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THERMODYNAMICS OF ASSOCIATED SOLUTIONS. PHASE EQUILIBRIA OF BINARY AND TERNARY WATER–ALCOHOL MIXTURES

ISAMU NAGATA

Department of Chemical Engineering, Kanazawa University, 2-40-20, Kodatsuno, Kanazawa, Ishikawa 920 (Japan)

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ABSTRACT

The UNIQUAC associated solution theory is applied to the accurate reproduction of binary vapor–liquid equilibrium data for water–alcohol mixtures. It is able to predict ternary liquid–liquid and vapor–liquid equilibria for mixtures containing water and alcohols using binary parameters obtained from phase equilibrium data for the constituting binary mixtures.

INTRODUCTION

Chemical models are well suited to the description of excess thermodynamic properties of associated solutions. Many investigators have studied vapor–liquid equilibria for binary alcohol–inert and –active component solutions with association models containing chemical and physical contribution terms to the excess Gibbs energy. Nath and Bender [1,2] for the first time successfully applied their association theory to binary aqueous mixtures and predicted isothermal vapor–liquid equilibria for ternary aqueous mixtures from binary parameters alone. However, Nath and Bender did not perform liquid–liquid equilibrium calculations for aqueous mixtures. The UNIQUAC associated solution theory [3,4] has been extended to associated solutions containing any number of alcohols to calculate vapor–liquid and liquid–liquid equilibria [5].

This paper presents an application of the UNIQUAC associated solution theory to phase equilibrium calculation for water–alcohol mixtures.

THEORY

Binary mixtures containing two associating components

The theory assumes three linear, polymer-forming reactions for self-association of components A and B and for solvation between the *i*-th polymer of component A and the j-th polymer of component B, thus

$$A_1 + A_i = A_{i+1} \tag{1}$$

$$B_1 + B_i = B_{i+1} \tag{2}$$

$$A_i + B_j = A_iB_j \tag{3}$$

The equilibrium constants for these reactions are given by

$$K_I = \left(\Phi_{I_{i+1}}/\Phi_{I_i}\Phi_{I_1}\right)i/(i+1) \tag{4}$$

for association of component I ($I =$ A, B), and

$$K_{\mathrm{AB}} = \left(\Phi_{\mathrm{A}_i\mathrm{B}_j}/\Phi_{\mathrm{A}_i}\Phi_{\mathrm{B}_j}\right)ij/\left(ir_{\mathrm{A}} + jr_{\mathrm{B}}\right) \tag{5}$$

for solvation

The activity coefficient of component A is expressed as

$$\begin{aligned}\ln \gamma_{\mathrm{A}} = {} & \ln\left(\Phi_{\mathrm{A}_1}/\Phi_{\mathrm{A}_1}^0 x_{\mathrm{A}}\right) + r_{\mathrm{A}}\left(1/V^0 - 1/V\right) \\ & - (Z/2)q_{\mathrm{A}}\left[\ln(\Phi_{\mathrm{A}}/\theta_{\mathrm{A}}) + 1 - \Phi_{\mathrm{A}}/\theta_{\mathrm{A}}\right] \\ & + q_{\mathrm{A}}\left\{-\ln(\theta_{\mathrm{A}} + \theta_{\mathrm{B}}\tau_{\mathrm{BA}}) + \theta_{\mathrm{B}}\left[\tau_{\mathrm{BA}}/(\theta_{\mathrm{A}} + \theta_{\mathrm{B}}\tau_{\mathrm{BA}}) - \tau_{\mathrm{AB}}/(\theta_{\mathrm{B}} + \theta_{\mathrm{A}}\tau_{\mathrm{AB}})\right]\right\}\end{aligned} \tag{6}$$

where the segment fraction, Φ, the surface fraction, θ, and adjustable binary parameter, τ, are defined by

$$\Phi_{\mathrm{A}} = r_{\mathrm{A}}x_{\mathrm{A}}/(r_{\mathrm{A}}x_{\mathrm{A}} + r_{\mathrm{B}}x_{\mathrm{B}}) \qquad \Phi_{\mathrm{B}} = 1 - \Phi_{\mathrm{A}} \tag{7}$$

$$\theta_{\mathrm{A}} = q_{\mathrm{A}}x_{\mathrm{A}}/(q_{\mathrm{A}}x_{\mathrm{A}} + q_{\mathrm{B}}x_{\mathrm{B}}) \qquad \theta_{\mathrm{B}} = 1 - \theta_{\mathrm{A}} \tag{8}$$

$$\tau_{\mathrm{BA}} = \exp(-a_{\mathrm{BA}}/T) \qquad \tau_{\mathrm{AB}} = \exp(-a_{\mathrm{AB}}/T) \tag{9}$$

The activity coefficient of component B is given by exchanging the subscripts A and B for B and A, respectively.

The nominal segment fractions of both components are expressed by the monomer segment fractions.

$$\Phi_{\mathrm{A}} = \left[\Phi_{\mathrm{A}_1}/\left(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1}\right)^2\right]\left[1 + r_{\mathrm{A}}K_{\mathrm{AB}}\theta_{\mathrm{B}_1}/\left(1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1}\right)\right] \tag{10}$$

$$\Phi_{\mathrm{B}} = \left[\Phi_{\mathrm{B}_1}/\left(1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1}\right)^2\right]\left[1 + r_{\mathrm{B}}K_{\mathrm{AB}}\Phi_{\mathrm{A}_1}/\left(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1}\right)\right] \tag{11}$$

and the true molar volume of the mixture is given by

$$\begin{aligned}1/V = {} & \Phi_{\mathrm{A}_1}/r_{\mathrm{A}}\left(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1}\right) + K_{\mathrm{AB}}\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}/\left[\left(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1}\right)\left(1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1}\right)\right] \\ & + \Phi_{\mathrm{B}_1}/r_{\mathrm{B}}\left(1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1}\right)\end{aligned} \tag{12}$$

For the pure component I eqns. (10)–(12) reduce to

$$\Phi_{I_1}^0 = \left[(2K_I + 1) - (1 + 4K_I)^{1/2}\right]/2K_I^2 \tag{13}$$

and

$$1/V_I^0 = \left(1 - K_{\mathrm{B}}\Phi_{I_1}^0\right)/r_I \tag{14}$$

when $K_B = 0$, the above equations reduce to those for associating active component mixtures and $\Phi^0_{B_1} = 1$.

Ternary mixtures containing three associating components

In a solution including three self-associating components, three general successive chemical reactions may proceed [5].

$$I_1 + I_i = I_{i+1} \qquad I = \mathrm{A, B, C} \tag{15}$$

$$I_i + J_j = I_iJ_j \qquad I = \mathrm{A, B};\ J = \mathrm{B, C} \tag{16}$$

$$\mathrm{A}_i + \mathrm{B}_j + \mathrm{C}_k = \mathrm{A}_i\mathrm{B}_j\mathrm{C}_k \tag{17}$$

The equilibrium constants for these reactions additional to eqns. (4) and (5) are defined as

$$K_{AC} = \left(\Phi_{A_iC_j}/\Phi_{A_i}\Phi_{C_j}\right)ij/\left(ir_A + jr_B\right) \tag{18}$$

$$K_{BC} = \left(\Phi_{B_iC_j}/\Phi_{B_i}\Phi_{C_j}\right)ij/\left(ir_B + jr_C\right) \tag{19}$$

$$K_{ABC} = \left(\Phi_{A_iB_jC_k}/\Phi_{A_i}\Phi_{B_j}\Phi_{C_k}\right)ijk/\left(ir_A + jr_B + kr_C\right) \tag{20}$$

The monomer segment fractions of three components are related to the stoichiometric segment fraction of each component as shown for binary mixtures.

$$\begin{aligned}\Phi_A = {} & \left[\Phi_{A_1}/\left(1 - K_A\Phi_{A_1}\right)\right]\Big(1 + r_A\Big\{K_{AB}\Phi_{B_1}/\left(1 - K_B\Phi_{B_1}\right) \\ & + K_{AC}\Phi_{C_1}/\left(1 - K_C\Phi_{C_1}\right) + K_{ABC}\Phi_{B_1}\Phi_{C_1}/\left[\left(1 - K_B\Phi_{B_1}\right)\left(1 - K_C\Phi_{C_1}\right)\right]\Big\}\Big)\end{aligned} \tag{21}$$

$$\begin{aligned}\Phi_B = {} & \left[\Phi_{B_1}/\left(1 - K_B\Phi_{B_1}\right)\right]\Big(1 + r_B\Big\{K_{AB}\Phi_{A_1}/\left(1 - K_C\Phi_{C_1}\right) \\ & + K_{BC}\Phi_{C_1}/\left(1 - K_C\Phi_{C_1}\right) + K_{ABC}\Phi_{A_1}\Phi_{C_1}/\left[\left(1 - K_A\Phi_{A_1}\right)\left(1 - K_C\Phi_{C_1}\right)\right]\Big\}\Big)\end{aligned} \tag{22}$$

$$\begin{aligned}\Phi_C = {} & \left[\Phi_{C_1}/\left(1 - K_C\Phi_{C_1}\right)\right]\Big(1 + r_C\Big\{K_{AC}\Phi_{A_1}/\left(1 - K_A\Phi_{A_1}\right) \\ & + K_{BC}\Phi_{B_1}/\left(1 - K_B\Phi_{B_1}\right) + K_{ABC}\Phi_{A_1}\Phi_{B_1}/\left[\left(1 - K_A\Phi_{A_1}\right)\left(1 - K_B\Phi_{B_1}\right)\right]\Big\}\Big)\end{aligned} \tag{23}$$

The true molar volume of the solution is given by

$$\begin{aligned}1/V = {} & \Phi_{A_1}/r_A\left(1 - K_A\Phi_{A_1}\right) + K_{AB}\Phi_{A_1}\Phi_{B_1}/\left[\left(1 - K_A\Phi_{A_1}\right)\left(1 - K_B\Phi_{B_1}\right)\right] \\ & + \Phi_{B_1}/r_B\left(1 - K_B\Phi_{B_1}\right) + K_{BC}\Phi_{B_1}\Phi_{C_1}/\left[\left(1 - K_B\Phi_{B_1}\right)\left(1 - K_C\Phi_{C_1}\right)\right] \\ & + \Phi_{C_1}/r_C\left(1 - K_C\Phi_{C_1}\right) + K_{AC}\Phi_{A_1}\Phi_{C_1}/\left[\left(1 - K_A\Phi_{A_1}\right)\left(1 - K_C\Phi_{C_1}\right)\right] \\ & + K_{ABC}\Phi_{A_1}\Phi_{B_1}\Phi_{C_1}/\left[\left(1 - K_A\Phi_{A_1}\right)\left(1 - K_B\Phi_{B_1}\right)\left(1 - K_C\Phi_{C_1}\right)\right]\end{aligned} \tag{24}$$

The activity coefficient of component I is

$$\ln \gamma_I = \ln\left(\Phi_{I_1}/\Phi_{I_1}^0 x_I\right) + r_I(1/V^0 - 1/V) - (Z/2)q_I[\ln(\Phi_I/\theta_I) + 1 - \Phi_I/\theta_I]$$
$$+ q_I\left[1 - \ln\left(\sum_J \theta_J \tau_{JI}\right) - \sum_J\left(\theta_J \tau_{IJ}/\sum_K \theta_K \tau_{KJ}\right)\right] \tag{25}$$

where

$$\theta_I = q_I x_I/\sum_J q_J x_J \tag{26}$$

$$\Phi_I = r_I x_I/\sum_J r_J x_J \tag{27}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{28}$$

If component I does not self-associate, $K_I = 0$ and $\Phi_I^0 = 1$.

CALCULATED RESULTS AND DISCUSSION

The association constants of pure alcohols at 50°C were taken from Brandani [6]: for methanol, 173.9; for ethanol, 110.4; for 1-propanol, 87.0; for 1-butanol, 69.5. That for water was assumed as 500 at 50°C. The enthalpy of hydrogen-bond formation for all alcohols and water which self-associate through the O–H bond was selected as -23.2 kJ mol^{-1}, which is equivalent to the enthalpy of dilution of ethanol in *n*-hexane at 25°C [7].

The temperature dependence of the equilibrium constant is expresed by

$$\frac{\partial \ln K}{\partial(1/T)} = -\frac{h}{R} \tag{29}$$

Table 1 presents the solvation equilibrium constants and their temperature dependencies [5]. Any complex formation was not assumed in binary mixtures of hydrocarbons, tetrachloromethane and trichloromethane with water.

Binary vapor–liquid equilibrium data were reduced to obtain the energy parameters of the UNIQUAC associated solution theory using the relation

$$\phi_I y_I P = \gamma_I x_I \phi_I^s P_I^s \exp\left[v_I^L(P - P_I^s)/RT\right] \tag{30}$$

where the fugacity coefficients, ϕ_I and ϕ_I^s, were calculated from

$$\ln \phi_I = \left(2\sum_J y_J B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ}\right)P/RT \tag{31}$$

The second virial coefficients B_{IJ} were calculated by the Hayden–O'Connell method [8]. The pure molar liquid volumes v_I^L were estimated by the modified Rackett equation [9]. Pure component vapor pressures, P_I^s, were obtained from the Antoine equation whose constants are available elsewhere [10,11]. Pure component structural parameters, r and q, were estimated by

TABLE 1

Solvation equilibrium constants and enthalpies of hydrogen bonding and of complex formation

A	B	K_{AB} (50°C)	$-h_{AB}$ (kJ mol^{-1})
Methanol	Ethanol	2500	23.2
Methanol	Water	3500	23.2
Ethanol	Water	3000	23.2
1-Propanol	Water	700	23.2
1-Butanol	Water	400	23.2
Methanol	Benzene	4	8.3
Ethanol	Benzene	3	8.3
Ethanol	Trichloromethane	15	13
1-Propanol	Benzene	2.5	8.3
1-Propanol	Tetrachloromethane	1	5.5
1-Butanol	Benzene	2.5	8.3

the method of Vera et al. [12]. The computer program used for parameter estimation was similar to that based on the maximum likelihood principle as described by Prausnitz et al. [13]. The values of the standard deviations in the measured variables were equal to those given by Prausnitz et al. [13]: for pressure, $\sigma_P = 1.0$ Torr; for temperature, $\sigma_T = 0.05$ K; for liquid and vapor mole fractions, $\sigma_x = 0.001$ and $\sigma_y = 0.003$.

Mutual solubility data were used to obtain energy parameters for a partially miscible mixture by solving eqn. (32) with a Newton–Raphson iterative technique.

$$(\gamma_I x_I)^{\mathrm{I}} = (\gamma_I x_I)^{\mathrm{II}} \qquad (32)$$

where the superscripts I and II indicate equilibrium liquid phases. The monomer segment fractions were obtained by solving related material balance equations with subroutine NOLBR built in a FACOM M-170F computer. Tables 2 and 3 give the binary calculated results as obtained from phase equilibrium data reduction and typical results are illustrated in Figs. 1 and 2. The calculated results in Fig. 2 show that the theory provided maxima in the plot of activity coefficient versus liquid mole fraction.

In ternary phase equilibrium calculations the ternary solvation constant, K_{ABC}, was neglected. The predicted vapor-phase mole fractions and total pressures were compared with the experimental vapor–liquid equilibrium data of the water(1)–methanol(2)–ethanol(3) system at 25°C [14]. The average deviations on vapor-phase mole fraction and pressure were calculated by using the following equations

$$\delta y_I = (100/N) \sum_i |\Delta y_I|_i \qquad (33)$$

$$\delta P = (1/N) \sum_i |\Delta P_i| \qquad (34)$$

TABLE 2

Root-mean square deviations as obtained from binary data reduction for water solutions

System (A–B)	Temp. (°C)	No. of data points	Root-mean square deviations				Parameters (K)		Ref.
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}	
Water–methanol	25	10	0.70	0.00	0.7	4.2	−217.36	−1.00	14
Water–ethanol	25	10	0.40	0.00	0.3	3.7	266.61	−149.06	14
Water–1-propanol	30	13	1.37	0.00	1.6	8.0	443.92	−173.97	15
Water–1-butanol	60	12	2.26	0.03	1.3	8.1	513.84	−140.10	15
Water–1-butanol	25	MS [a]					412.66	−134.58	16
Water–benzene	25	MS					638.72	156.69	17
	30	MS					652.03	153.54	16
Water–tetrachloromethane	20	MS					611.00	483.17	16
Water–trichloromethane	20	MS					580.52	82.93	16
Water–cyclohexane	25	MS					727.84	583.76	16
Water–*n*-heptane	25	MS					709.56	606.74	16
Water–*n*-hexane	25	MS					697.45	623.58	16

[a] MS = mutual solubility.

TABLE 3

Root-mean square deviations as obtained from binary data reduction for alcohol solutions

System (A–B)	Temp. (°C)	No. of data points	Root-mean square deviations				Parameters (K)		Ref.
			δP (torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}	
Methanol–benzene	35	9	1.03	0.03	1.2	5.5	−174.19	344.10	18
Ethanol–*n*-hexane	25	25	0.85	0.00	0.2		165.83	−74.30	19
Ethanol–*n*-heptane	30	31	0.58	0.00	0.2		66.97	−2.41	20
Ethanol–cyclohexane	20	7	0.77	0.01	0.3	3.3	103.02	−29.63	18
Ethanol–benzene	25	11	0.76	0.00	1.0	5.5	−35.50	141.02	21
Ethanol–trichloromethane	35	26	0.88	0.02	0.3	2.2	−106.99	324.03	18
1-Propanol–cyclohexane	25	27	0.72	0.00	0.1		250.39	−130.94	19
1-Propanol–benzene	45	11	0.14	0.00	0.1	1.4	114.53	−8.23	18
1-Propanol–tetrachloromethane	35	20	0.89	0.02	0.7	7.0	−68.11	146.86	19
1-Butanol–benzene	45	9	0.41	0.01	0.2	4.2	129.95	−11.32	22
Methanol–ethanol	25	11	2.77	0.00	1.6	10.2	−52.69	−64.25	19
Methanol–cyclohexane	25	MS[a]					7.86	86.15	23

[a] MS = mutual solubility.

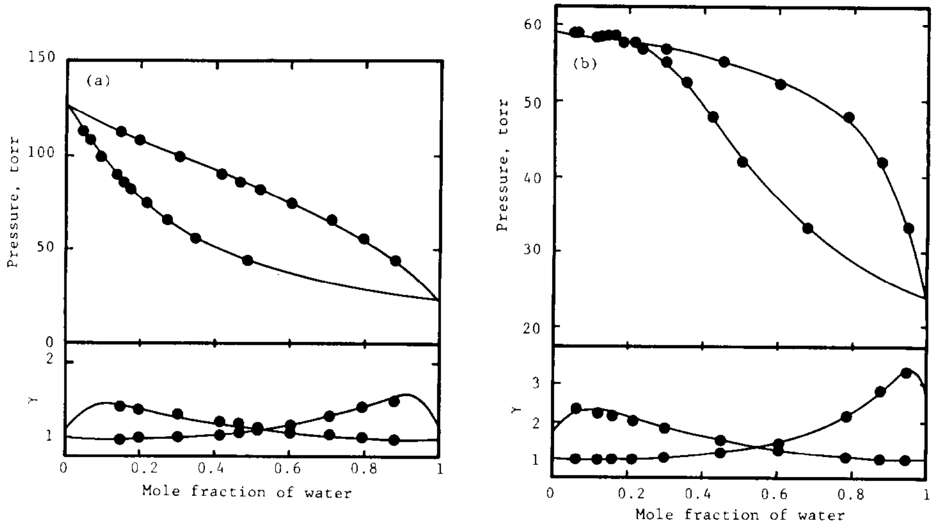

Fig. 1. Vapor–liquid equilibria for (a) water–methanol and (b) water–ethanol at 25°C. Experimental (●) [14]. Calculated (———).

$$\delta P/P = (100/N)\sum_{i} |\Delta P_i|/P_i \tag{35}$$

where $\delta y_i = 2.3$, $\delta y_2 = 3.6$, $\delta y_3 = 3.8$, $\delta P = 6.4$ Torr and $\delta P/P = 9.2\%$. Nath and Bender [2] presented the predictions of vapor–liquid equilibria for

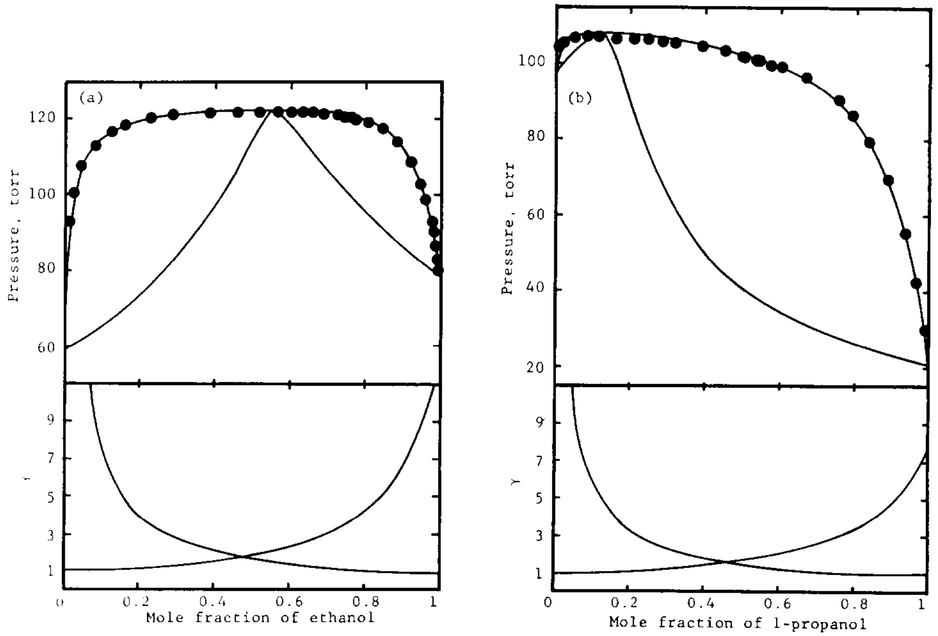

Fig. 2. Vapor–liquid equilibria for (a) ethanol–*n*-heptane at 30°C and (b) 1-propanol–cyclohexane at 25°C. Experimental: (●), ethanol–*n*-heptane [20]; 1-propanol–cyclohexane [19]. Calculated (———).

TABLE 4

Ternary systems tested

No.	System	Temp. (°C)	Type	Ref.
1	Cyclohexane–methanol–water	25	II	24
2	Benzene–methanol–water	30	I	24
3	*n*-Hexane–ethanol–water	25	I	24
4	Cyclohexane–ethanol–water	25	I	24
5	*n*-Heptane–ethanol–water	25	I	24
6	Benzene–ethanol–water	25	I	24
7	Trichloromethane–ethanol–water	20	I	24
8	Cyclohexane–1-propanol–water	25	I	24
9	Benzene–1-propanol–water	30	I	24
10	Tetrachloromethane–1-propanol–water	20	I	24
11	Benzene–1-butanol–water	25	II	25

ternary mixtures containing water and ethanol based on their association theory and the calculated results show exceedingly larger deviations than those obtained in this work. Table 4 lists eleven ternary, partially miscible systems chosen to test the ability of the theory: nine type-I systems, i.e., including only one partially miscible binary; two type-II systems, i.e., containing two partially miscible binaries. Figure 3 compares the calculated values obtained from the theory with the experimental data [24,25]. The agreement for mixtures of normal alcohols with water is comparable to that obtained by commonly used models for the excess Gibbs energy.

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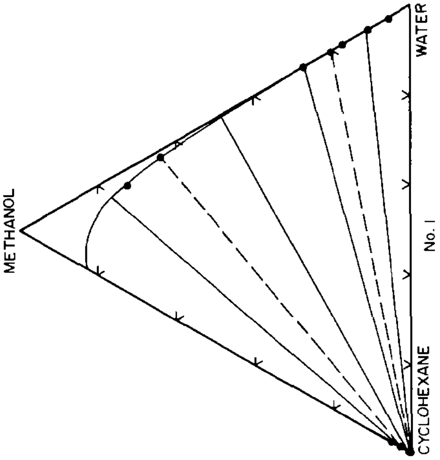
LIST OF SYMBOLS

A, B, C	components
a_{IJ}	binary interaction parameter
B_{IJ}	second virial coefficient
h_A, h_{AB}	molar enthalpies of hydrogen bond formation
K_I	equilibrium constant for chain association of component I



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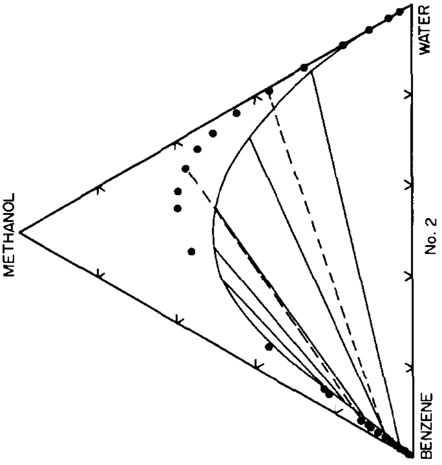

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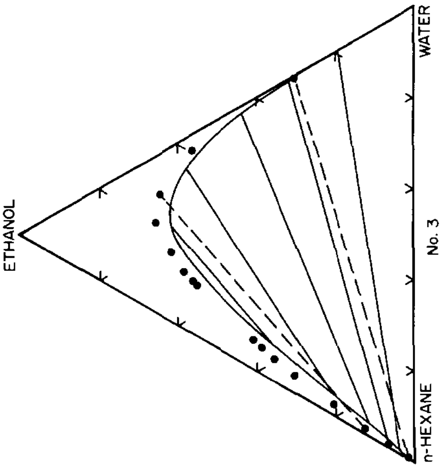

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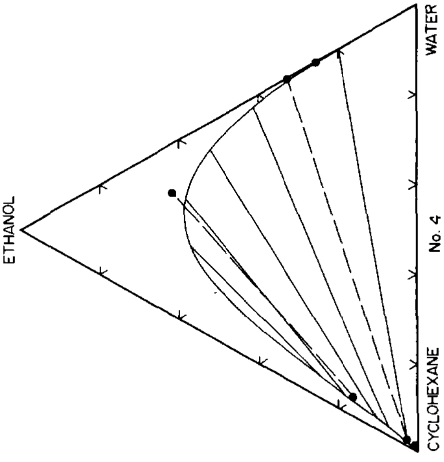

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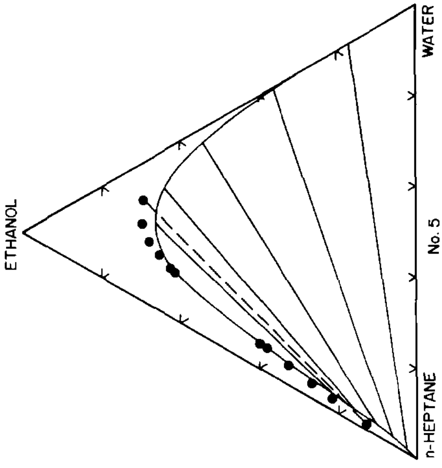

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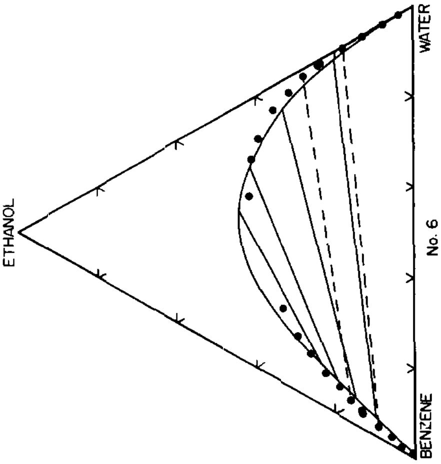

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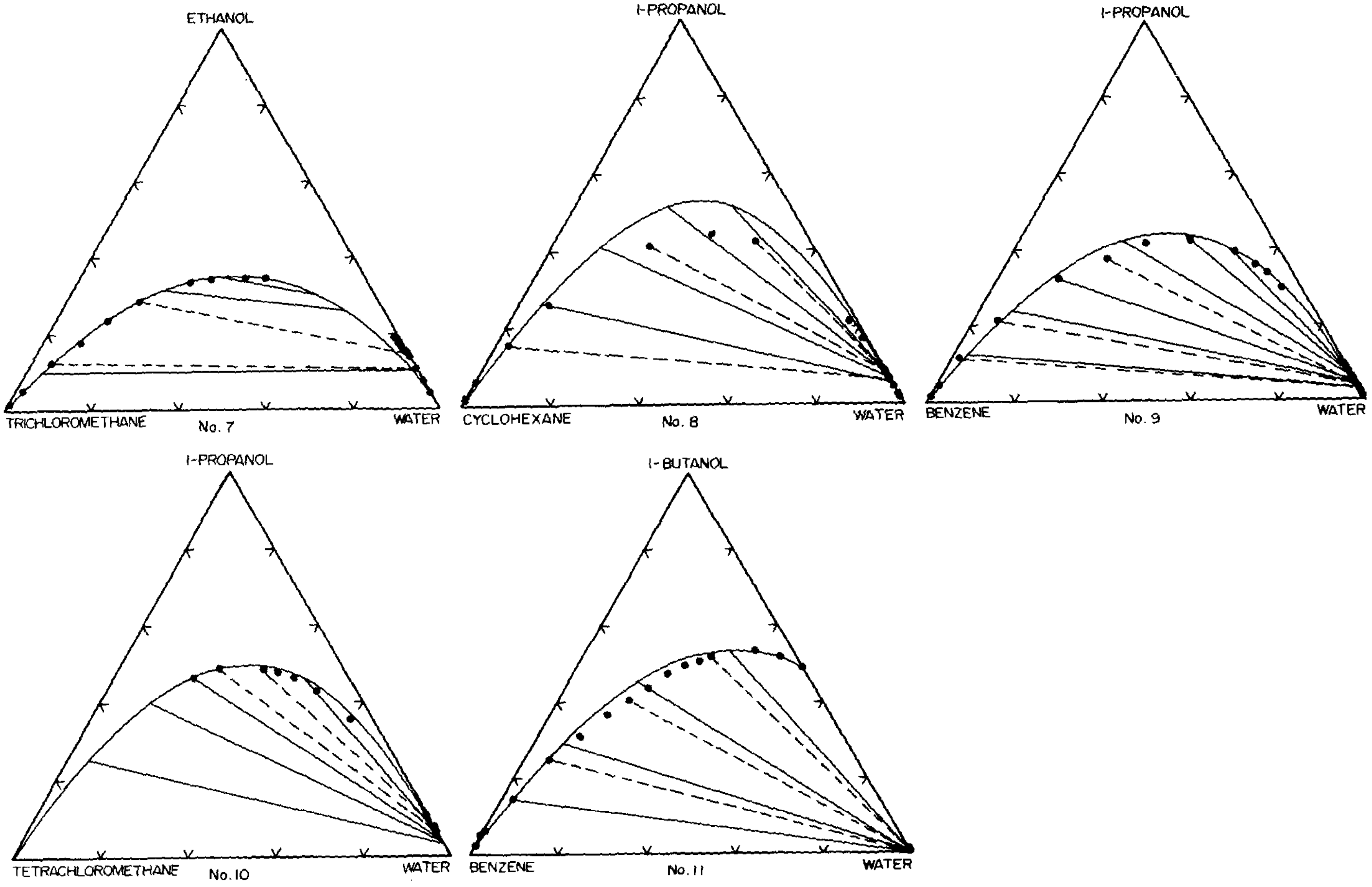

Fig. 3. Calculated and experimental liquid–liquid equilibria. The number refers to Table 4. Experimental tie-line (●------●). Calculated (———). Compositions are expressed as mole fractions.

K_{AB}, K_{AC}, K_{BC}, K_{ABC}	equilibrium constants for solvation
P	total pressure
P_I^s	saturated vapor pressure of pure component I
q_I	molecular geometric area parameter of pure component I
R	universal gas constant
r_I	molecular geometric size parameter of pure component I
T	absolute temperature
v_I^L	liquid molar volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
Z	coordination number (equal to 10)

Greek letters

γ_I	activity coefficient of component I
θ_I	area fraction of component I
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid mole fraction and vapor mole fraction
τ_{IJ}	$\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{A_1}, Φ_{B_1}, Φ_{C_1}	monomer segment fractions of components A, B and C
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, B, C	components
A_1, A_i, B_1, B_i	monomer and i-mer of components A and B
A_iB_j	binary complex containing i molecules of component A and j molecules of component B
$A_iB_jC_k$	ternary complex containing i molecules of component A, j molecules of component B and k molecules of component C
AB, ABC	complex containing components A and B, or A, B and C, respectively
i, j, k	i-mer, j-mer and k-mer
I, J, K	components I, J and K

Superscripts

s	saturated
0	pure component
L	liquid

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