] \tag{6}$$

where $\gamma_{A_1}^0$ is the activity coefficient of the monomer in the pure alcohol, $x_{A_1}^0$ is the mole fraction of the monomer in the pure alcohol, P_h^S is the vapour pressure of the hypothetical monomer, and v_A^L is the molar volume of pure alcohol obtained by using the modified Rackett equation [8]. B_A^F is the free contribution to the second virial coefficient which is calculated by the method of Hayden and O'Connell [9]. The related parameters used are taken from Prausnitz et al. [10].

$\gamma^0_{A_1}$ is given by

$$\ln \gamma^0_{A_1} = \ln\left(\frac{\Phi^{0\prime}_{A_1}}{x^0_{A_1}}\right) + 1 - \frac{\Phi^{0\prime}_{A_1}}{x^0_{A_1}} \tag{7}$$

where the modified segment fraction of the pure alcohol monomer $\Phi^{0\prime}_{A_1}$ and $x^0_{A_1}$ are expressed as

$$\Phi^{0\prime}_{A_1} = \frac{1}{1+K_A} \tag{8}$$

$$x^0_{A_1} = -\frac{K_A \Phi^{0\prime}_{A_1}}{\ln(1 - K_A \Phi^{0\prime}_{A_1})} \tag{9}$$

The methyl-R ethers were assumed to be the homomorphs with the same number of carbon atoms as in the pertinent alcohol [11,12]. Ambrose et al. [13] measured the vapour pressures of many ethers and presented a general equation to reproduce their experimental vapour pressure data for the ethers in terms of the effective number of carbon atoms in the ether molecule n^*

$$\begin{aligned}\log_{10} P(\text{kPa}) = {} & 7.1972 + 0.1752n^* - (916.74 + 184.766n^*)T^{-1} \\ & - (9.6590 + 1.17110n^*)10^{-4}T \\ & - (1.34082 - 0.152687n^*)10^{-6}T^2 \end{aligned} \tag{10}$$

The values of n^* were taken from Refs. [12] and [13].

K_A at 50°C and h_A for eight aliphatic alcohols were calculated by minimizing the objective function

$$F = \sum_{i=1}^{n} [P^S_{Ai(\text{exp})} - P^S_{Ai(\text{calc})}]^2 \tag{11}$$

where $P^S_{A(\text{calc})}$ was calculated from Eq. (6) and $P^S_{A(\text{exp})}$ was evaluated using the Antoine equation [14] at equally spaced points within the temperature range listed in Table 1, where the values of association constants and enthalpies of hydrogen-bond formation

Table 1
Association parameters and results of fit of vapour pressure data for alcohols

Substance	K_A (at 50°C)	$-\Delta_r H_A$/kJ mol^{-1}	Temperature range/°C	Abs. arith. mean dev./Torr
Methanol	143.0	22.5	1.7–60	0.64
Ethanol	119.2	22.2	19.6–75	0.36
1-Propanol	104.3	22.0	48.1–90	0.06
2-Propanol	84.6	22.2	52.3–80	0.05
1-Butanol	95.6	21.5	78.6–115	0.27
2-Butanol	68.6	20.8	67.7–95	0.32
iso-Butanol	78.7	21.2	69.9–105	0.33
tert-Butanol	38.1	19.7	56.8–80	0.28

are shown, along with the absolute arithmetic mean deviations between the calculated and experimental vapour pressure. The values of the enthalpy for hydrogen-bond formation calculated in this work are comparable to the enthalpy of dilution of ethanol in saturated hydrocarbons at 25°C [15]. The molar latent heat of vaporization for the associated fluid λ is expressed by the equation [4]

$$\lambda = \lambda_{\mathrm{h}} - K_{\mathrm{A}} \Phi^{0\prime}_{\mathrm{A}_1} \Delta_{\mathrm{r}} H_{\mathrm{A}} \tag{12}$$

where λ_{h} is the molar latent heat of vaporization for the alcohol's homomorph, which is taken from Ref. [16]. Table 2 presents the evaluated and experimental molar latent heats of vaporization for alcohols at 25°C, indicating that agreement is good and that the association parameters obtained in this work are physically reasonable.

3. Association model

The excess Gibbs free energy of a ternary mixture involving an alcohol (A) and two non-associated components (B and C) is expressed as the sum of the chemical and physical contribution terms. The chemical contribution term [2, 3] based on Eq. (1), is expressed by

$$\frac{g^{\mathrm{E}}_{\mathrm{chem}}}{RT} = x_{\mathrm{A}} \ln\left(\frac{\Phi'_{\mathrm{A}_1}}{\Phi^{0\prime}_{\mathrm{A}_1} x_{\mathrm{A}}}\right) + x_{\mathrm{B}} \ln\left(\frac{\Phi'_{\mathrm{B}_1}}{x_{\mathrm{B}}}\right) + x_{\mathrm{C}} \ln\left(\frac{\Phi'_{\mathrm{C}_1}}{x_{\mathrm{C}}}\right)$$

$$- \frac{\sum_{I=1}^{3} r'_I x_I}{V'} + \frac{r'_{\mathrm{A}} x_{\mathrm{A}}}{V^{0\prime}} + x_{\mathrm{B}} + x_{\mathrm{C}} \tag{13}$$

where r_I was estimated by the method of Vera et al. [19] and r'_I is given by $r'_I = r_I^{2/3}$. Table 3 gives the values of the molecular size parameters r. The solvation constants

Table 2
Comparison of calculated and experimental molar latent heats of vaporization at 25°C

Substance	Molar latent heat of vaporization		Deviation/%	Ref.
	Calculated/kJ mol^{-1}	Experimental/kJ mol^{-1}		
Ethanol	42.73	42.26	1.11	[17]
1-Propanol	47.89	47.49	0.85	[17]
2-Propanol	46.70	45.34	3.00	[17]
1-Butanol	52.78	52.34	0.83	[17]
2-Butanol	50.44	49.74	1.41	[17]
iso-Butanol	51.40	50.79	1.20	[17]
tert-Butanol	47.24	46.69	1.19	[18]

Table 3
Values of molecular size parameter r for pure components

Component	r	Component	r
Methanol	1.15	*n*-Decane	5.77
Ethanol	1.69	*n*-Hexadecane	9.01
1-Propanol	2.23	Benzene	2.56
2-Propanol	2.23	Toluene	3.10
1-Butanol	2.77	*p*-Xylene	3.65
2-Butanol	2.77	Tetrachloromethane	2.71
iso-Butanol	2.77	Acetonitrile	1.50
tert-Butanol	2.77	Methyl acetate	2.25
n-Hexane	3.61	Ethyl acetate	2.79
Cyclohexane	3.18	Tetrahydrofuran	2.36
Methylcyclohexane	3.72	2-Propanone	2.06
n-Heptane	4.15	2-Butanone	2.60
n-Octane	4.69		

K_{AB} and K_{AC} between alcohol (A) and an active non-associated component (B or C) are defined by

$$\begin{aligned} K_{AB} &= \frac{\Phi'_{A_iB_1}}{\Phi'_{A_i}\Phi'_{B_1}} \quad \text{for } A_i + B_1 = A_iB_1 \\ &= K^*_{AB}\exp\left[-\frac{\Delta_r H_{AB}}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \end{aligned} \tag{14}$$

$$\begin{aligned} K_{AC} &= \frac{\Phi'_{A_iC_1}}{\Phi'_{A_i}\Phi'_{C_1}} \quad \text{for } A_i + C_1 = A_iC_1 \\ &= K^*_{AC}\exp\left[-\frac{\Delta_r H_{AC}}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \end{aligned} \tag{15}$$

where $\Delta_r H_{AB}$ and $\Delta_r H_{AC}$ are the molar enthalpies for chemical complex formation between alcohol (A) and component (B or C), and K^*_{AB} and K^*_{AC} are the values of K_{AB} and K_{AC} at $T^* = 323.15$ K. The solvation constants are not concerned with the association degree of alcohol molecules.

The modified monomer segment fractions of three components, Φ'_{A_1}, Φ'_{B_1} and Φ'_{C_1}, are obtained by solving the following mass balance equations

$$\begin{aligned} \Phi'_A &= \frac{\Phi'_{A_1}}{1-K_A\Phi'_{A_1}} + K_{AB}\Phi'_{A_1}\Phi'_{B_1}\left(\frac{1}{1-K_A\Phi'_{A_1}} - \frac{\rho'_{AB}f_{AB}}{K_A\Phi'_{A_1}}\right) \\ &\quad + K_{AC}\Phi'_{A_1}\Phi'_{C_1}\left(\frac{1}{1-K_A\Phi'_{A_1}} - \frac{\rho'_{AC}f_{AC}}{K_A\Phi'_{A_1}}\right) \end{aligned} \tag{16}$$

$$\Phi'_B = \Phi'_{B_1}\left(1 + \frac{K_{AB}\,\rho'_{AB}f_{AB}}{K_A}\right) \tag{17}$$

$$\Phi'_C = \Phi'_{C_1}\left(1 + \frac{K_{AC}\,\rho'_{AC}f_{AC}}{K_A}\right). \tag{18}$$

where ρ'_{AB} and ρ'_{AC} are given by $\rho'_{AB}=(r_B/r_A)^{2/3}$ and $\rho'_{AC}=(r_C/r_A)^{2/3}$. f_{AB} and f_{AC} are expressed by

$$f_{AB}=\sum_{i=1}^{\infty}\frac{(K_A\Phi'_{A_1})^i}{i+\rho'_{AB}} \tag{19}$$

$$f_{AC}=\sum_{i=1}^{\infty}\frac{(K_A\Phi'_{A_1})^i}{i+\rho'_{AC}} \tag{20}$$

The values of f_{AB} and f_{AC} are obtained as the relative errors of these quantities become less than 10^{-6}.

Substituting the values of Φ'_{A_1}, Φ'_{B_1}, Φ'_{C_1}, f_{AB}, and f_{AC} obtained from Eqs. (16)–(20) into Eq. (21) gives the modified molar volume of the ternary mixture V'

$$\frac{1}{V'}=-\frac{\ln(1-K_A\Phi'_{A_1})}{K_A r'_A}+\frac{\Phi'_{B_1}}{r'_B}\left(1+\frac{K_{AB}\rho'_{AB}f_{AB}}{K_A}\right)+\frac{\Phi'_{C_1}}{r'_C}\left(1+\frac{K_{AC}\rho'_{AC}f_{AC}}{K_A}\right) \tag{21}$$

The modified molar volume of the pure alcohol $V^{0\prime}$ is calculated by substituting the value of $\Phi^{0\prime}_{A_1}$ obtained from Eq. (8) into Eq. (22),

$$\frac{1}{V^{0\prime}}=-\frac{\ln(1-K_A\Phi^{0\prime}_{A_1})}{K_A r'_A} \tag{22}$$

The physical contribution term is given by the residual term of Eq. (1)

$$\frac{g^E_{\text{phys}}}{RT}=-\sum_{I=1}^{3}x_I\ln\left(\sum_{J=1}^{3}\Phi_J\tau_{JI}\right) \tag{23}$$

The activity coefficients of the components A, B and C are expressed by

$$\ln\gamma_A=\ln\left(\frac{\Phi'_{A_1}}{\Phi^{0\prime}_{A_1}x_A}\right)-\frac{r'_A}{V'}+\frac{r'_A}{V^{0\prime}}-\ln\left(\sum_{J=1}^{3}\Phi_J\tau_{JA}\right)+\frac{\Phi_A}{x_A}-\sum_{K=1}^{3}\frac{\Phi_K\tau_{AK}(r_A/r_K)}{\sum_{J=1}^{3}\Phi_J\tau_{JK}} \tag{24}$$

$$\ln\gamma_B=\ln\left(\frac{\Phi'_{B_1}}{x_B}\right)-\frac{r'_B}{V'}+1-\ln\left(\sum_{J=1}^{3}\Phi_J\tau_{JB}\right)+\frac{\Phi_B}{x_B}-\sum_{K=1}^{3}\frac{\Phi_K\tau_{BK}(r_B/r_K)}{\sum_{J=1}^{3}\Phi_J\tau_{JK}} \tag{25}$$

$$\ln\gamma_C=\ln\left(\frac{\Phi'_{C_1}}{x_C}\right)-\frac{r'_C}{V'}+1-\ln\left(\sum_{J=1}^{3}\Phi_J\tau_{JC}\right)+\frac{\Phi_C}{x_C}-\sum_{K=1}^{3}\frac{\Phi_K\tau_{CK}(r_C/r_K)}{\sum_{J=1}^{3}\Phi_J\tau_{JK}} \tag{26}$$

The excess molar enthalpy of the mixture is given as the sum of the chemical and the physical contribution

$$H^{\mathrm{E}} = H^{\mathrm{E}}_{\mathrm{chem}} + H^{\mathrm{E}}_{\mathrm{phys}} \tag{27}$$

The total enthalpy for the formation of chemical species in the ternary mixture is expressed by

$$H_f = \Delta_{\mathrm{r}} H_{\mathrm{A}} \sum_{i=1}^{\infty} (i-1)(n_{\mathrm{A}_i} + n_{\mathrm{A}_i\mathrm{B}} + n_{\mathrm{A}_i\mathrm{C}}) + \Delta_{\mathrm{r}} H_{\mathrm{AB}} \sum_{i=1}^{\infty} n_{\mathrm{A}_i\mathrm{B}} + \Delta_{\mathrm{r}} H_{\mathrm{AC}} \sum_{i=1}^{\infty} n_{\mathrm{A}_i\mathrm{C}} \tag{28}$$

The chemical contribution term of the excess molar enthalpy is given by

$$\begin{aligned} H^{\mathrm{E}}_{\mathrm{chem}} &= H_f - x_{\mathrm{A}} H^0_{\mathrm{fA}} \\ &= \frac{\Delta_{\mathrm{r}} H_{\mathrm{A}}}{K_{\mathrm{A}}}[x_{\mathrm{A}} \ln(1+K_{\mathrm{A}}) + (x_{\mathrm{A}} + \rho'_{\mathrm{AB}} x_{\mathrm{B}} + \rho'_{\mathrm{AC}} x_{\mathrm{C}}) \ln(1 - K_{\mathrm{A}} \Phi'_{\mathrm{A}_1})] \\ &+ (\Delta_{\mathrm{r}} H_{\mathrm{AB}} - \Delta_{\mathrm{r}} H_{\mathrm{A}}) \frac{K_{\mathrm{AB}} \rho'_{\mathrm{AB}} f_{\mathrm{AB}} x_{\mathrm{B}}}{K_{\mathrm{A}} + K_{\mathrm{AB}} \rho'_{\mathrm{AB}} f_{\mathrm{AB}}} \\ &+ (\Delta_{\mathrm{r}} H_{\mathrm{AC}} - \Delta_{\mathrm{r}} H_{\mathrm{A}}) \frac{K_{\mathrm{AC}} \rho'_{\mathrm{AC}} f_{\mathrm{AC}} x_{\mathrm{C}}}{K_{\mathrm{A}} + K_{\mathrm{AC}} \rho'_{\mathrm{AC}} f_{\mathrm{AC}}} \end{aligned} \tag{29}$$

where H^0_{fA} is the value of H_{f} for the pure alcohol.

The physical contribution term is derived by applying the Gibbs–Helmholtz relation to Eq. (23)

$$H^{\mathrm{E}}_{\mathrm{phys}} = \frac{\partial(g^{\mathrm{E}}_{\mathrm{phys}}/T)}{\partial(1/T)} = -R \sum_{I=1}^{3} x_I \frac{\sum_{J=1}^{3} \Phi_J \frac{\partial \tau_{JI}}{\partial(1/T)}}{\sum_{J=1}^{3} \tau_{JI} \Phi_J} \tag{30}$$

where the binary energy parameter a_{IJ} is assumed to be a linear function of temperature

$$a_{IJ} = C_{IJ} + D_{IJ}(T - 273.15) \tag{31}$$

4. Calculation procedure

Vapour–liquid equilibria of the binary and ternary mixtures were calculated using the relation

$$\phi_I y_I P = \gamma_I x_I P^{\mathrm{S}}_I \phi^{\mathrm{S}}_I \exp\left[\frac{v^{\mathrm{L}}_I (P - P^{\mathrm{S}}_I)}{RT}\right] \tag{32}$$

where y_I is the vapour mole fraction of component I, P the total pressure, P^{S}_I the vapour pressure of pure component obtained using the Antoine equation whose parameters were given by the literature [20, 21]. The fugacity coefficients, ϕ_I and ϕ^{S}_I, were calculated from the volume-explicit virial equation of state truncated after the second term. The second virial coefficients were obtained from the method of Hayden and O'Connell [9].

Binary vapour–liquid equilibrium data were reduced using a computer program based on the maximum likelihood principle described by Prausnitz et al. [10]. The standard deviations in the measured variable were used as $\sigma_P = 1.0$ Torr, $\sigma_T = 0.001$

and $\sigma_y = 0.003$. The energy parameters for partially miscible systems were obtained by solving the equations of isoactivity for the components (Eqs. (33) and (34)) in equilibriated phases

$$(\gamma_I x_I)^\alpha = (\gamma_I x_I)^\beta \tag{33}$$

$$\sum_{I=1}^{2} x_I^\alpha = 1 \quad \text{and} \quad \sum_{I=1}^{2} x_I^\beta = 1 \tag{34}$$

where the superscripts α and β indicate equilibrium liquid phases. The binary parameters C_{IJ} and D_{IJ} of Eq. (31) were obtained by minimizing the sum-of-squares of deviations between experimental and calculated values using the simplex method [22].

5. Calculated results

5.1. Phase equilibria

A single value of $\Delta_r H_A = -23.2\,\text{kJ mol}^{-1}$ [15] is used for all alcohols studied here. Table 4 shows the values of the solvation parameters. The enthalpies of complex

Table 4
Solvation parrameters

System (A + B)	K_{AB} (at 50°C)	$-\Delta_r H_{AB}$/kJ mol^{-1}
Methanol + benzene	8.0	8.3
Ethanol + benzene	7.5	8.3
1-Propanol + benzene	7.0	8.3
2-Propanol + benzene	7.0	8.3
1-Butanol + benzene	6.5	8.3
2-Butanol + benzene	6.5	8.3
tert-Butanol + benzene	6.5	8.3
Ethanol + toluene	7.5	8.3
2-Propanol + toluene	7.0	8.3
Ethanol + *p*-xylene	5.5	8.3
1-Propanol + *p*-xylene	5.0	8.3
2-Propanol + *p*-xylene	5.0	8.3
1-Butanol + *p*-xylene	4.5	8.3
Methanol + tetrachloromethane	1.5	5.5
1-Propanol + tetrachloromethane	1.0	5.5
2-Propanol + tetrachloromethane	1.0	5.5
Methanol + acetonitrile	75.0	17.0
Ethanol + acetonitrile	55.0	17.0
1-Propanol + acetonitrile	45.0	17.0
2-Propanol + acetonitrile	35.0	17.0
Methanol + methyl acetate	35.0	17.0
1-Propanol + ethyl acetate	30.0	17.0
2-Propanol + ethyl acetate	30.0	17.0
Methanol + tetrahydrofuran	40.0	20.0
Methanol + 2-propanone	70.0	21.0
Ethanol + 2-propanone	55.0	21.0
1-Propanol + 2-propanone	40.0	21.0
Ethanol + 2-butanone	45.0	21.0
1-Propanol + 2-butanone	30.0	21.0

formation $\Delta_r H_{AB}$ were estimated approximately by taking the difference between the enthalpy of infinite dilution of ethanol in saturated hydrocarbons and that of ethanol in active solvents and were assumed to be independent of the number of carbon atoms in alcohol molecules and are the same as those estimated by Nagata et al. [23–26]. The solvation constants K_{AB} were estimated by fitting the model to mixture properties (vapour–liquid equilibria and excess enthalpy data); they decrease with increasing number of carbon atoms in the alcohol. Nagata and Miyamoto [23] reproduced well IR spectroscopic results for 1-propanol + tetrachloromethane using the UNIQUAC associated-solution model with four association constants and a small value of the solvation constant; we adopted a small value of K_{AB} for this system. The complex formation of A_iB complexes for the system does not yield a significant negative excess enthalpy. The final calculated results for H^E due to the presence of negative H^E_{phys} represent adequately the calorimetric measurements. The values of $-\Delta_r H_{AB}$ are in the order: ketones > tetrahydrofuran > esters, and acetonitrile > hydrocarbons > tetrachloromethane. The values of K_{AB} for methanol + active solvent mixtures are in the order: acetonitrile > 2-propanone > tetrahydrofuran > methyl acetate > ethyl acetate > benzene > toluene > *p*-xylene > tetrachloromethane. Table 5 gives the binary calculated results obtained by fitting the model to experimental phase equilibria data. Figs. 1 and 2 illustrate examples for selected binary mixtures. The ternary predicted vapour–liquid equilibrium results obtained from the model with only binary parameters agree well with experimental values as shown in Table 1. Furthermore, Figs. 3 and 4 demonstrate the good workability of the model in predicting ternary liquid–liquid equilibria using binary parameters alone.

In representing the binary coexistence curves over a wide temperature range, we assume the quadratic temperature dependence of the energy parameters.

$$a_{BA} = A_{BA} + B_{BA} T + C_{BA} T^2 \tag{35}$$

$$a_{AB} = A_{AB} + B_{AB} T + C_{AB} T^2 \tag{36}$$

Calculated results are given in Table 7 and are compared with the experimental data for four mixtures as shown in Fig. 5. Each experimental data point was analyzed using the model parameters, which are assumed to be linearly or quadratically temperature-dependent. For each system Table 7 shows the parameter set, which provides a smaller deviation between the experimental and calculated liquid compositions than the other one. The precision of the measurements in the systems studied affects the quality of correlation. The parameters listed in Table 7 were used to predict activity coefficients in the miscible regions to verify their physical significance. The predicted values are well compared with the experimental ones as shown in Figs. 6–9.

5.2. *Excess enthalpy*

The binary calculated results for excess enthalpy data are presented in Table 8 and are compared with the experimental values of selected mixtures in Fig. 10. Table 9 gives

Table 5
Calculated results for binary phase equilibrium data

System (A + B)	Temp./°C	No. of data points	Root-mean-squared devs.				Parameters		Ref.
			δP/Torr	$\delta T/K$	$\delta x \times 10^3$	$\delta y \times 10^3$	a_{AB}/K	a_{BA}/K	
Methanol + *n*-hexane	35	22	0.97	0.04	0.9		327.93	63.14	[27]
	50	22	0.40	0.03	0.9		293.40	67.71	[27]
Ethanol + *n*-hexane	35	9	1.19	0.04	0.2	9.3	251.23	15.69	[27]
Ethanol + cyclohexane	20	7	0.95	0.00	0.2	3.7	253.63	23.12	[27]
	35	7	2.15	0.05	0.1	3.1	230.90	25.50	[27]
Ethanol + *n*-heptane	30	22	1.11	0.02	0.3		310.23	16.37	[28]
Ethanol + *n*-octane	45	17	1.57	0.03	2.8	4.2	346.13	16.37	[29]
Ethanol + *n*-hexadecane	52.1	29	1.54	0.00	1.4		−508.89	300.08	[30]
1-Propanol + cyclohexane	25	27	1.46	0.00	0.2		382.18	−65.64	[29]
2-Propanol + cyclohexane	50	9	2.49	0.09	0.6	11.4	399.34	−107.05	[31]
2-Propanol + *n*-heptane	30	11	1.63	0.02	0.7		476.05	−89.88	[32]
1-Butanol + cyclohexane	25	14	1.56	0.02	0.6	13.0	176.60	−56.08	[31]
	45	43	1.61	0.03	0.4		288.92	−102.35	[33]
1-Butanol + *n*-heptane	60	19	2.25	0.05	0.7	6.5	401.68	−100.04	[34]
iso-Butanol + *n*-heptane	30	22	0.58	0.00	0.0		269.95	−39.55	[28]
Methanol + cyclohexane	25	MS[a]					295.45	76.15	[35]
	40	MS					261.24	79.06	[36]
Methanol + *n*-heptane	25	MS					312.28	71.27	[37]
Methanol + benzene	35	9	0.93	0.03	1.1	5.1	−159.44	268.67	[27]
	55	9	0.80	0.00	1.9	5.5	−7.01	136.52	[27]
Methanol + tetrachloromethane	35	9	1.67	0.05	0.7	8.6	−351.12	412.81	[27]
Methanol + acetonitrile	25	10	1.44	0.02	0.5	5.8	228.19	231.58	[38]
	55	13	0.64	0.04	0.3	2.5	356.58	−5.06	[36]

Methanol + methyl acetate	30	7	2.87	0.10	0.8	8.6	121.36	76.40	[27]
Methanol + tetrahydrofuran	25	19	0.37	0.01	0.0		−50.32	163.60	[29]
Methanol + 2-propanone	35	11	1.10	0.04	0.4	2.9	302.88	13.58	[27]
Ethanol + benzene	25	11	0.91	0.01	1.0	7.4	−120.92	309.28	[39]
	45	12	0.63	0.01	0.5	3.6	38.18	115.19	[27]
Ethanol + toluene	35	10	0.54	0.01	0.6	3.8	−132.42	259.91	[27]
Ethanol + acetonitrile	50	12	0.67	0.02	0.3		499.90	−33.91	[29]
Ethanol + 2-butanone	25	12	1.07	0.01	0.7	6.2	199.82	99.35	[39]
	55	14	1.09	0.04	1.3	9.8	553.55	−133.82	[27]
1-Propanol + benzene	45	11	0.41	0.00	0.4	2.1	75.35	45.10	[27]
1-Propanol + acetonitrile	55	10	1.30	0.04	0.7	5.2	583.02	−104.41	[40]
2-Propanol + benzene	50	15	1.61	0.05	1.1	5.2	288.90	−56.45	[31]
2-Propanol + acetonitrile	50	15	0.51	0.02	0.6	3.5	550.32	−101.95	[35]
Benzene + cyclohexane	20	11	0.91	0.00	0.1	0.9	49.95	97.42	[41]
	39.99	7	0.29	0.01	0.2	1.9	33.62	112.10	[41]
Tetrachloromethane + cyclohexane	40	9	0.48	0.01	0.2	1.8	107.80	−44.06	[41]
Tetrachloromethane + benzene	40	8	0.46	0.01	0.2	1.9	164.49	−98.52	[42]
Acetonitrile + benzene	45	11	0.68	0.02	0.4	3.2	−18.93	367.26	[42]
	55	12	1.15	0.04	0.6	7.0	−56.39	426.28	[43]
Tetrahydrofuran + cyclohexane	25	19	0.78	0.00	0.1		−78.77	296.92	[44]
Methyl acetate + cyclohexane	35	8	1.19	0.04	0.6	7.9	211.01	279.52	[45]
2-propanone + cyclohexane	25	12	0.93	0.00	0.3	4.7	191.76	561.75	[46]
Cyclohexane + *n*-heptane	25	30	0.07	0.00	0.1	0.7	71.72	−26.25	[47]
Acetonitrile + cyclohexane	25	MS					630.87	1321.7	[48]
	40	MS					523.65	1244.2	[35]
	50	MS					496.60	1169.1	[35]
Acetonitrile + *n*-hexane	40	MS					458.45	1151.7	[49]

[a] MS, mutual solubilities.

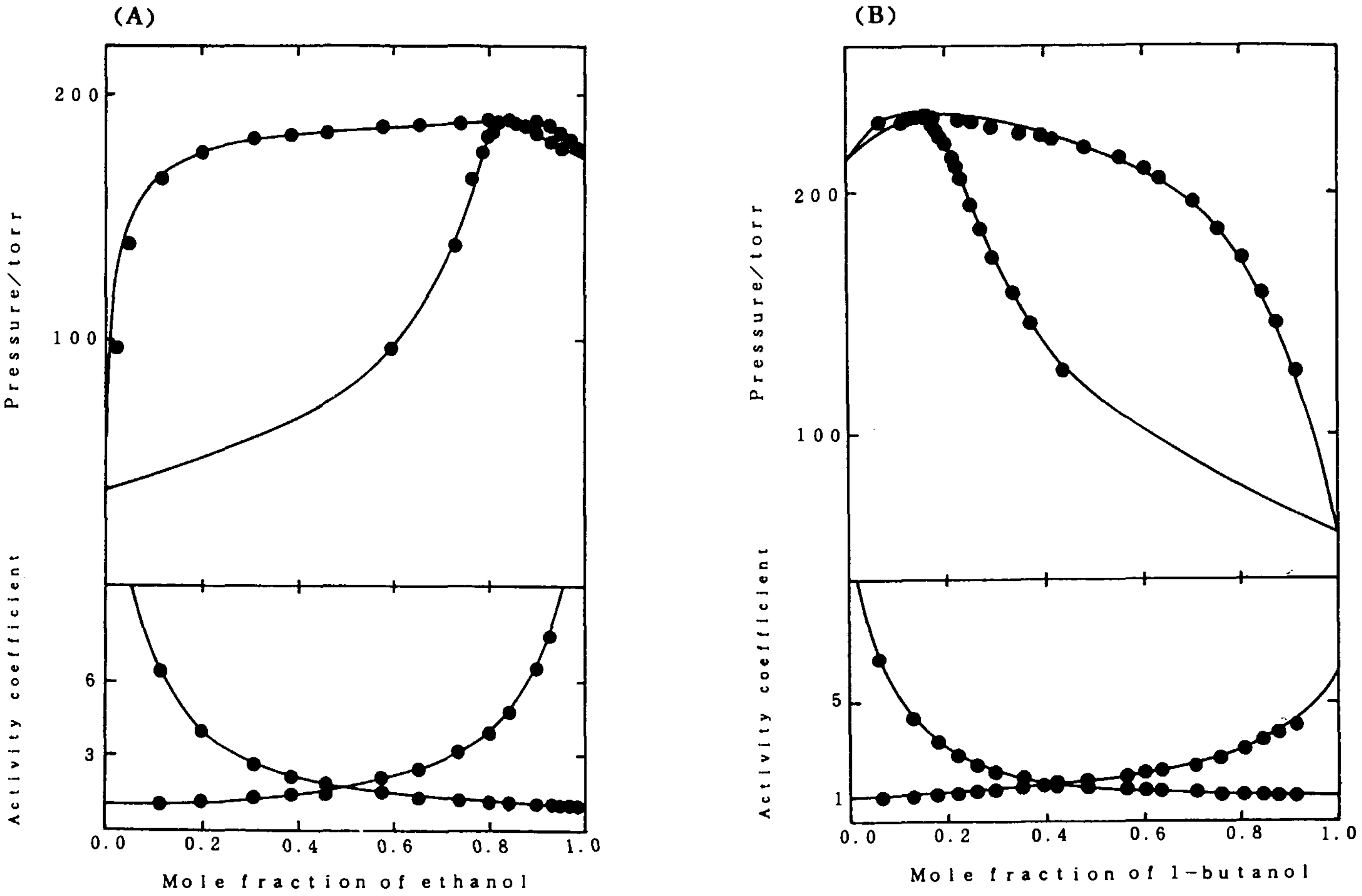


Fig. 1. Vapour–liquid equilibria for binary mixtures consisting of one alcohol and one inert component. Calculated, ——. Experimental: ●, (A) ethanol + *n*-octane at 45°C [29]; (B) 1-butanol + *n*-heptane at 60°C [34].

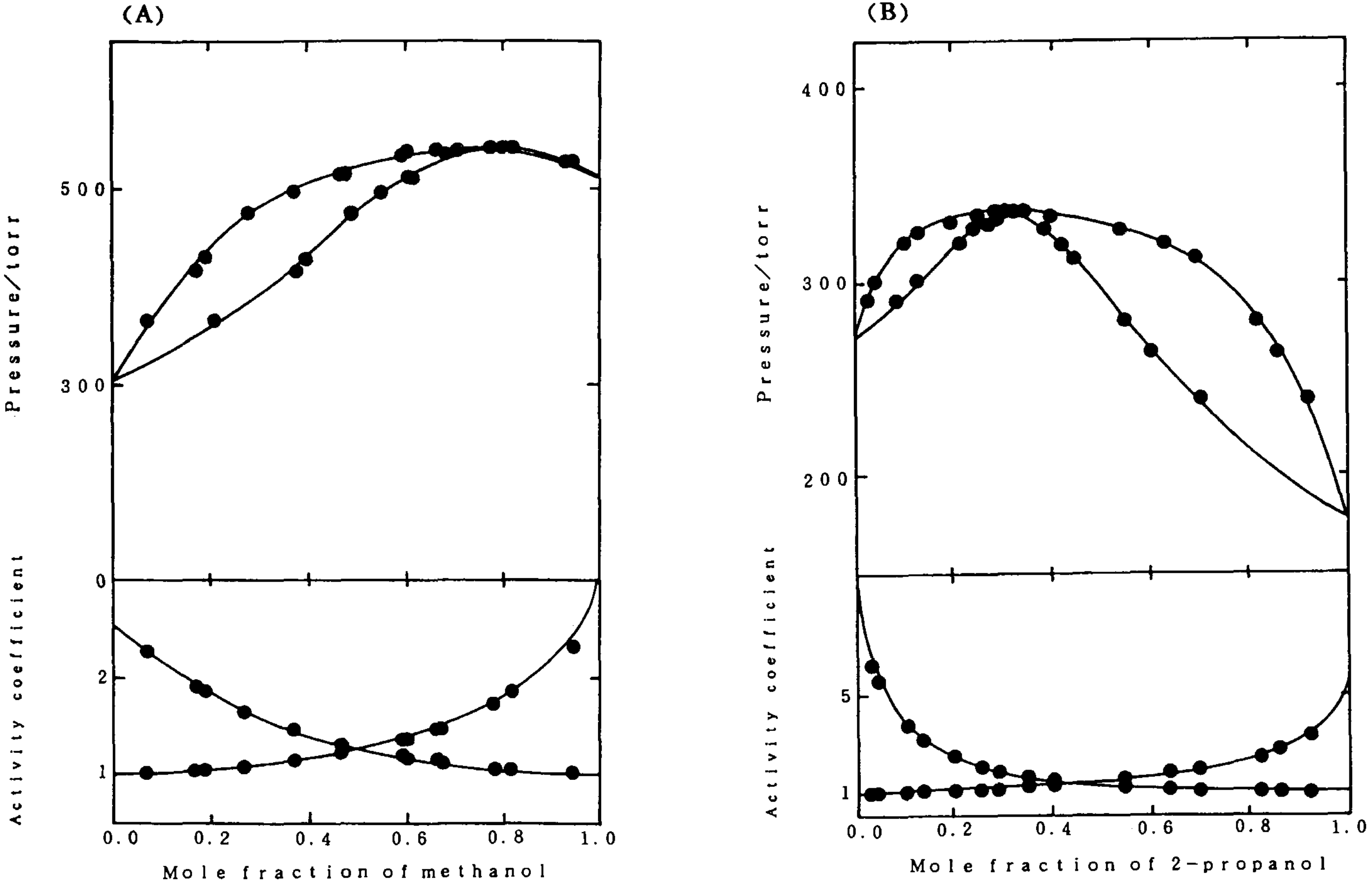


Fig. 2. Vapour–liquid equilibria for binary mixtures consisting of one alcohol and one active component. Calculated, ——. Experimental: ●, (A) Methanol + acetonitrile 55°C [36]; (B) 2-propanol + benzene at 50°C [31].

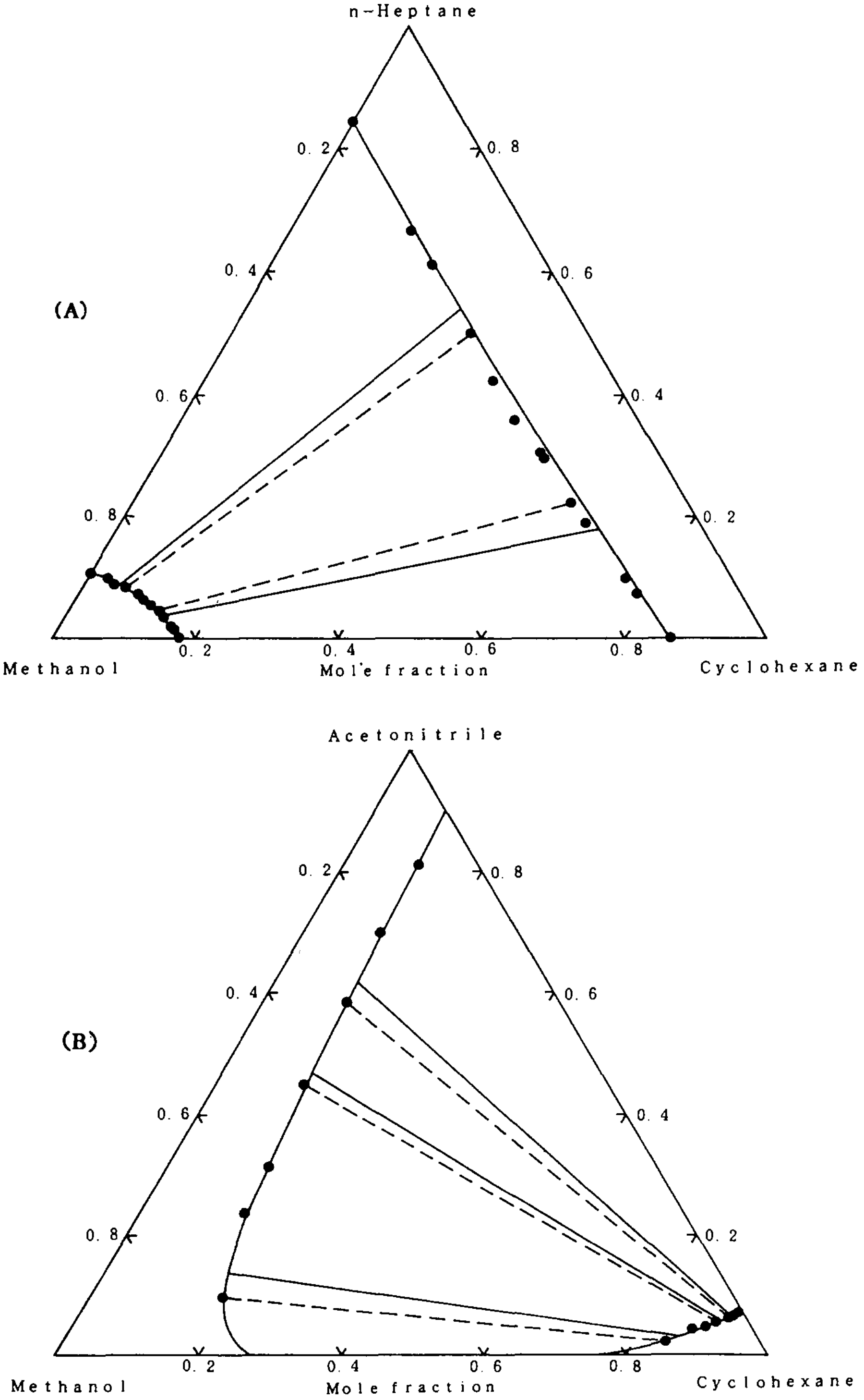


Fig. 3. Ternary liquid–liquid equilibria for systems where two binaries are partially miscible. Calculated, ——. Experimental tie-line: ● — — ●, (A) methanol + *n*-heptane + cyclohexane at 25°C [51]; (B) methanol + acetonitrile + cyclohexane at 40°C [52].

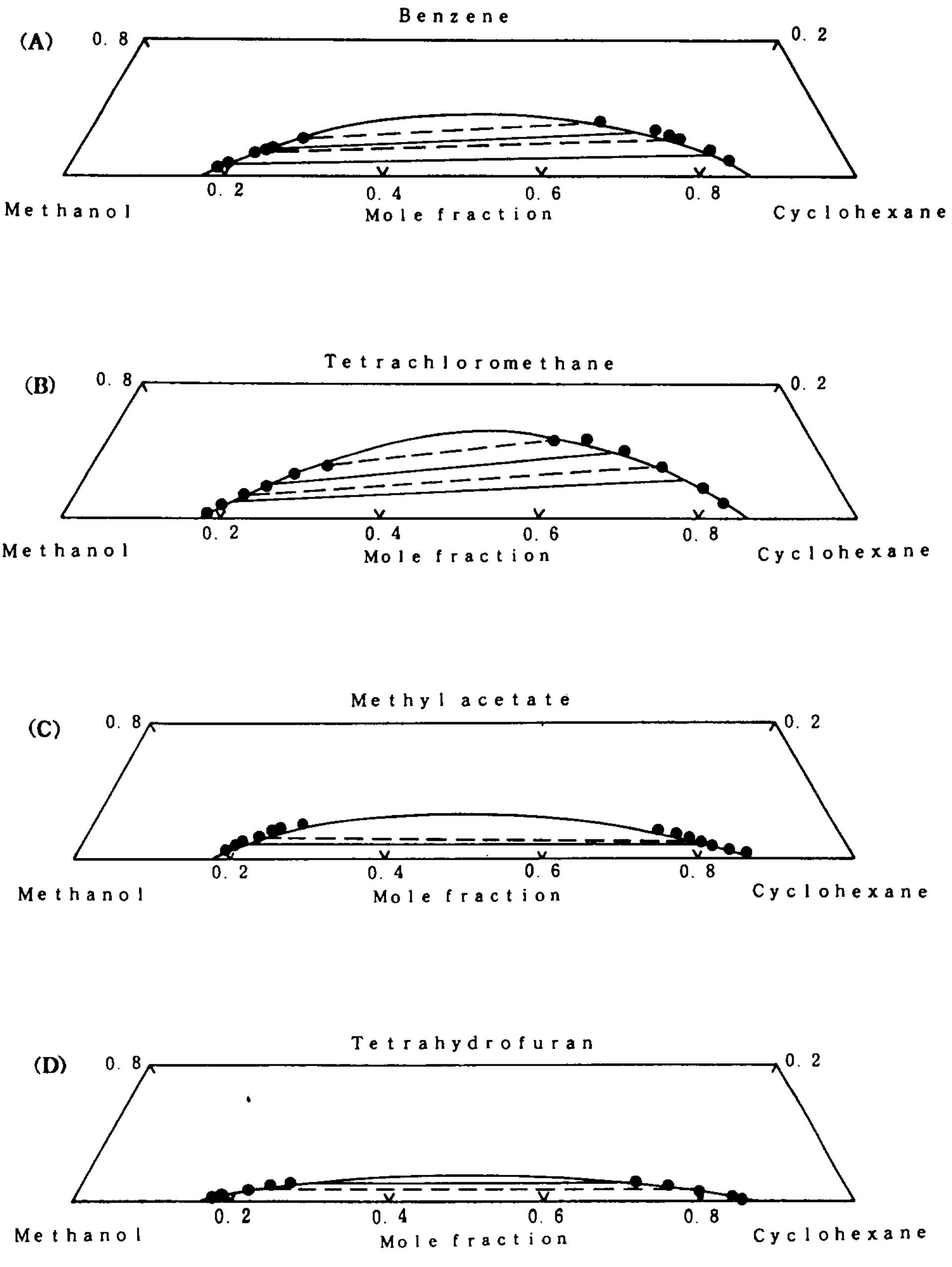


Fig. 4. Ternary liquid–liquid equlibria for systems where only one binary is partially miscible. Calculated, ——. Experimental tie-line: ● — — ●, (A) methanol + benzene + cyclohexane at 25°C [52]; (B) methanol + tetrachloromethane + cyclohexane at 25°C [53]; (C) methanol + methyl acetate + cyclohexane at 25°C [54]; (D) methanol + tetrahydrofuran + cyclohexane at 25°C [54]; (E) methanol + 2-propanone + cyclohexane at 25°C [52]; (F) 2-propanol + acetonitorile + cyclohexane at 50°C [52]; (G) ethanol + acetonitrile + *n*-hexane at 40°C [54].

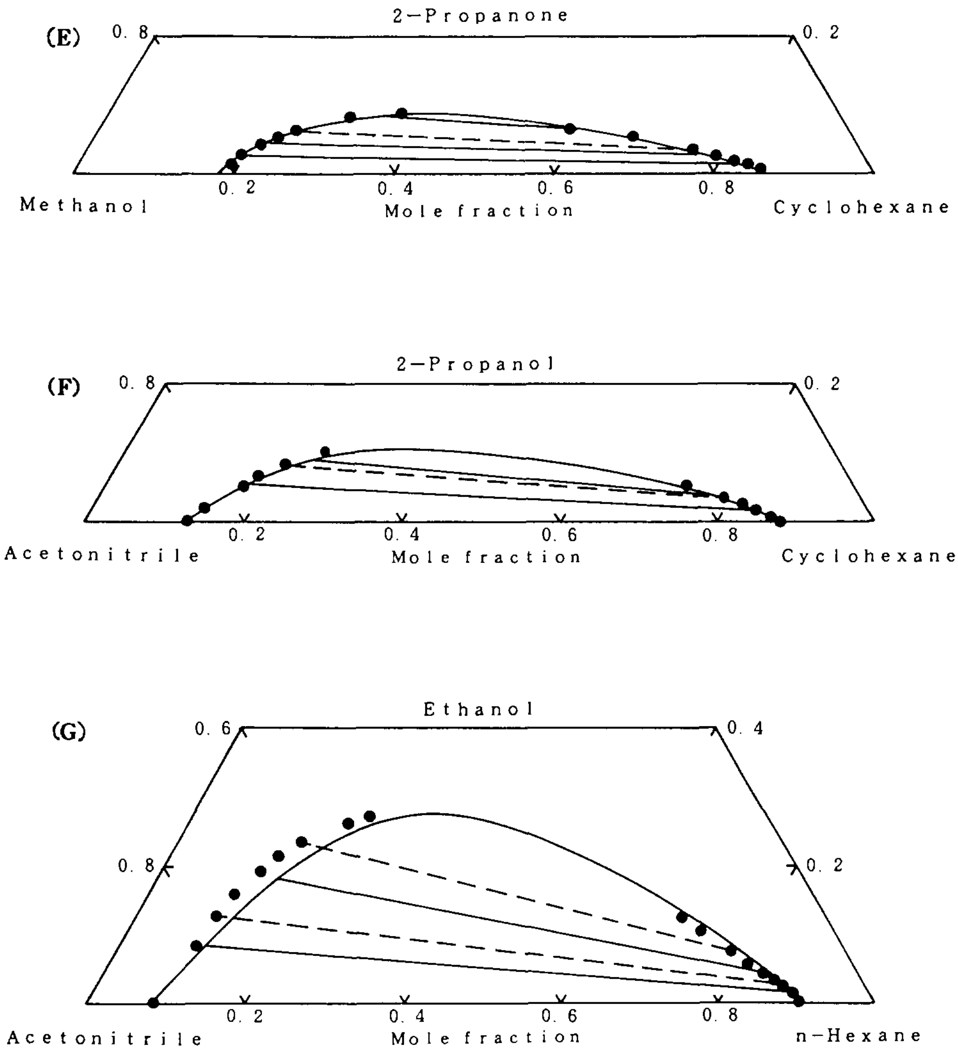


Fig. 4. *(continued)*

the predicted results for twelve ternary mixtures. These results confirm that the model works satisfactorily for binary and ternary alcohol mixtures.

6. Conclusions

The proposed association model is able to reproduce well vapour–liquid equilibria, coexistence curves and excess enthalpy data for binary alcohol mixutres and also to predict ternary phase equilibria and excess enthalpies from only binary information with good accuracy.

Table 6
Ternary predicted results for vapour–liquid equilibria

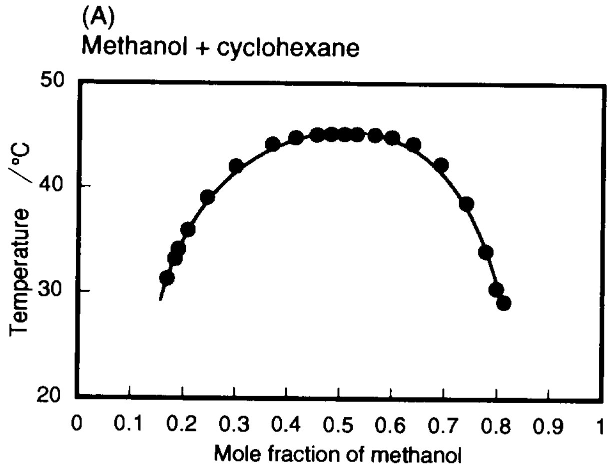
System (A + B + C)	Temp. /°C	No. of data points	Absolute arithmetic mean deviations					Ref.
			$\delta y_A \times 10^3$	$\delta y_B \times 10^3$	$\delta y_C \times 10^3$	δP /Torr	$\delta P/P$ /%	
Methanol + tetrachloromethane + benzene	55	8	1.9	3.0	2.8	2.4	0.4	[27]
Methanol + acetonitrile + benzene	55	17	6.1	4.6	6.5	5.4	1.0	[40]
Ethanol + benzene + cyclohexane	50	19	7.1	4.8	8.4	5.6	1.3	[27]
Ethanol + acetonitrile + benzene	45	21	6.6	6.9	8.5	4.3	1.4	[40]
1-Propanol + acetonitrile + benzene	45	27	5.7	7.9	9.7	3.4	1.4	[40]
2-Propanol + benzene + cyclohexane	40	6	6.3	2.1	5.5	1.5	0.6	[31]
	55	6	8.3	4.0	4.7	4.2	1.0	[31]
2-Propanol + acetonitrile + benzene	50	23	5.8	7.7	7.0	4.6	1.3	[50]

Table 7
Calculated results for mutual solubility data

System (A + B)	Temperature range/°C	Average abs. dev./mol%		Parameters			Ref.
		I[a]	II[b]	A_{AB} A_{BA}	B_{AB} B_{BA}	C_{AB} C_{BA}	
Methanol + cyclohexane	2.46–45.78	1.63	1.27	18370.6754 −2288.2310	−116.4343 15.3783	0.1876 −0.0250	[55]
	29.19–45.14	1.44	0.97	14214.5213 −3311.5416	−87.2200 21.7842	0.1362 −0.0350	[56]
Methanol + *n*-hexane	−28.00–33.36	2.12	1.85	2423.1229 −214.9091	−10.7700 1.6553	0.0125 −0.0024	[57]
	−18.15–32.85	0.89	0.66	2023.0718 −238.2734	−9.3203 1.9022	0.0121 −0.0030	[58]
Methanol + *n*-heptane	−19.50–50.91	1.76	1.87	1223.3910 −19.4855	−3.0593 0.2957		[55]
	18.00–50.00	0.47	0.13	1612.4355 −512.4692	−6.9209 3.7518	0.0083 −0.0060	[59]
	−3.15–50.85	1.32	0.78	−130.1021 −186.9953	6.1049 1.4514	−0.0154 −0.0020	[58]
	25.00–50.00	0.34	0.33	113.4234 −44.8989	2.1438 0.7158	−0.0047 −0.0011	[37]
Methanol + *n*-octane	11.85–61.85	0.40	0.26	2142.4758 −307.4294	−9.3567 2.2824	0.0109 −0.0033	[58]
	25.00–60.00	0.27	0.18	7310.0163 −688.3309	−42.0463 4.6993	0.0625 −0.0072	[37]
Methanol + *n*-hexadecane	26.85–136.85	1.26	1.40	2115.5522 −11.3755	−5.4714 0.3521		[58]
Ethanol + *n*-hexadecane	25.00–52.10	1.77	0.58	18632.7077 −1750.8946	−113.4959 11.4965	0.1761 −0.0183	[30]
	26.85–51.85	0.72	0.43	15599.3832 −1388.3573	−93.4688 9.0915	0.1431 −0.0143	[58]

[a] I, linear temperature dependence of the energy parameters assumed.

[b] II, quadratic temperature dependence of the energy parameters assumed.



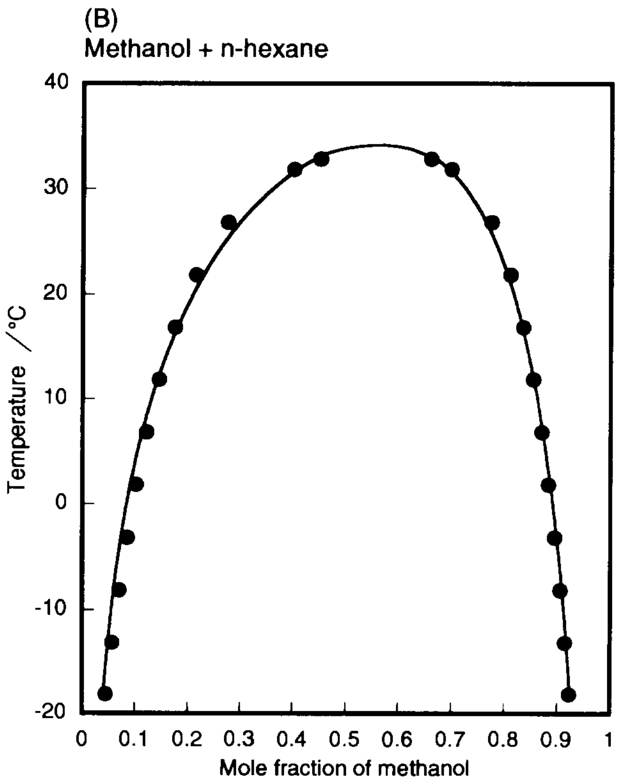
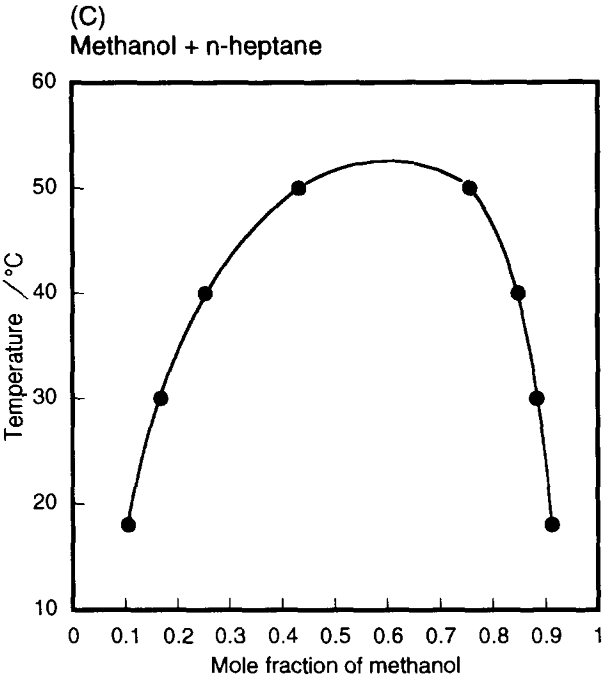


Fig. 5. Calculated coexistence curves for alcohol + saturated hydrocarbon mixtures: Calculated, ——. Experimental: ●, (A) methanol + cyclohexane [56]; (B) methanol + *n*-hexane [58]; (C) methanol + *n*-heptane [59]; (D) ethanol + *n*-hexadecane [58].



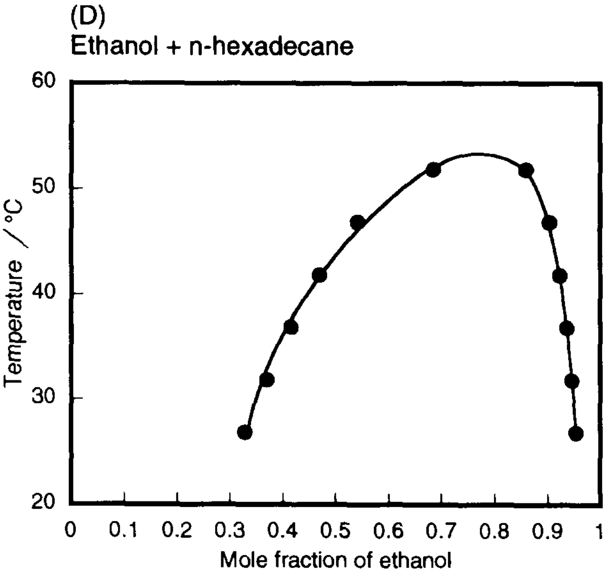
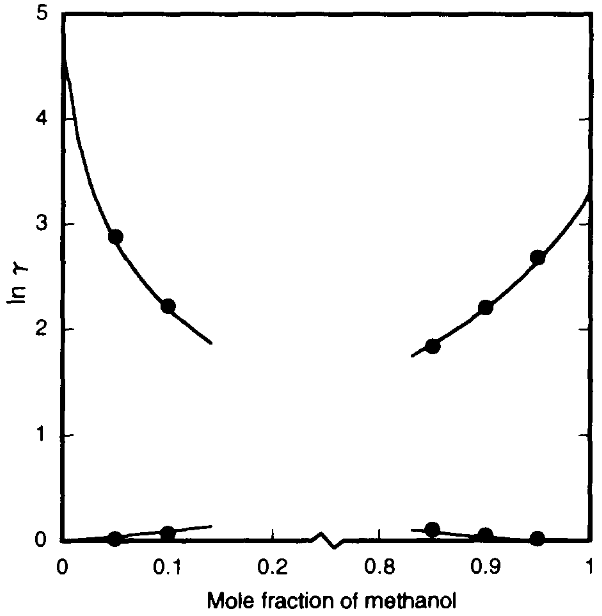


Fig. 5. *(continued)*

(A)
Methanol + cyclohexane at 25°C



(B)
Methanol + cyclohexane at 30°C

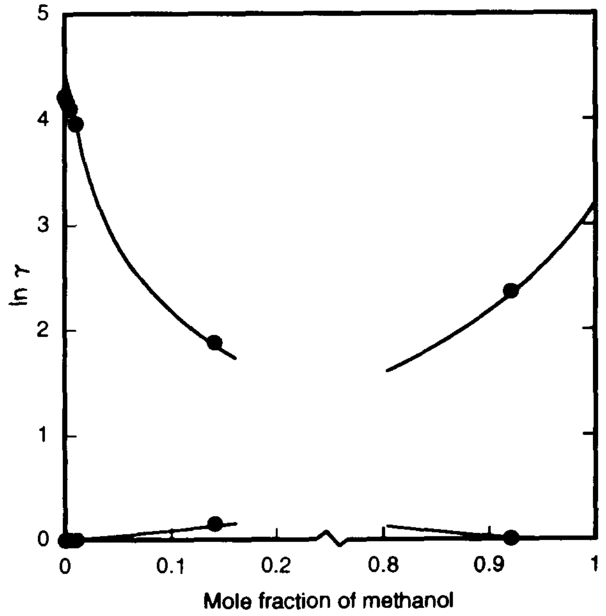
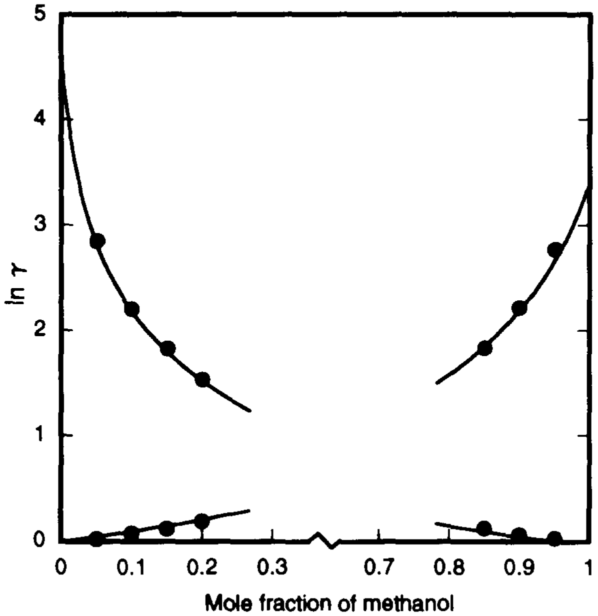


Fig. 6. Activity coefficients for methanol + cyclohexane. Predicted, ——. Experimental: ●, (A) data of Hwang and Robinson [60] at 25°C; (B) data of Goral et al. [40] at 30°C.


(A)
Methanol + n-hexane at 25°C

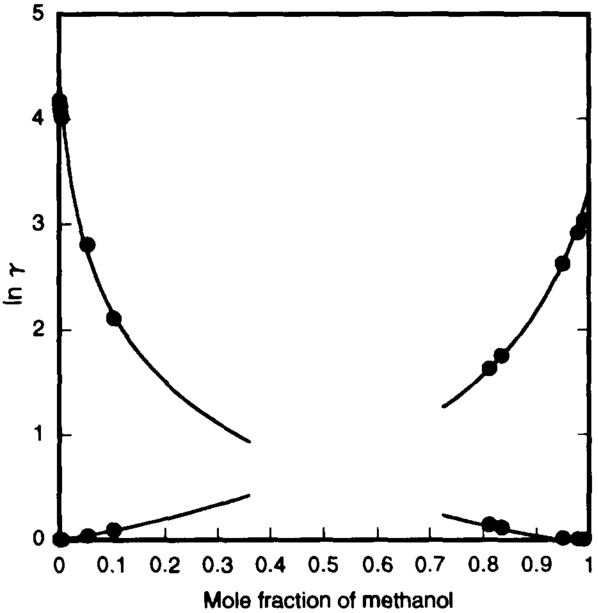
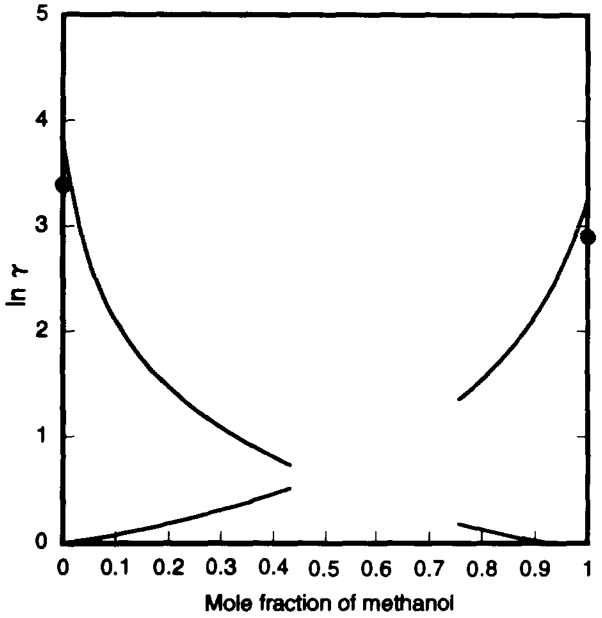

(B)
Methanol + n-hexane at 30°C

Fig. 7. Activity coefficients for methanol + n-hexane. Predicted, ——. Experimental: ●, (A) data of Hwang and Robinson [60] at 25°C; (B) data of Goral et al. [40] at 30°C.

(A)
Methanol + n-heptane at 50°C



(B)
Methanol + n-octane at 20°C

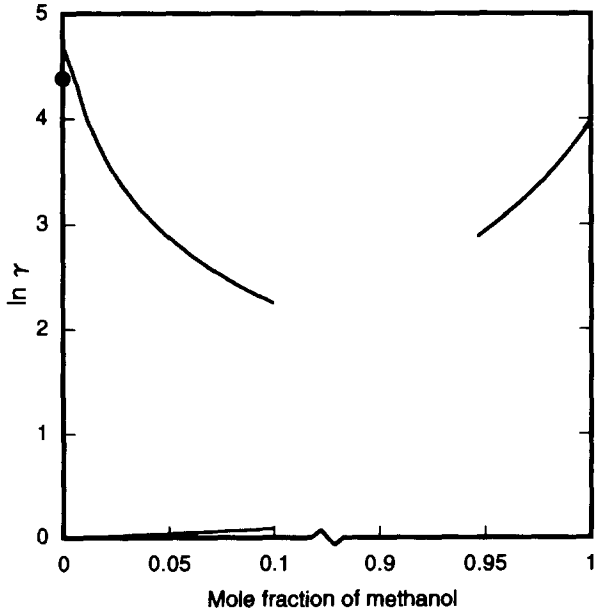


Fig. 8. Activity coefficients for (A) methanol + n-heptane and (B) methanol + n-octane. Predicted, —; Experimental: ●, (A) data of Tochigi and Kojima [61] at 50°C; (B) data of Thomas et al. [62] at 20°C

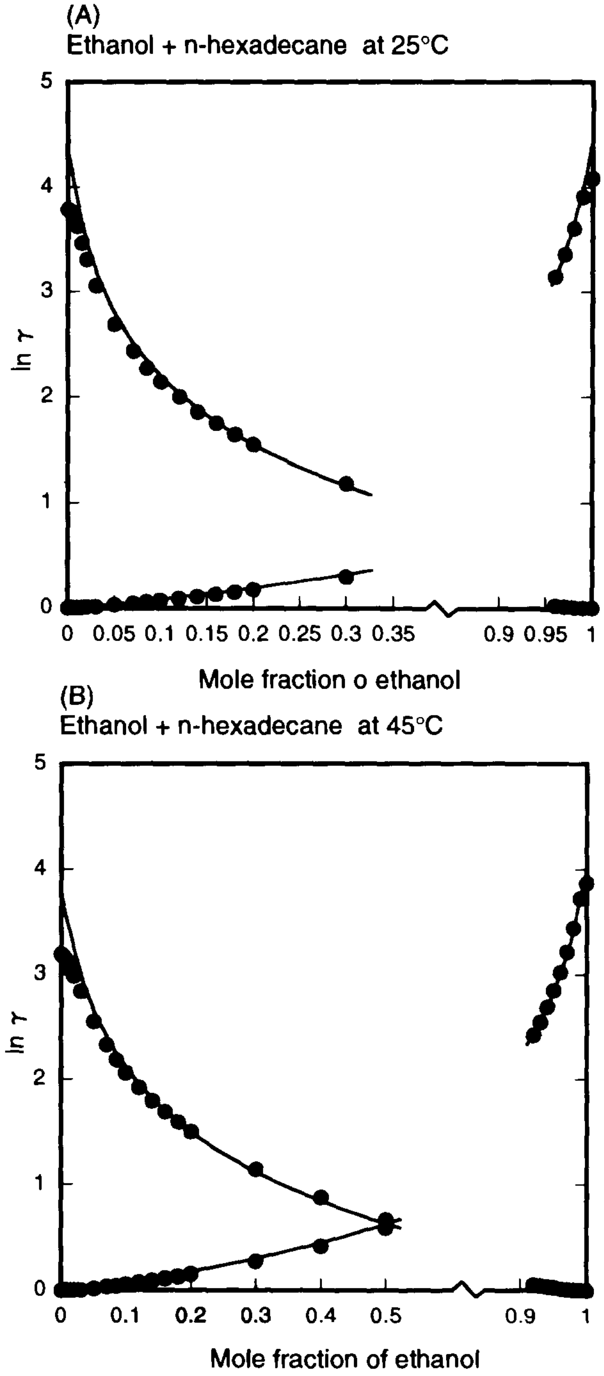


Fig. 9. Activity coefficients for ethanol + *n*-hexadecane [30]. Predicted, ——. Experimental: ●, (A) at 25°C; (B) at 45°C.

Table 8
Calculated results for binary excess molar enthalpies

System (A + B)	Temp./°C	No. of data points	Abs. arith. mean dev. /J mol^{-1}	Parameters				Ref.
				C_{AB}/K	D_{AB}	C_{BA}/K	D_{BA}	
Methanol + benzene	25	10	8.54	364.53	3.3339	−510.10	−2.4960	[63]
Methanol + tetrachloromethane	25	19	2.58	633.54	2.9134	141.58	1.2471	[64]
Methanol + acetonitrile	25	14	3.42	238.70	0.7110	573.08	1.1868	[64]
	35	14	3.12	143.18	0.3382	604.35	1.0823	[64]
Methanol + 2-propanone	25	19	4.05	198.47	0.0925	744.13	1.4873	[65]
	50	20	7.87	610.43	1.7449	168.41	−0.7452	[63]
Ethanol + cyclohexane	25	20	5.52	436.92	1.5470	107.14	−0.6289	[63]
Ethanol + *n*-hexane	25	14	3.82	634.62	2.2414	107.07	−0.3943	[63]
	45	8	2.51	561.79	1.7038	124.75	−0.3403	[63]
Ethanol + benzene	25	10	1.86	1141.26	2.4803	401.46	2.0255	[66]
Ethanol + *p*-xylene	25	16	4.49	1689.15	2.1693	167.18	0.9145	[63]
Ethanol + 2-propanone	25	19	2.07	182.13	−0.6203	497.42	0.0273	[67]
Ethanol + 2-butanone	25	17	6.49	208.70	−0.6830	884.89	0.7828	[64]
1-Propanol + *n*-heptane	25	19	2.27	574.82	2.1434	−156.37	−1.0933	[66]
1-Propanol + cyclohexane	25	18	3.73	174.19	0.2172	−136.39	−0.6663	[63]
1-Propanol + benzene	25	10	6.80	400.50	0.5603	718.56	3.2081	[68]
1-Propanol + *p*-xylene	25	16	7.22	574.47	1.2814	256.21	1.0989	[63]
1-Propanol + tetrachloromethane	25	19	4.51	151.14	−0.4906	104.81	1.8893	[64]
1-Propanol + acetonitrile	25	22	2.85	−60.21	−1.6788	660.64	0.6705	[69]

1-Propanol + ethyl acetate	25	23	10.80	31.65	−1.1073	1015.94	2.1516	[70]
1-Propanol + 2-propanone	25	19	1.38	45.50	−1.4230	520.91	0.0785	[71]
1-Propanol + 2-butanone	25	19	1.98	113.88	−1.1115	519.83	0.3064	[72]
2-Propanol + cyclohexane	25	18	2.70	810.37	3.9985	−135.93	−1.3873	[63]
2-Propanol + methylcyclohexane	25	19	8.67	168.50	0.9836	−105.20	−1.4240	[63]
2-Propanol + benzene	25	17	8.51	405.42	1.5162	−60.28	−0.9512	[63]
2-Propanol + toluene	25	10	9.18	815.12	2.5611	20.92	−0.4679	[68]
2-Propanol + *p*-xylene	25	17	4.27	1543.18	3.4844	−24.32	−0.7599	[63]
2-Propanol + tetrachloromethane	25	19	6.76	−47.90	−1.5686	167.73	3.0640	[64]
2-Propanol + acetonitrile	25	19	3.38	−76.08	−1.7680	625.04	−0.1469	[69]
2-Propanol + ethyl acetate	25	19	6.80	−32.32	−1.5486	911.99	2.4360	[70]
1-Butanol + cyclohexane	25	26	5.15	775.35	3.3835	−197.31	−1.2366	[64]
1-Butanol + *n*-decane	25	48	2.90	720.30	2.6662	−145.99	−1.2800	[63]
1-Butanol + benzene	25	25	9.56	138.94	−0.8623	169.78	1.2744	[68]
1-Butanol + *p*-xylene	25	32	9.01	355.70	0.3174	111.45	0.6293	[63]
2-Butanol + benzene	25	18	6.97	443.27	2.5800	73.33	−1.1139	[73]
tert-Butanol + benzene	27	8	10.82	1469.93	3.0557	514.66	−0.6856	[63]
	35	8	9.16	838.40	2.9791	488.28	−0.4177	[63]
Benzene + cyclohexane	25	24	1.53	467.26	1.5183	28.52	−1.3781	[74]
Benzene + methylcyclohexane	25	17	2.01	297.77	0.9555	39.26	−1.4523	[74]
p-Xylene + cyclohexane	25	18	0.42	286.78	0.7762	−34.64	−0.8511	[74]
Toluene + cyclohexane	25	12	4.66	341.88	1.1794	−18.32	−1.0876	[74]
2-Propanone + benzene	25	19	2.05	298.33	0.7977	295.87	0.9190	[64]
2-Butanone + benzene	25	24	5.08	98.78	−0.0528	27.44	0.5476	[63]

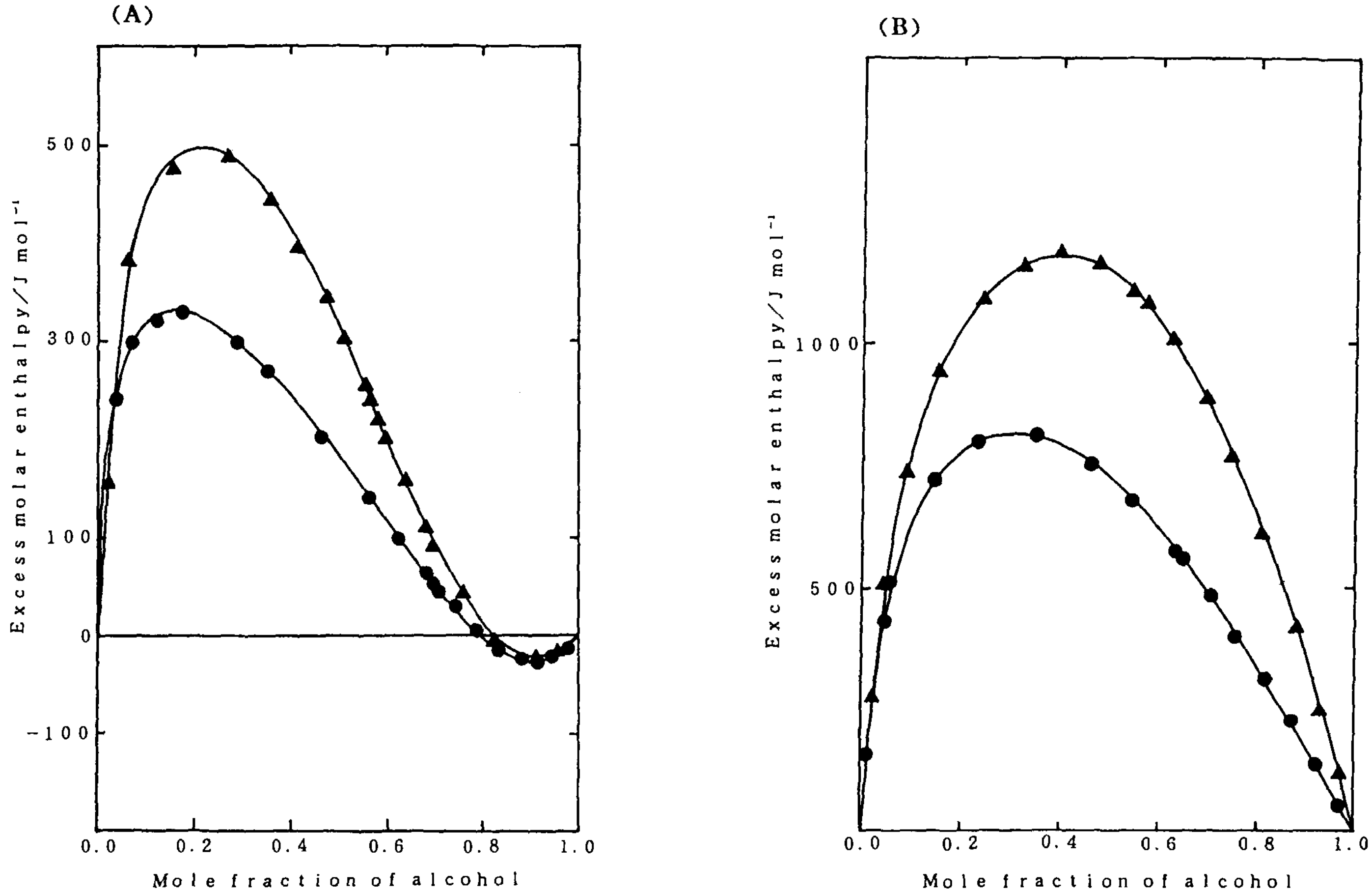


Fig. 10. Excess molar enthalpies for binary mixtures containing one alcohol at 25°C. Calculated, ——. Experimental: (A) ●, methanol + tetrachloromethane [64]; ▲, 1-propanol + tetrachloromethane [64]; (B) ●, ethanol + *p*-xylene [62]; ▲, 2-propanol + *p*-xylene [62].

Table 9
Ternary predicted results for excess molar enthalpies at 25°C

System (A + B + C)	No. of data points	Absolute arithmetic mean dev. ΔH^E/J mol^{-1}	Absolute arithmetic mean dev. $\Delta H^E/H^E$/%	Ref.
Methanol + 2-propanone + benzene	57	13.60	2.70	[65]
Ethanol + *p*-xylene + cyclohexane	59	9.58	1.50	[64]
Ethanol-2-propanone + benzene	57	10.60	1.57	[67]
Ethanol + 2-butanone + benzene	42	14.40	2.46	[75]
1-Propanol + *p*-xylene + cyclohexane	42	12.51	1.53	[64]
1-Propanol + 2-propanone + benzene	57	8.31	1.12	[71]
1-Propanol + 2-butanone + benzene	54	9.55	1.64	[72]
2-Propanol + bezene + cyclohexane	67	19.80	2.20	[64]
2-Propanol + benzene + methylcyclohexane	61	12.27	1.27	[74]
2-Propanol + toluene + cyclohexane	56	10.55	1.47	[74]
2-Propanol + *p*-xylene + cyclohexane	55	15.08	1.67	[64]
1-Butanol + benzene + cyclohexane	43	15.46	1.58	[64]

References

[1] W. E. Acree, Jr., Thermodynamic Properties of Nonelectrolyte Solutions, Academic Press, Orlando, FL, 1984.
[2] I. Nagata, Z. Phys. Chem. N. F., 107 (1977) 39–52.
[3] I. Nagata, Z. Phys. Chem., Leipzig, 259 (1978) 1151–1159.
[4] V. Brandani, Fluid Phase Equilibria, 12 (1983) 87–104.
[5] I. Nagata, M. Rogalski and K. Miyamoto, Thermochim. Acta, 224 (1993) 59–69.
[6] I. Nagata and K. Takeuchi, Thermochim. Acta, 240 (1994) 31–46.
[7] I. Nagata and M. Notoh, Thermochim. Acta, 242 (1994) 117–130.
[8] C. F. Spencer and R. P. Danner, J. Chem. Eng. Data, 17 (1972) 236–241.
[9] J. G. Hayden and J. P. O'Connell, Ind. Eng. Chem., Process Des. Dev., 14 (1975) 209–216.
[10] J. M. Prausnitz, T. F. Anderson, E. A. Grens, C. A. Eckert, R. Hsieh and J. P. O'Connell, Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice-Hall, Englewood Cliffs, NJ, 1980.
[11] T. Hofman and I. Nagata, Fluid Phase Equilibria, 25 (1986) 113–128.
[12] I. Nagata, Thermochim. Acta, 107 (1986) 199–217.
[13] D. Ambrose, J. H. Ellender, C. H. S. Sprake and R. Towsend, J. Chem. Thermodyn., 8 (1976) 165–178.
[14] T. Boublik, V. Fried and E. Hála, The Vapour Pressures of Pure Substances, 2nd edn., Elsevier, Amsterdam, 1984.
[15] R. H. Stokes and C. Burfitt, J. Chem. Thermodyn., 5 (1973) 623–631.
[16] T. Hofman and I. Nagata, Fluid Phase Equilibria, 28 (1986) 233–252.
[17] J. Polak and G. C. Benson, J. Chem. Thermodyn., 3 (1971) 235–242.
[18] V. Majer, V. Svoboda and V. Hynek, J. Chem. Thermodyn., 16 (1984) 1054–1066.
[19] S. H. Vera, S. G. Sayegh and G. A. Ratcliff, Fluid Phase Equilibria, 1(1977) 113–135.
[20] J. A. Riddick and W. B. Bunger, Organic Solvents, Wiley-Interscience, New York, 3rd edn., 1970.
[21] I. Brown and J. Smith, Aust. J. Chem., 7 (1954) 269–272.
[22] J. A. Nelder and R. Mead, Comput. J., 7 (1965) 308–313.
[23] I. Nagata and K. Miyamoto, Fluid Phase Equilibria, 56 (1990) 203–218.
[24] I. Nagata, Fluid Phase Equilibria, 19 (1985) 153–174.
[25] I. Nagata and K. Tamura, Thermochim. Acta, 77 (1984) 281–297.
[26] I. Nagata and K. Tamura, Thermochim. Acta, 57 (1982) 331–349.

[27] J. Gmehling and U. Onken, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols, DECHEMA Chemistry Data Ser., Vol. I, Part 2a, DECHEMA, Frankfurt am Main, Germany, 1977.

[28] V. R. Bhethanabotla and S. W. Campbell, Fluid Phase Equilibria, 62 (1991) 239–258

[29] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Supplement 1), DECHEMA Chemistry Data Ser., Vol. I, Part 2c, DECHEMA, Frankfurt am Main, Germany, 1982.

[30] H. T. French, A. Richards and R. H. Stokes, J. Chem. Thermodyn., 11 (1979) 671–686.

[31] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols, DECHEMA Chemistry Data Ser., Vol. I, Part 2b, DECHEMA, Frankfurt am Main, Germany, 1978.

[32] H. C. Van Ness and M. M. Abbott, Int. Data Ser., Ser. A, 5 (1977) 13–14.

[33] H. T. French, J. Solution Chem., 12 (1983) 869–887.

[34] C. Berro and A. Péneloux, J. Chem. Eng. Data, 29 (1984) 206–210.

[35] I. Nagata and K. Katoh, Thermochim. Acta, 39 (1980) 45–62.

[36] I. Nagata, K. Katoh and J. Koyabu, Thermochim. Acta, 47 (1981) 225–233.

[37] H. Higashiuchi, Y. Sakurai, Y. Iwai, Y. Arai and M. Nagatani, Fluid Phase Equilibria, 36 (1987) 35–47.

[38] I. Nagata, Thermochim. Acta, 114 (1987) 227–238.

[39] T. Ohta, J. Koyabu and I. Nagata, Fluid Phase Equilibria, 7 (1981) 65–73.

[40] J. Gmehling, U. Onken and J. R. Rarey-Nies, Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Supplement 3), DECHEMA Chemistry Data Ser., Vol. I. Part 2e, DECHEMA, Frankfurt am Main, Germany, 1988.

[41] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aliphatic Hydrocarbons C_4–C_6, DECHEMA Chemistry Data Ser., Vol. I, Part 6a, DECHEMA, Frankfurt am Main, Germany, 1980.

[42] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aromatic Hydrocarrbons, DECHEMA Chemistry Data Ser., Vol. 1, Part 7, DECHEMA, Frankfurt am Main, Germany, 1980.

[43] T. Ohta and I. Nagata, J. Chem. Eng. Data, 28 (1983) 398–402.

[44] H. Arm and D. Bankay, Helv. Chim. Acta, 52 (1969) 279–281.

[45] I. Nagata, T. Ohta, T. Takahashi and K. Gotoh, J. Chem Eng. Jpn., 6 (1973) 129–134.

[46] S. P. Puri, J. Polak and J. A. Ruether, J. Chem. Eng. Data, 19 (1974) 87–89.

[47] J. Gmehling, U. Onken and B. Kolbe, Vapor–Liquid Equilibrium Data Collection, Aliphatic Hydrocarbons (Supplement 1), DECHEMA Chemistry Data Ser., Vol. I, Part 6c, DECHEMA, Frankfurt am Main, 1983.

[48] I. Nagata and T. Ohta, J. Chem. Eng. Data, 28 (1983) 256–259.

[49] J. M. Sørensen and W. Arlt, Liquid–Liquid Equilibrium Data Collection, Binary Systems, DECHEMA Chemistry Data Ser., Vol. V, Part 1, DECHEMA, Frankfurt am Main, Germany, 1979.

[50] I. Nagata, J. Chem. Eng. Data, 30 (1985) 363–365

[51] I. Nagata, Thermochim. Acta, 208 (1992) 61–71.

[52] E. A. Macedo and P. Rasmussen, Liquid–Liquid Equilibrium Data Collection (Supplement 1), DECHEMA Chemistry Data Ser., Vol. V, Part 4, DECHEMA, Frankfurt am Main, Germany, 1987.

[53] M. Yasuda, H. Kawade and T. Katayama, Kagaku Kogaku Ronbunshu, 1 (1975) 172–175.

[54] J. M. Sørensen and W. Arlt, Liquid–Liquid Equilibrium Data Collection, Ternary Systems, DECHEMA Chemistry Data Ser., Vol. V, Part 2, DECHEMA, Frankfurt am Main, Germany, 1980.

[55] H. Hradetzky and J. H. Bittrich, Int. Data Ser., Ser. A, 14 (1986) 218.

[56] E. L. Eckfeldt and W. W. Lucasse, J. Phys. Chem., 47 (1943) 164–183.

[57] H. Hradetzky and D. A. Lempe, Fluid Phase Equilibria, 69 (1991) 285–301.

[58] A. Skrzecz, Thermochim. Acta, 182 (1991) 123–131.

[59] G. Tagliavini and G. Arich, Ric. Sci., 28 (1958) 1902–1910.

[60] S. C. Hwang and R. L. Robinson, Jr., J. Chem. Eng. Data, 22 (1977) 319–325.

[61] K. Tochigi and K. Kojima, J. Chem. Eng. Jpn., 9 (1976) 267–273.

[62] E. R. Thomas, B. A. Newman, T. C. Long, D. A. Wood and C. A. Eckert, J. Chem. Eng. Data, 27 (1982) 399–405.

[63] C. Christensen, J. Gmehling, R. Rasmussen and U. Weidlich, Heats of Mixing Data Collection, Binary Systems, DECHEMA Chemistry Data Ser., Vol. III, Part 1, DECHEMA, Frankfurt am Main, Germany, 1984.
[64] J. Gmehling and T. Holderbaum, Heats of Mixing Data Collection, Binary and Multicomponent Systems (Supplement 1), DECHEMA Chemistry Data Ser., Vol. III, Part 3, DECHEMA, Frankfurt am Main, Germany, 1989.
[65] I. Nagata, Thermochim. Acta, 236 (1994) 23–30.
[66] M. Bender, J. Hauser and A. Heintz, Ber. Bunsenges. Phys. Chem., 95 (1991) 801–811.
[67] I. Nagata and A. Książczak, J. Chem. Thermodyn., 26 (1994) 165–169.
[68] R. V. Mrazek and H. C. Van Ness, AIChE J., 7 (1961) 190–195.
[69] K. Tamura and I. Nagata, J. Chem. Eng. Data, 31 (1986) 410–413.
[70] J. P. E. Grolier and A. Viallard, J. Chim. Phys., 68 (1971) 1442–1448.
[71] I. Nagata and K. Takeuchi, Thermochim. Acta, 242 (1994) 103–110.
[72] K. Tamura and I. Nagata, J. Chem. Thermodyn., 23 (1991) 359–364.
[73] I. Nagata and K. Tamura, Fluid Phase Equilibria, 41 (1988) 127–139.
[74] C. Christensen, J. Gmehling, R. Rasmussen and U. Weidlich, Heats of Mixing Data Collection, Binary and Multicomponent Systems, DECHEMA Chemistry Data Ser., Vol. III, Part 2, DECHEMA, Frankfurt am Main, Germany, 1984.
[75] I. Nagata and K. Tamura, J. Chem. Thermodyn., 22 (1990) 279–283.