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THERMODYNAMICS OF SOLUTIONS OF METHANOL AND SOLVATING COMPONENTS

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ABSTRACT

A model is proposed to correlate the excess Gibbs free energies and excess enthalpies of binary solutions of methanol and a solvating component. Solution nonideality from ideal solutions is given by the sum of the chemical contribution term, which is due to self-association of methanol and solvation between methanol and a nonassociating component, and the physical contribution term with allowance for the NRTL equation. The model uses the following data for methanol: two enthalpies for formation of the hydrogen bonds for the dimer and all larger polymeric species; three equilibrium constants of stepwise association for the dimer, trimer and other polymeric species, and an equilibrium constant for cyclic species of more than tetramer. The association model further includes an additional solvation equilibrium to allow for the interaction between the terminal hydroxyl group of methanol polymeric species and a solvating component. The model is extended to predict vapor–liquid equilibria, liquid–liquid equilibria and excess enthalpies for ternary solutions containing methanol and two nonassociating components from only binary information. Calculated results are in good agreement with experimental data as shown by selected illustrative examples.

NOTATION

C_i, D_i	constants of eqn. (54)
G_{ij}	coefficients 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 dimer
h_A	enthalpy of hydrogen bond formation in i-mer
h_{AB}, h_{AC}	enthalpies of formation of chemical complexes A_iB and A_iC
h_{BC}	enthalpy of formation of chemical complex B_1C_1
h_{B_2C}	enthalpy of formation of chemical complex B_2C_1

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h_f	total enthalpy of chemical complex formation in solution
h^E	excess enthalpy
K_2	equilibrium constant of dimer formation
K_3	equilibrium constant of open chain trimer formation
K	equilibrium constant of open chain i-mer formation, $i>3$
K_{cy}	equilibrium constant for cyclization of open chain i-mer as defined by θ/i, $i>4$
K_{AB}, K_{AC}	equilibrium constants of formation of chemical complexes A_iB and A_iC
K_{BC}	equilibrium constant of formation of chemical complex B_1C_1
K_{B_2C}	equilibrium constant of formation of chemical complex B_2C_1
n	number of moles of a particular species
P	total pressure
P_i^s	saturated vapor pressure of pure component i
R	gas constant
S	stoichiometric sum
T	absolute temperature
v_i^L	molar liquid volume of pure component i
x_i	liquid phase mole fraction of component i
y_i	vapor phase mole fraction of component i
z	coefficient as defined by Kx_{A_1}

Greek letters

α_{ij}	nonrandomness parameter of NRTL equation
γ_i	activity coefficient of component i
θ	constant related to K_{cy}
τ_{ji}	coefficient as defined by $(g_{ji}-g_{ii})/RT$
ϕ_i	vapor phase fugacity coefficient of component i
ϕ_i^s	vapor phase fugacity coefficient of pure component i at system temperature T and pressure P_i^s

Subscripts

A	methanol
A_1, A_i	methanol monomer and i-mer
A_iB, A_iC	complex formation between methanol i-mer and component B or C
BC	1 : 1 complex between components B and C
B_2C	2 : 1 complex between components B and C
chem	chemical
f	complex formation
i, j, k	components
phys	physical
1, 2, 3	methanol and unassociated components

Superscripts

E	excess
L	liquid
s	saturation
*	pure methanol

INTRODUCTION

Stokes [1] presented a chemical association model which can account for the thermodynamic, spectroscopic and dielectric properties of dilute solutions of ethanol in cyclohexane. The model contains three equilibrium constants for the formation of open chains of any length, an equilibrium constant for the formation of cyclic species of more than tetramer, and the Scatchard–Hildebrand interaction term. Vapor pressure and excess enthalpy data for the system ethanol-*p*-xylene [2] were interpreted by the association model with an addition of a solvation equilibrium to allow for the interaction between the terminal hydroxyl group of ethanol chains and *p*-xylene. The theory of Stokes gives generally a good fit to the experimental data in the low concentration range of ethanol and cannot treat excess enthalpy data over the whole concentration range. This may be due to the inadequacy of the Scatchard–Hildebrand equation for molecular interactions. One must present a refined version of the model of Stokes to reproduce well the thermodynamic properties of alcohol solutions over the entire concentration range. This paper is concerned with such a modified model to calculate vapor–liquid and liquid–liquid equilibria and excess enthalpies for binary and ternary solutions of methanol and nonassociating components, because a considerable amount of experimental data for these properties have been available in the literature.

THEORY

Binary systems

Following Stokes' method, we assume four stepwise equilibrium constants defined in terms of mole fraction statistics for highly associated alcohol. Open chain reactions are:

$$\mathrm{A}+\mathrm{A}=\mathrm{A}_2 \qquad K_2=x_{\mathrm{A}_2}/x_{\mathrm{A}_1}^2 \tag{1}$$

$$\mathrm{A}_2+\mathrm{A}=\mathrm{A}_3 \qquad K_3=x_{\mathrm{A}_3}/x_{\mathrm{A}_2}x_{\mathrm{A}_1} \tag{2}$$

$$\mathrm{A}_i+\mathrm{A}=\mathrm{A}_{i+1} \qquad K=x_{\mathrm{A}_{i+1}}/x_{\mathrm{A}_i}x_{\mathrm{A}_1} \qquad i\geqslant 3 \tag{3}$$

Cyclic groups are defined in equilibrium with the open chains bigger than tetramer.

$$\mathrm{A}_{i(\mathrm{linear})}=\mathrm{A}_{i(\mathrm{cyclic})} \qquad K_{\mathrm{cy}}=\theta/i,\ i>4 \tag{4}$$

Additionally we assume a solvation equilibrium between the terminal hydroxyl group of alcohol chains and one solvating component such as benzene, carbon tetrachloride, chloroform, acetone and ethyl ether.

$$A_{i(\text{linear})} + B = A_iB \quad K_{AB} = x_{A_iB_1}/x_{A_i}x_{B_1} \tag{5}$$

According to Prigogine and Defay [3] the excess Gibbs free energy and the activity coefficients of associated component (= component 1) and nonassociated component (= component 2) for the chemical contribution due to association and solvation are given by

$$g^E_{\text{chem}}/RT = x_1 \ln(x_{A_1}/x^*_{A_1}x_1) + x_2 \ln(x_{B_1}/x_2) \tag{6}$$

$$(\ln \gamma_1)_{\text{chem}} = \ln(x_{A_1}/x^*_{A_1}x_1) \tag{7}$$

$$(\ln \gamma_2)_{\text{chem}} = \ln(x_{B_1}/x_2) \tag{8}$$

For the physical contribution we take the NRTL equation of Renon and Prausnitz [4] in place of the Scatchard–Hildebrand equation used by Stokes.

$$g^E_{\text{phys}}/RT = x_1x_2[\tau_{21}G_{21}/(x_1 + x_2G_{21}) + \tau_{12}G_{12}/(x_2 + x_1G_{12})] \tag{9}$$

$$(\ln \gamma_1)_{\text{phys}} = x_2^2[\tau_{21}G_{21}^2/(x_1 + x_2G_{21})^2 + \tau_{12}G_{12}/(x_2 + x_1G_{12})^2] \tag{10}$$

$$(\ln \gamma_2)_{\text{phys}} = x_1^2[\tau_{12}G_{12}^2/(x_2 + x_1G_{12})^2 + \tau_{21}G_{21}/(x_1 + x_2G_{21})^2] \tag{11}$$

where

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

$$G_{21} = \exp(-\alpha_{21}\tau_{21}) \qquad G_{12} = \exp(-\alpha_{12}\tau_{12}) \tag{13}$$

Then the final expressions of the excess Gibbs free energy and activity coefficients are given by the sum of these two contributions.

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

$$\ln \gamma_1 = (\ln \gamma_1)_{\text{chem}} + (\ln \gamma_1)_{\text{phys}} \tag{15}$$

$$\ln \gamma_2 = (\ln \gamma_2)_{\text{chem}} + (\ln \gamma_2)_{\text{phys}} \tag{16}$$

The following mass balance equations [eqns. (17)–(21)] are used to obtain the mole fractions of the monometric species, x_{A_1}, $x^*_{A_1}$ and x_{B_1}.

$$\begin{aligned} x_1 &= n_1/(n_1 + n_2) \\ &= \frac{\sum_{i=1}^{\infty} in_{A_i(\text{linear})} + \sum_{i=1}^{\infty} in_{A_iB_1} + \sum_{i=5}^{\infty} in_{A_i(\text{cyclic})}}{\sum_{i=1}^{\infty} in_{A_i(\text{linear})} + \sum_{i=1}^{\infty} in_{A_iB_1} + \sum_{i=5}^{\infty} in_{A_i(\text{cyclic})} + \sum_{i=0}^{\infty} n_{A_iB_1}} \\ &= \Big\{(1 + K_{AB}x_{B_1})\big[x_{A_1} + 2K_2x_{A_1}^2 + K_2K_3(3 - 2z)x_{A_1}^3/(1 - z)^2\big] \\ &\quad + K_2K_3K^2\theta x_{A_1}^5/(1 - z)\Big\}/S \end{aligned} \tag{17}$$

$$x_2 = n_2/(n_1+n_2)$$

$$= \frac{\sum_{i=0}^{\infty} n_{\mathrm{A}_i\mathrm{B}_1}}{\sum_{i=1}^{\infty} i n_{\mathrm{A}_i(\mathrm{linear})} + \sum_{i=1}^{\infty} i n_{\mathrm{A}_i\mathrm{B}_1} + \sum_{i=5}^{\infty} i n_{\mathrm{A}_i(\mathrm{cyclic})} + \sum_{i=0}^{\infty} n_{\mathrm{A}_i\mathrm{B}_1}}$$

$$= \left\{K_{\mathrm{AB}} x_{\mathrm{B}_1}\left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3/(1-z)\right] + x_{\mathrm{B}_1}\right\}/S \tag{18}$$

where $z = K x_{\mathrm{A}_1}$ and S is the stoichiometric sum given by

$$S = (1 + K_{\mathrm{AB}} x_{\mathrm{B}_1})\left[x_{\mathrm{A}_1} + 2K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 (3-2z) x_{\mathrm{A}_1}^3/(1-z)^2\right]$$
$$+ K_2 K_3 K^2 \theta x_{\mathrm{A}_1}^5/(1-z)$$
$$+ K_{\mathrm{AB}} x_{\mathrm{B}_1}\left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3/(1-z)\right] + x_{\mathrm{B}_1} \tag{19}$$

The mole fractions of chemical species in the solution keep the following relation.

$$\sum_{i=1}^{\infty} x_{\mathrm{A}_i(\mathrm{linear})} + \sum_{i=5}^{\infty} x_{\mathrm{A}_i(\mathrm{cyclic})} + \sum_{i=0}^{\infty} x_{\mathrm{A}_i\mathrm{B}_1}$$
$$= (1 + K_{\mathrm{AB}} x_{\mathrm{B}_1})\left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + \frac{K_2 K_3 x_{\mathrm{A}_1}^3}{(1-z)}\right] - \frac{K_2 K_3 \theta}{K^3}$$
$$\times\left[\ln(1-z) + z + \frac{z^2}{2} + \frac{z^3}{3} + \frac{z^4}{4}\right]$$
$$+ K_{\mathrm{AB}} x_{\mathrm{B}_1}\left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3/(1-z)\right] + x_{\mathrm{B}_1} = 1 \tag{20}$$

At pure alcohol state eqn. (20) reduces to

$$\sum_{i=1}^{\infty} x_{\mathrm{A}_i(\mathrm{linear})}^* + \sum_{i=5}^{\infty} x_{\mathrm{A}_i(\mathrm{cyclic})}^*$$
$$= \left[x^*_{\mathrm{A}_1} + K_2 x^{*2}_{\mathrm{A}_1} + K_2 K_3 x^{*3}_{\mathrm{A}_1}/(1-z^*)\right] - \frac{K_2 K_3 \theta}{K^3}$$
$$\times\left[\ln(1-z^*) + z^* + z^{*2}/2 + z^{*3}/3 + z^{*4}/4\right] = 1 \tag{21}$$

The excess enthalpy is similarly given by the sum of two contributions: one is chemical and the other physical.

$$h^{\mathrm{E}} = h^{\mathrm{E}}_{\mathrm{chem}} + h^{\mathrm{E}}_{\mathrm{phys}} \tag{22}$$

The chemical contribution term is defined as

$$h^{\mathrm{E}}_{\mathrm{chem}} = h_{\mathrm{f}} - x_1 h_{\mathrm{f}}^* \tag{23}$$

where h_{f} is the total enthalpy of the solution and h_{f}^* is the value of h_{f} at pure alcohol state.

$$h_{\mathrm{f}}=\Bigg\{h_2(n_{\mathrm{A}_2}+n_{\mathrm{A}_2\mathrm{B}_1})+h_{\mathrm{A}}\Bigg[\sum_{i=3}^{\infty}(i-1)n_{\mathrm{A}_i,(\text{linear})}+\sum_{i=5}^{\infty}in_{\mathrm{A}_i,(\text{cyclic})}$$

$$+\sum_{i=3}^{\infty}(i-1)n_{\mathrm{A}_i\mathrm{B}_1}\Bigg]+h_{\mathrm{AB}}\sum_{i=1}^{\infty}n_{\mathrm{A}_i\mathrm{B}_1}\Bigg\}/(n_1+n_2)$$

$$=\Big\{(1+K_{\mathrm{AB}}x_{\mathrm{B}_1})\big[h_2K_2x_{\mathrm{A}_1}^2+h_{\mathrm{A}}K_2K_3x_{\mathrm{A}_1}^3(2-z)/(1-z)^2\big]$$

$$+h_{\mathrm{A}}K_2K_3K^2\theta x_{\mathrm{A}_1}^5/(1-z)$$

$$+h_{\mathrm{AB}}K_{\mathrm{AB}}x_{\mathrm{B}_1}\big[x_{\mathrm{A}_1}+K_2x_{\mathrm{A}_1}^2+K_2K_3x_{\mathrm{A}_1}^3/(1-z)\big]\Big\}/S \tag{24}$$

$$h_{\mathrm{f}}^*=\big[h_2K_2x^{*2}_{\mathrm{A}_1}+h_{\mathrm{A}}K_2K_3x^{*3}_{\mathrm{A}_1}(2-z^*)/(1-z^*)^2$$

$$+h_{\mathrm{A}}K_2K_3K^2\theta x^{*5}_{\mathrm{A}_1}/(1-z^*)\big]/S^* \tag{25}$$

where h_2 is the enthalpy of formation of dimer, h_{A} is the enthalpy of hydrogen bond formation for all open chain alcohol i-mers ($i>2$) as well as cyclic ones, and S^* is the value of S at pure alcohol state.

$$S^*=x^*_{\mathrm{A}_1}+2K_2x^{*2}_{\mathrm{A}_1}+K_2K_3x^{*3}_{\mathrm{A}_1}(3-2z^*)/(1-z^*)^2$$

$$+K_2K_3K^2\theta x^{*5}_{\mathrm{A}_1}/(1-z^*) \tag{26}$$

Application of the Gibbs–Helmholtz equation to $g^{\mathrm{E}}_{\mathrm{phys}}/T$ gives the physical contribution term to the excess enthalpy.

$$h^{\mathrm{E}}_{\mathrm{phys}}=\frac{\partial(g^{\mathrm{E}}_{\mathrm{phys}}/T)}{\partial(1/T)}=Rx_1x_2\Bigg\{\frac{\tau'_{21}G_{21}}{x_1+x_2G_{21}}+\frac{\tau'_{12}G_{12}}{x_2+x_1G_{12}}$$

$$-\alpha_{12}\Bigg[\frac{x_1\tau_{21}G_{21}\tau'_{21}}{(x_1+x_2G_{21})^2}+\frac{x_2\tau_{12}G_{12}\tau'_{12}}{(x_2+x_1G_{12})^2}\Bigg]\Bigg\} \tag{27}$$

where

$$\tau'_{21}=\partial\tau_{21}/\partial(1/T)\qquad \tau'_{12}=\partial\tau_{12}/\partial(1/T) \tag{28}$$

In the correlation of experimental excess enthalpy data, we assume that the energy parameters could be expressed by a linear function of temperature.

$$g_{21}-g_{11}=C_1+D_1(T-273.15)\qquad g_{12}-g_{22}=C_2+D_2(T-273.15) \tag{29}$$

Investigations of complex formation in binary mixtures of chloroform (B = component 1) and acetone (C = component 2) [5,6] justify that the physical contribution can be negligible compared to the chemical contribution so that two complex forming reactions are responsible for all deviations from ideal solution. The McGlashan–Rastogi method of analysis [7] evaluates the equilibrium constants (K_{BC} and K_{B_2C}) and the enthalpies of complex formation (h_{BC} and h_{B_2C}) for the reactions represented by

$$\mathrm{B}+\mathrm{C}=\mathrm{BC} \qquad K_{BC}=x_{B_1C_1}/x_{B_1}x_{C_1} \tag{30}$$

$$2\,\mathrm{B}+\mathrm{C}=\mathrm{B_2C} \qquad K_{B_2C}=x_{B_2C_1}/x_{B_1}^2x_{C_1} \tag{31}$$

The excess Gibbs free energy and excess enthalpy are given by

$$g^E/RT=x_1\ln\frac{x_{B_1}}{x_1}+x_2\ln\frac{1-x_{B_1}}{\left(1+K_{BC}x_{B_1}+K_{B_2C}x_{B_1}^2\right)x_2} \tag{32}$$

$$h^E=x_{B_1}x_{C_1}\left(K_{BC}h_{BC}+x_{B_1}K_{B_2C}h_{B_2C}\right)/\left[1+x_{B_1}x_{C_1}\left(K_{BC}+2x_{B_1}K_{B_2C}\right)\right] \tag{33}$$

The mole fractions of monometric B and C are obtained from eqns. (34) and (35).

$$x_1=\frac{(1+K_{BC})x_{B_1}+K_{B_2C}x_{B_1}^2(2-x_{B_1})}{1+K_{BC}x_{B_1}(2-x_{B_1})+K_{B_2C}x_{B_1}^2(3-2x_{B_1})} \tag{34}$$

$$x_{B_1}+K_{BC}x_{B_1}x_{C_1}+K_{B_2C}x_{B_1}^2x_{C_1}+x_{C_1}=1 \tag{35}$$

In the system benzene–tetrachloromethane only BC complex formation is assumed and the physical interaction term is also included according to the analysis of McGlashan et al. [8]. When there is no complex formation, solution nonideality is described in terms of the physical contribution.

TERNARY SYSTEMS

As a typical example, we present our ternary expressions of the excess Gibbs free energy and excess enthalpy for mixtures of methanol (A = component 1), chloroform (B = component 2) and acetone (C = component 3). We consider self-association of methanol and binary complex formation between two different component molecules, but we do not assume any ternary complexes.

Ternary extension of eqns. (6) and (9) gives g_{chem}^E and g_{phys}^E.

$$g_{\text{chem}}^E=RT\left[x_1\ln\left(x_{A_1}/x_{A_1}^*x_1\right)+x_2\ln\left(x_{B_1}/x_2\right)+x_3\ln\left(x_{C_1}/x_3\right)\right] \tag{36}$$

$$g_{\text{phys}}^E=RT\sum_{i=1}^{3}x_i\frac{\sum_{j=1}^{3}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{3}G_{ki}x_k} \tag{37}$$

where

$$\tau_{ji}=(g_{ji}-g_{ii})/RT \tag{38}$$

$$G_{ji}=\exp(-\alpha_{ji}\tau_{ji}) \tag{39}$$

where $(\ln \gamma_i)_{\mathrm{chem}}$ and $(\ln \gamma_i)_{\mathrm{phys}}$ are separately expressed by

$$(\ln \gamma_1)_{\mathrm{chem}}=\ln(x_{\mathrm{A}_1}/x^*_{\mathrm{A}_1}x_1) \tag{40}$$

$$(\ln \gamma_2)_{\mathrm{chem}}=\ln(x_{\mathrm{B}_1}/x_2) \tag{41}$$

$$(\ln \gamma_3)_{\mathrm{chem}}=\ln(x_{\mathrm{C}_1}/x_3) \tag{42}$$

$$(\ln \gamma_i)_{\mathrm{phys}}=\frac{\sum_{j=1}^{3}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{3}G_{ki}x_k}+\sum_{j=1}^{3}\frac{\sum_{j=1}^{3}x_jG_{ij}}{\sum_{k=1}^{3}G_{kj}x_k}\left(\tau_{ij}-\frac{\sum_{r=1}^{3}x_r\tau_{rj}G_{rj}}{\sum_{k=1}^{3}G_{kj}x_k}\right) \tag{43}$$

The mole number of each component is equal to the sum of mole numbers of chemical species in the mixtures.

$$n_1=\sum_{i=1}^{\infty} in_{\mathrm{A}_i(\mathrm{linear})}+\sum_{i=1}^{\infty} in_{\mathrm{A}_i\mathrm{B}_1}+\sum_{i=1}^{\infty} in_{\mathrm{A}_i\mathrm{C}_1}+\sum_{i=5}^{\infty} in_{\mathrm{A}_i(\mathrm{cyclic})} \tag{44}$$

$$n_2=n_{\mathrm{B}_1}+n_{\mathrm{B}_1\mathrm{C}_1}+2\,n_{\mathrm{B}_2\mathrm{C}_1}+\sum_{i=1}^{\infty} n_{\mathrm{A}_i\mathrm{B}_1} \tag{45}$$

$$n_3=n_{\mathrm{C}_1}+n_{\mathrm{B}_1\mathrm{C}_1}+n_{\mathrm{B}_2\mathrm{C}_1}+\sum_{i=1}^{\infty} n_{\mathrm{A}_i\mathrm{C}_1} \tag{46}$$

Then, the mole fractions of monometric A, B and C are related to the nominal mole fraction of each component and are obtained by solving eqns. (47)–(51).

$$\begin{aligned}x_1=\frac{n_1}{n_1+n_2+n_3}=\Big\{&(1+K_{\mathrm{AB}}x_{\mathrm{B}_1}+K_{\mathrm{AC}}x_{\mathrm{C}_1})\big[x_{\mathrm{A}_1}+2\,K_2x^2_{\mathrm{A}_1}\\&+K_2K_3x^3_{\mathrm{A}_1}(3-2z)/(1-z)^2\big]+K_2K_3K^2\theta x^5_{\mathrm{A}_1}/(1-z)\Big\}/S\end{aligned} \tag{47}$$

$$\begin{aligned}x_2=\frac{n_2}{n_1+n_2+n_3}=\Big\{&x_{\mathrm{B}_1}+K_{\mathrm{BC}}x_{\mathrm{B}_1}x_{\mathrm{C}_1}+2\,K_{\mathrm{B}_2\mathrm{C}}x^2_{\mathrm{B}_1}x_{\mathrm{C}_1}+K_{\mathrm{AB}}x_{\mathrm{B}_1}\\&\times\big[x_{\mathrm{A}_1}+K_2x^2_{\mathrm{A}_1}+K_2K_3x^3_{\mathrm{A}_1}/(1-z)\big]\Big\}/S\end{aligned} \tag{48}$$

$$\begin{aligned}x_3=\frac{n_3}{n_1+n_2+n_3}=\Big\{&x_{\mathrm{C}_1}+K_{\mathrm{BC}}x_{\mathrm{B}_1}x_{\mathrm{C}_1}+K_{\mathrm{B}_2\mathrm{C}}x^2_{\mathrm{B}_1}x_{\mathrm{C}_1}+K_{\mathrm{AC}}x_{\mathrm{C}_1}\\&\times\big[x_{\mathrm{A}_1}+K_2x^2_{\mathrm{A}_1}+K_2K_3x^3_{\mathrm{A}_1}/(1-z)\big]\Big\}/S\end{aligned} \tag{49}$$

where the stoichiometric sum is

$$S=(1+K_{AB}x_{B_1}+K_{AC}x_{C_1})\left[x_{A_1}+2\,K_2x_{A_1}^2+K_2K_3x_{A_1}^3(3-2z)/(1-z)^2\right]$$
$$+K_2K_3K^2\theta x_{A_1}^5/(1-z)+(K_{AB}x_{B_1}+K_{AC}x_{C_1})\left[x_{A_1}+K_2x_{A_1}^2\right.$$
$$\left.+K_2K_3x_{A_1}^3/(1-z)\right]+2\,K_{BC}x_{B_1}x_{C_1}+3\,K_{B_2C}x_{B_1}^2x_{C_1}+x_{B_1}+x_{C_1} \qquad (50)$$

The sum of mole fractions of all chemical species is equal to unity.

$$\sum_{i=1}^{\infty}x_{A_i(\text{linear})}+\sum_{i=1}^{\infty}x_{A_iB_1}+\sum_{i=1}^{\infty}x_{A_iC_1}+\sum_{i=5}^{\infty}x_{A_i(\text{cyclic})}+x_{B_1C_1}+x_{B_2C_1}+x_{B_1}+x_{C_1}$$
$$=(1+K_{AB}x_{B_1}+K_{AC}x_{C_1})\left[x_{A_1}+K_2x_{A_1}^2+\frac{K_2K_3x_{A_1}^3}{(1-z)}\right]$$
$$-\frac{K_2K_3\theta}{K^3}\left[\ln(1-z)+z+\frac{z^2}{2}+\frac{z^3}{3}+\frac{z^4}{4}\right]$$
$$+K_{BC}x_{B_1}x_{C_1}+K_{B_2C}x_{B_1}^2x_{C_1}+x_{B_1}+x_{C_1}=1 \qquad (51)$$

The total molar enthalpy of all chemical species in the ternary mixtures is given by

$$h_f=\left\{h_2(n_{A_2}+n_{A_2B_1}+n_{A_2C_1})+h_A\left[\sum_{i=3}^{\infty}(i-1)n_{A_i(\text{linear})}+\sum_{i=5}^{\infty}in_{A_i(\text{cyclic})}\right.\right.$$
$$\left.+\sum_{i=3}^{\infty}(i-1)(n_{A_iB_1}+n_{A_iC_1})\right]+h_{AB}\sum_{i=1}^{\infty}n_{A_iB_1}+h_{AC}\sum_{i=1}^{\infty}n_{A_iC_1}+h_{BC}n_{B_1C_1}$$
$$\left.+h_{B_2C}n_{B_2C_1}\right\}/(n_1+n_2+n_3)$$
$$=\left\{(1+K_{AB}x_{B_1}+K_{AC}x_{C_1})\left[h_2K_2x_{A_1}^2+h_AK_2K_3x_{A_1}^3(2-z)/(1-z)^2\right]\right.$$
$$+h_AK_2K_3K^2\theta x_{A_1}^5/(1-z)$$
$$+(h_{AB}K_{AB}x_{B_1}+h_{AC}K_{AC}x_{C_1})\left[x_{A_1}+K_2x_{A_1}^2+K_2K_3x_{A_1}^3/(1-z)\right]$$
$$\left.+h_{BC}K_{BC}x_{B_1}x_{C_1}+h_{B_2C}K_{B_2C}x_{B_1}^2x_{C_1}\right\}/S \qquad (52)$$

Substitution of eqns. (52) and (25) into eqn. (23) gives h_{chem}^E. h_{phys}^E is obtained by differentiating g_{phys}^E with respect to temperature.

$$h^{\mathrm{E}}_{\mathrm{phys}} = \frac{\partial(g^{\mathrm{E}}_{\mathrm{phys}}/T)}{\partial(1/T)} = R\sum_{i=1}^{3} x_i \left(\frac{\sum_{j=1}^{3} x_j \frac{\partial(\tau_{ji}G_{ji})}{\partial(1/T)}}{\sum_{k=1}^{3} G_{ki}x_k} - \frac{\sum_{j=1}^{3} \tau_{ji}G_{ji}x_j \sum_{k=1}^{3} x_k \frac{\partial G_{ki}}{\partial(1/T)}}{\left(\sum_{k=1}^{3} G_{ki}x_k\right)^2} \right) \quad (53)$$

and the energy parameters are assumed to change linearly with temperature.

$$g_{ji} - g_{ii} = C_i + D_i(T - 273.15) \quad (54)$$

CALCULATED RESULTS

Reproduction of binary experimental data

The equilibrium constants and enthalpies of hydrogen bond formation for methanol are $K_2 = 70$, $K_3 = 120$, $K = 100$ and $\theta = iK_{cy(i)} = 90$ at 25°C, $h_2 = -21.2$ kJ mole^{-1} and $h_A = -23.5$ kJ mole^{-1} [1]. h_2 and h_A are assumed independent of temperature. The temperature dependence of K_2 gives h_2, that of K or θ gives a value of h_A, and that of K_3 corresponds to $2h_A - h_2$, since the value of K_2K_3/K^2 should be independent of temperature according to the model.

$$\partial \ln K_2/\partial(1/T) = -h_2/R, \qquad \partial \ln K/\partial(1/T) = -h_A/R,$$

$$\partial \ln \theta/\partial(1/T) = -h_A/R, \qquad \partial \ln K_3/\partial(1/T) = -(2h_A - h_2)/R \quad (55)$$

Similarly the temperature dependence of K_{AB} gives h_{AB}.

To test the present association model, experimental vapor–liquid equilibrium and excess enthalpy data, which were selected for representative binary systems, were analyzed.

Vapor–liquid equilibrium data were reduced by

$$\phi_i y_i P = x_i \gamma_i \phi_i^s P_i^s \exp[v_i^L(P - P_i^s)/RT] \quad (56)$$

where y is the vapor mole fraction, P is the total pressure, v_i^L is the molar liquid volume of pure component i, P_i^s is the saturated vapor pressure of pure component i and the Antoine equation is used to calculate P_i^s [9]. The volume-explicit virial equation truncated after the second term is used to obtain the fugacity coefficient ϕ and the pure component and cross-virial coefficients are estimated by the method of Hayden and O'Connell [10]. The nonrandomness parameter of the NRTL equation $\alpha_{ij}(=\alpha_{ji})$ is set to 0.3 for all binary combinations studied in this work [4]. The energy parameters were obtained by minimizing the squares of deviations in $\ln(\gamma_1/\gamma_2)$ for all data

TABLE 1

Solvation equilibrium constants and their enthalpies of complex formation

System	Temp. (°C)	K	h (kJ mole^{-1})
Methanol–acetone	50	15.0	−21.0
Methanol–benzene	55	3.0	−8.2
Methanol–chloroform	50	28.0	−24.5
Methanol–ethyl ether	25	15.0	−22.0
Methanol–methyl acetate	50	10.0	−17.0
Methanol–tetrachloromethane	25	1.5	−5.5
Methanol–tetrahydrofuran	25	25.0	−20.0
Benzene–tetrachloromethane	25	0.215	−5.28
Chloroform–acetone, 1:1 complex	25	0.967	−10.5
2:1 complex	25	1.117	−13.2
1:1 complex	50	0.698	
2:1 complex	50	0.668	

points. The Simplex method [11] was used for this purpose. Liquid–liquid equilibria are described in terms of the equality of activities in two liquid phases for each component. Table 1 lists the solvation equilibrium constants and their enthalpies of complex formation. Stokes and Burfitt [12] reported enthalpies of dilution of ethanol in cyclohexane, tetrachloromethane and benzene at 25°C. We estimated the enthalpies of complex formation between methanol and tetrachloromethane or benzene by taking the difference between the value of enthalpy of dilution of ethanol in cyclohexane and that in tetrachloromethane or benzene. Enthalpies of complex formation for other solvents (acetone, ethyl ether, methyl acetate, tetrahydrofuran except chloroform) were similarly estimated. The equilibrium constant and enthalpy of complex formation of the system benzene–tetrachloromethane were taken from McGlashan et al. [8]. The equilibrium constants of the system chloroform–acetone are the same as obtained by Kearns [5], and the enthalpies of complex formation of this system at 25°C were taken from a previous paper [13]. Tables 2 and 3 present typical results for representative systems. Figures 1–6 are examples of representative sets of binary data which we have correlated. The association model represents very well skewed excess enthalpy curves showing both endo- and exothermic regions for the systems methanol–tetrachloromethane and methanol–chloroform (Figs. 5 and 6).

TABLE 2

Binary parameters and absolute arithmetic mean deviations as obtained from vapor–liquid equilibrium data reduction

System (1–2)	Temp (°C)	No. of data points	Parameters		Deviations		Ref.
			$g_{21} - g_{11}$ (J mole^{-1})	$g_{12} - g_{22}$ (J mole^{-1})	Vapor mole fraction (×1000)	Pressure (mmHg)	
Methanol–acetone	35	11	1021.00	−1937.01	6.0	3.1	14
	50	35	1030.76	−1907.72	7.4	4.6	15
Methanol–benzene	35	9	1412.84	−768.43	9.3	3.2	16
	55	9	1455.08	−648.68	8.0	3.4	
Methanol–chloroform	50	25	7852.05	−2548.58	7.7	3.4	15
Methanol–ethyl ether	25	19	3117.19	−2485.35		3.2	17
Methanol–methyl acetate	20	7	3328.13	−2772.95	8.2	1.2	18
	30	7	3341.80	−2789.06	6.6	4.5	
	50	15	1108.64	−1674.07	5.1	2.1	15
Methanol–tetrachloromethane	35	9	2061.89	−1104.74	11.9	3.2	16
	55	6	1817.87	−740.23	8.7	8.9	19
Methanol–tetrahydrofuran	25	19	3486.45	−3099.37		1.8	20
Acetone–methyl acetate	50	35	−53.22	385.25	2.7	1.8	15
Benzene–cyclohexane	39.99	7	434.20	735.72	1.6	0.9	21
	69.98	7	325.68	720.22	2.0	0.9	
Chloroform–acetone	50	29	0.0	0.0	6.8	1.9	15
Ethyl ether–cyclohexane	25	19	2190.67	−929.44		4.2	22
Methyl acetate–cyclohexane	35	8	2063.99	2227.66	2.5	8.5	23
	40	9	2083.68	2234.19	5.6	4.1	
Tetrachloromethane–benzene	40	8	−58.11	884.49	0.8	1.4	24
	70	8	197.98	560.08	0.8	2.8	
Tetrachloromethane–cyclohexane	40	9	410.18	−138.12	0.5	0.1	25
	70	9	−631.54	932.54	0.4	0.6	
Tetrahydrofuran–cyclohexane	25	19	2888.67	−703.13		1.1	26
Methanol–cyclohexane	25	MS[a]	−147.84	1832.48			27

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[a] MS=mutual solubility data.

TABLE 3

Binary parameters and absolute arithmetic mean deviations as obtained from excess enthalpy data reduction

System (1–2)	Temp (°C)	No. of data points	Parameters				Deviation (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})		
Methanol–acetone	25	22	−1762.97	2170.56	−7.6350	6.1596	8.0	28
Methanol–benzene	25	10	−5332.94	3711.11	−8.2463	−12.0038	5.4	29
	35	10	−9168.56	470.89	−31.5925	1.5479	2.7	
	45	10	−10659.10	275.87	−37.3338	1.9839	5.7	
Methanol–chloroform	25	15	7262.22	965.31	−12.7532	19.5736	21.1	28
	35	9	8979.71	3012.68	−6.6929	23.9245	20.5	30
Methanol–ethyl ether	25	19	2890.49	−493.72	2.0247	1.4799	10.7	17
Methanol–*n*-hexane	45	17	11408.3	3827.16	28.2364	3.6452	7.8	31
Methanol–methyl acetate	25	16	14569.0	2831.04	64.2601	10.7244	10.5	32
Methanol–tetrachloromethane	0	18	−6751.22	5940.68	−22.9142	24.5063	3.5	33
	20	14	−8010.75	7574.45	−26.7144	25.9177	5.9	
	35	13	−8360.83	8293.72	−27.4832	25.3150	7.4	
	50	25	−9194.42	9046.20	−30.4346	27.4275	10.2	
Methanol–tetrahydrofuran	25	19	12696.7	512.86	53.3860	4.9052	8.1	20

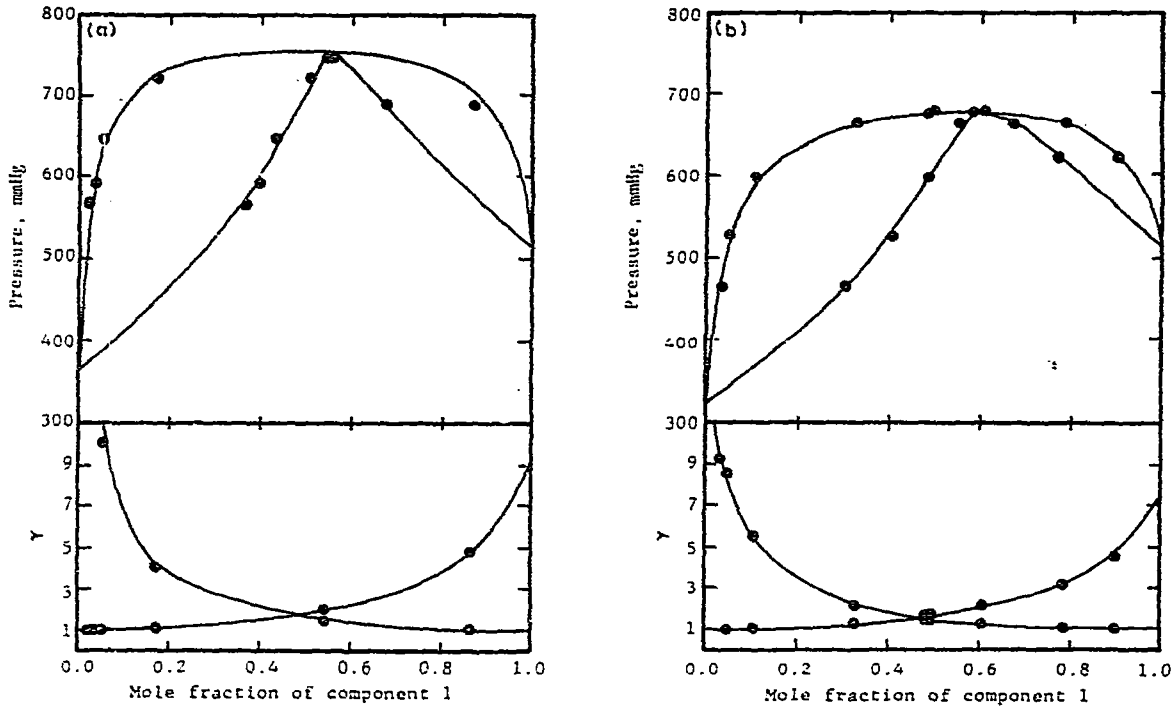

Fig. 1. Vapor–liquid equilibria for (a) methanol (1)–tetrachloromethane (2), and (b) methanol (1)–benzene (2) at 55°C. Calculated (———). Experimental (●) methanol–tetrachloromethane, data of Scatchard et al. [16]; methanol–benzene, data of Scatchard and Ticknor [19].

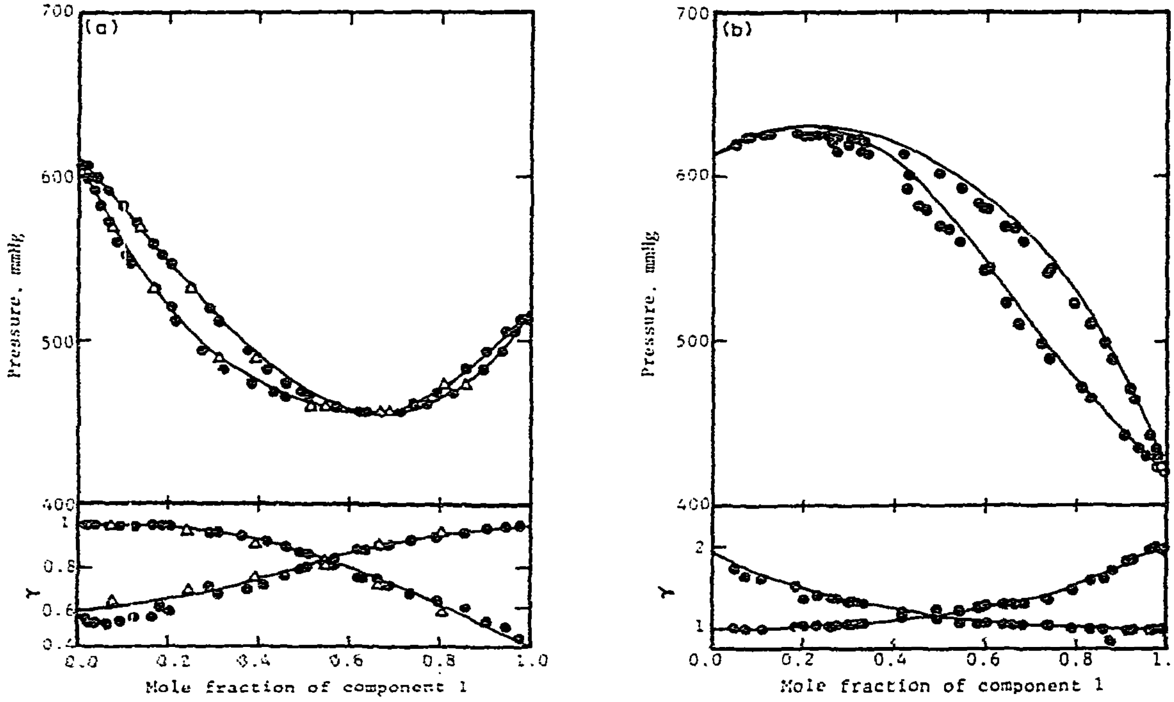

Fig. 2. Vapor–liquid equilibria for (a) chloroform (1)–acetone(2), and (b) methanol(1)–acetone (2) at 50°C. Calculated (———). Experimental: chloroform–acetone, data of Severns et al. [15] (●), and Mueller and Kearns [34] (△); methanol–acetone, data of Severns et al. [15] (●).

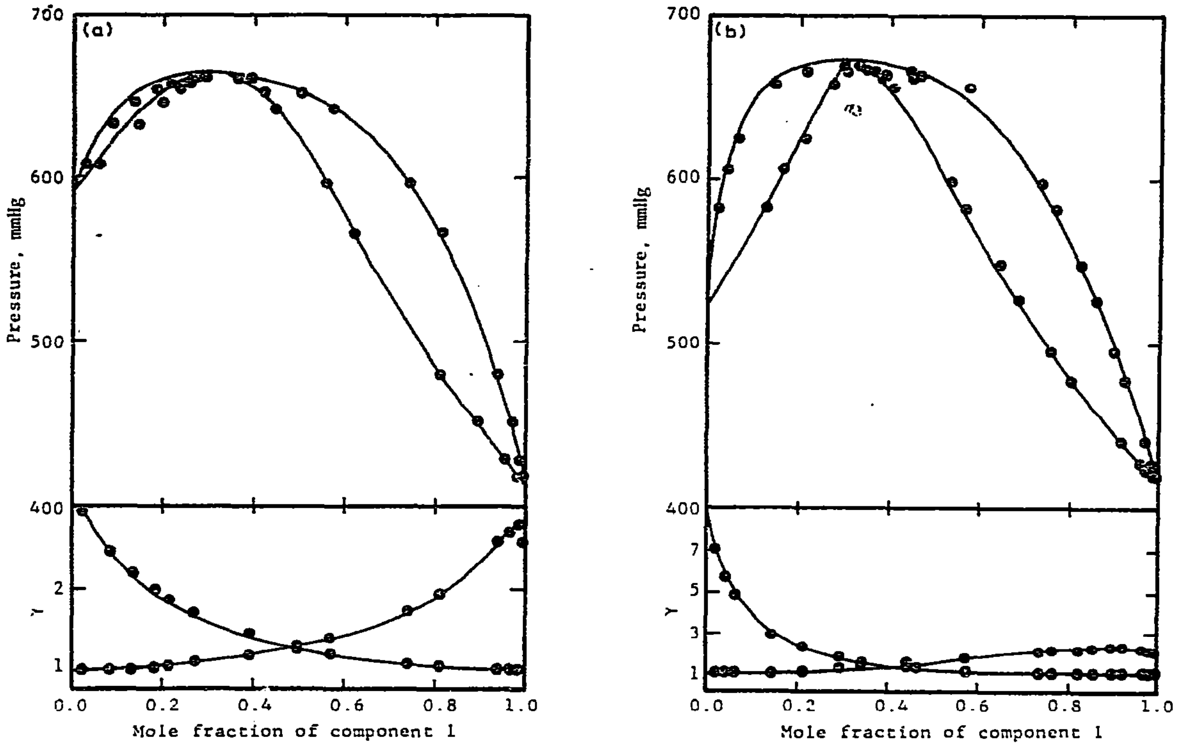

Fig. 3. Vapor–liquid equilibria for (a) methanol (1)–methyl acetate (2), and (b) methanol (1)–chloroform (2) at 50°C. Calculated (———). Experimental (●) data of Severns et al. [15].

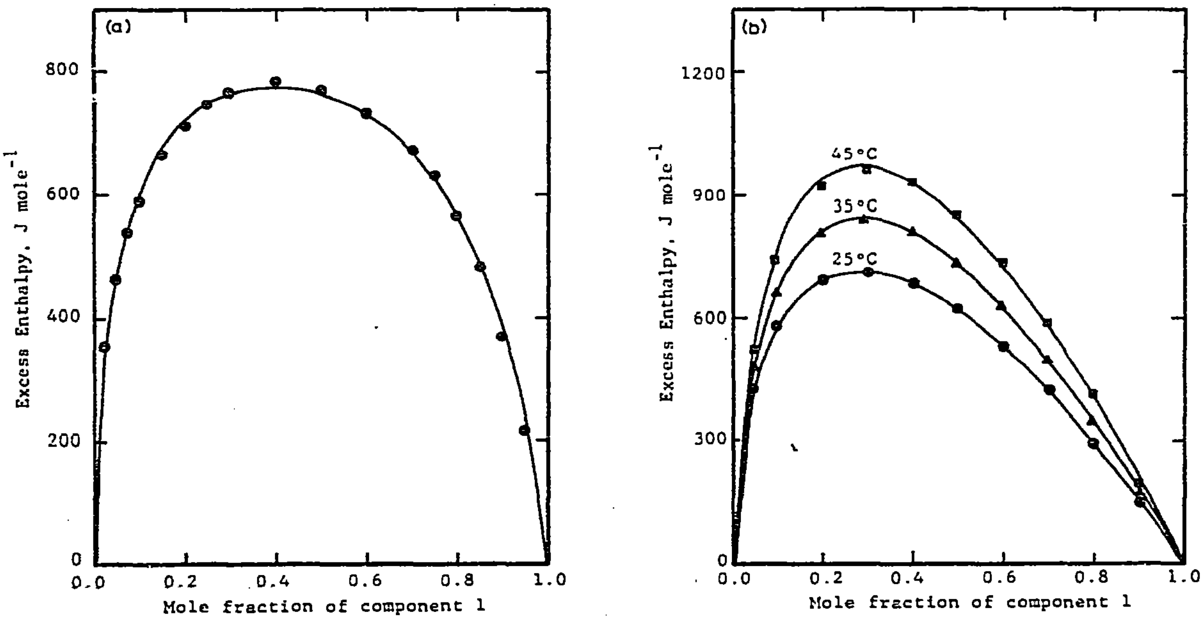

Fig. 4. Excess enthalpies for (a) methanol (1)–*n*-hexane (2), and (b) methanol (1)–benzene (2). Calculated (———). Experimental: methanol–*n*-hexane data of Savini et al. [31] at 45°C; methanol–benzene (●) 25°C, (▲) 35°C, (■) 45°C, data of Mrazek and Van Ness [29].

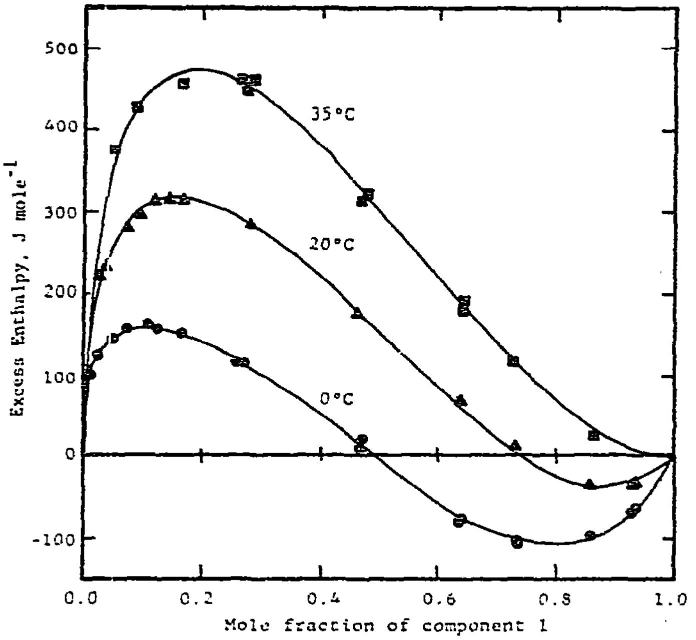

Fig. 5. Excess enthalpies for methanol (1)–tetrachloromethane (2). Calculated (———). Experimental: (●) 0°C, (▲) 20°C, (▦) 35°C, data of Otterstedt and Missen [33].

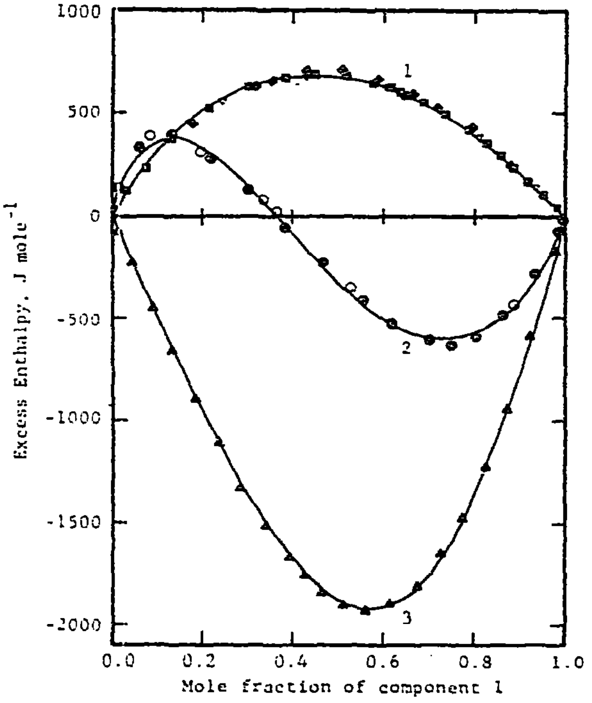

Fig. 6. Excess enthalpies for three binary systems at 25°C. Calculated (———). Experimental: 1 methanol (1)–acetone (2), data of Nagata and Tamura [28] (▦), Coomber and Wormald [35] (◆), Hirobe [36] (▽); 2 methanol (1)–chloroform (2), data of Nagata and Tamura [28] (●), Hirobe [36] (○); 3 chloroform (1)–acetone (2), data of Nagata et al. [13] (▲).

TABLE 4

Predicted results for ternary vapor–liquid equilibria as obtained from binary parameters

System	Temp. (°C)	No. of data points	Deviations		Ref.
			Vapor mole fraction (×1000)	Pressure (mm Hg)	
Methanol–			9.5		
tetrachloromethane–	34.68	6	5.0	6.2	19
benzene			6.1		
Methanol–			6.6		
tetrachloromethane–	55	8	2.2	6.0	19
benzene			5.9		
Methanol–			13.6		
acetone–	50	35	6.6	5.3	15
methyl acetate			10.1		
Methanol–			9.4		
chloroform–	50	30	9.2	8.8	15
acetone			8.6		

Ternary predictions from binary parameters alone

Table 4 summarizes vapor–liquid equilibrium predictions for four representative ternary systems. Agreement is good between calculated and experimental vapor mole fractions and pressures. The absolute arithmetic mean deviation of excess enthalpy between calculated and observed results for 51 data points of the system methanol–chloroform–acetone at 25°C [28] is 28.3 J mole^{-1}. It is often difficult to predict well ternary liquid–liquid equilibria with a plait point by using binary parameters. Figures 7–11 demonstrate

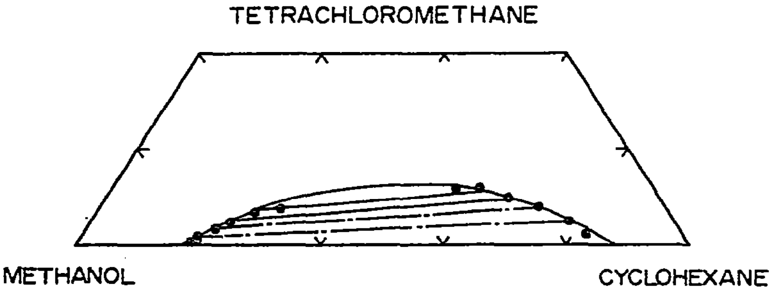

Fig. 7. Ternary liquid–liquid equilibria for methanol–tetrachloromethane–cyclohexane at 25°C. Calculated (———). Experimental data of Yasuda et al. [27]. (●---●) Tie line. Concentrations are in mole fractions.

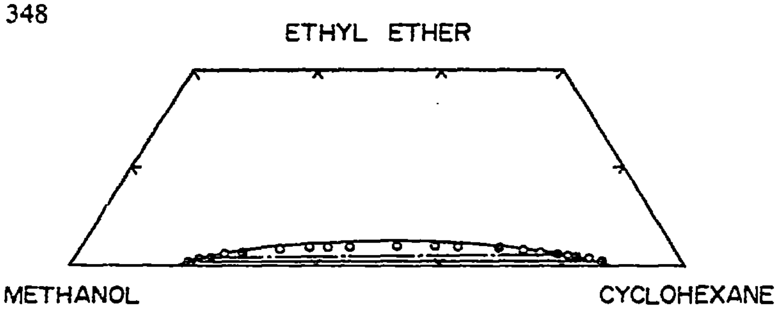

Fig. 8. Ternary liquid–liquid equilibria for methanol–ethyl ether–cyclohexane at 25°C. Calculated (———). Experimental data of Sugi et al. [37]. (○) Solubility; (●---●) tie line. Concentrations are in mole fractions.

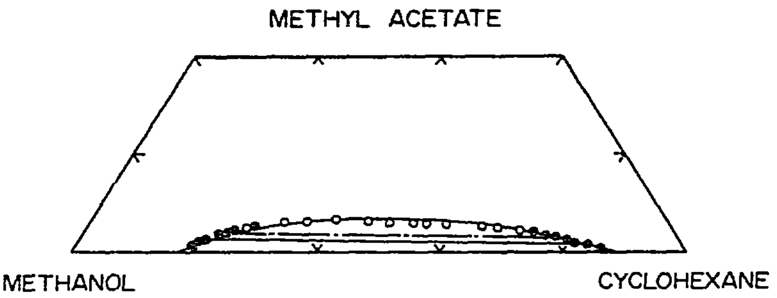

Fig. 9. Ternary liquid–liquid equilibria for methanol–methyl acetate–cyclohexane at 25°C. Calculated (———). Experimental data of Sugi et al. [37]. (○) Solubility. (●---●) tie line. Concentrations are in mole fractions.

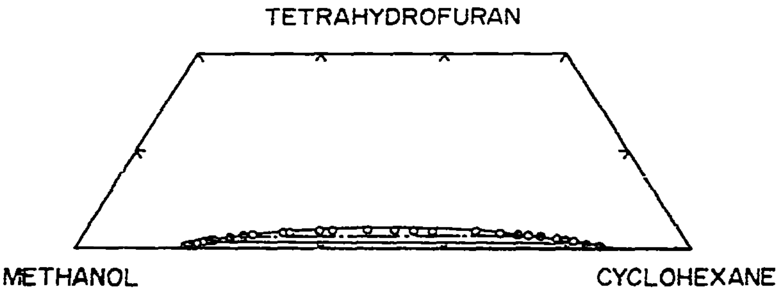

Fig. 10. Ternary liquid–liquid equilibria for methanol–tetrahydrofuran–cyclohexane at 25°C. Calculated (———). Experimental data of Sugi et al. [37]. (○) Solubility: (●---●) tie line. Concentrations are in mole fractions.

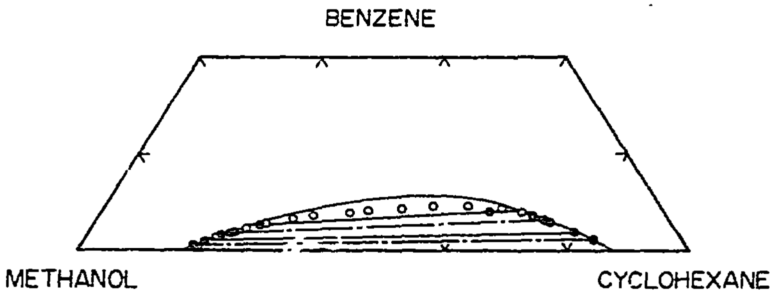

Fig. 11. Ternary liquid–liquid equilibria for methanol–benzene–cyclohexane at 25°C. Calculated (———). Experimental data of Nagata [38]. (○) Solubility; (●---●) tie line. Concentrations are in mole fractions.

clearly that the model also works very well for this problem, although the original NRTL equation failed to do so.

We may conclude that the proposed association model has a good ability in reproducing the thermodynamic properties of binary and ternary methanol solutions over the whole mole fraction range.

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