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THERMODYNAMICS OF ASSOCIATED MIXTURES OF THE MECKE—KEMPTER TYPE

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ABSTRACT

A chain-forming associated solution theory based on the UNIQUAC equation is presented for alcohol-unassociated active component liquid mixtures of the Mecke—Kempter type. The capability of the theory in reproducing the excess Gibbs free energy and excess enthalpy data for many binary mixtures is successfully shown. Ternary extension of the theory is presented in the calculations of vapor—liquid and liquid—liquid equilibria and excess enthalpy data from binary data.

NOTATION

C, D	constants of eqn. (34)
f	summation as defined by eqn. (24)
g^E	excess Gibbs free energy
h	enthalpy of formation of a hydrogen bond or alcohol-unassociated component bond
h^E	excess enthalpy
K	chemical equilibrium constant
l_i	bulk factor of pure component i as defined by eqn. (14)
n	number of moles of a particular species
P	total pressure
P_i^s	saturated vapor pressure of pure component i
q_i	surface parameter of pure component i
r_i	volume parameter of pure component i
R	gas constant
T	absolute temperature
u_{ji}	binary interaction parameter
V	segment number of one true mole of solution in which alcohol complexes and alcohol-unassociated active component complexes are considered as chemical species
v_i^L	molar liquid volume of pure component i
x_i	liquid-phase mole fraction of component i

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y_i	vapor-phase mole fraction of component i
Z	lattice coordination number, a constant here set equal to 10

Greek symbols

γ_i	activity coefficient of component i
θ_i	surface fraction of component i
ρ_{AB}	r_B/r_A
ρ_{AC}	r_C/r_A
τ_{ji}	$\exp[-(u_{ji} - u_{ii})/RT]$
ϕ_i	volume fraction of component i
ψ_i	vapor-phase fugacity coefficient of component i
ψ_i^s	vapor-phase fugacity coefficient of pure component i at system temperature T and pressure P_i^s

Superscripts

L	liquid
M	mixing
0	pure alcohol
s	saturation
I, II	phases

Subscripts

A	alcohol, component 1
A_1, A_i	alcohol monomer and i-mer, respectively
AB	complex formation between alcohol and component B
A_iB	alcohol i-mer-unassociated component B complex
AC	complex formation between alcohol and component C
A_iC	alcohol i-mer-unassociated component C complex
B, C	unassociated components 2, 3, respectively
chem	chemical
f	complex formation
i, j, k	components
phys	physical
T	total

INTRODUCTION

Previous studies on concentrated alcohol solutions have shown that the thermodynamic properties of alcohols in unassociated components could be correlated in terms of continuous association models which are based on the alcohol self-association concept. The thermodynamic properties of athermal associated mixtures consisting of a continuously associated component (species A_i, $i = 1, 2, 3 \ldots$) and a chemically inert component (one species) have been theoretically investigated on the basis of the Mecke—Kempter model using Flory's approximation for the entropic term [1,2]. In the representation of the excess enthalpies of these mixtures, the residual interaction expressed by the Scatchard—Hildebrand equation is further included [3,4]. Wiehe and Bagley [5] considered the ratio of the molar volumes of the components as an adjustable parameter in the derivation of a theory of solutions of alcohols in inert components by using the athermal Flory equation. The theory of Wiehe and Bagley fails to predict liquid—liquid phase separation and is unable to give a good description of excess enthalpy. Wiehe et al. [6] have coupled the two-parameter Flory—Huggins equation with stoichiometric models of association and interaction with unassociated active components to obtain a good prediction of ternary vapor—liquid equilibria from binary data. The failure of the previous approaches in the successful correlation of the three thermodynamic properties (vapor—liquid and liquid—liquid equilibria and excess enthalpy) of alcohol solutions of the Mecke—Kempter type is mainly due to the deficiencies of the equations used. A more flexible equation than the Flory—Huggins equation should be adopted as the basic equation to improve the associated solution theory. The UNIQUAC equation is applicable to binary and multicomponent mixtures of nonpolar and polar liquids as well as polymer solutions to give good representation of both vapor—liquid and liquid—liquid equilibria [7]. We have applied the UNIQUAC equation to the associated solution theory for alcohol-saturated hydrocarbon mixtures [8].

The resultant theory has been shown to be more useful than the previous approaches in the correlation of the excess Gibbs free energy and excess enthalpy.

In the present extension of our previous theory [8], the Mecke—Kempter model is derived for the calculation of the three thermodynamic properties of binary and ternary alcohol mixtures including unassociated active components.

THEORY

For a ternary mixture of an alcohol (A = component 1) and two unassociated active components (B = component 2, and C = component 3), we [9] have derived the expressions of the activity coefficients and the excess Gibbs free energy, which are given as the sum of the chemical and physical terms, by using the UNIQUAC equation with the following assumptions.

(1) The alcohol self-associates to form open chain hydrogen-bonded complexes (A_i) given by successive chemical reaction

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

Alcohol i-mers and unassociated active component form chemical complexes (A_iB and A_iC) according to

$$A_i + B = A_iB \tag{2}$$

$$A_i + C = A_iC \tag{3}$$

(2) Structural parameters of chemical complexes are expressed by those for pure components, i.e.

$r_{A_i} =$ [illegible] $= ir_1$, $q_{A_i} = iq_1$, $r_{A_iB} = ir_1 + r_2$; and $q_{A_iB} = iq_1 + q_2$

(3) Physical interactions between all the components can be given by the residual term of the UNIQUAC equation.

$$\ln \gamma_i = \ln(\gamma_i)_{\mathrm{chem}} + \ln(\gamma_i)_{\mathrm{phys}} \tag{4}$$

$$\ln(\gamma_1)_{\mathrm{chem}} = \ln\left(\frac{\phi_{A_1}}{\phi^0_{A_1} x_1}\right) + \frac{r_1}{V^0} - \frac{r_1}{V} + \left(\frac{Z}{2}\right) q_1 \ln\left(\frac{\theta_1}{\phi_1}\right) + (1 - l_1)\phi_1 + (1 - l_2)\phi_2 \frac{r_1}{r_2} + (1 - l_3)\phi_3 \frac{r_1}{r_3} + l_1 - 1 \tag{5}$$

$$\ln(\gamma_2)_{\mathrm{chem}} = \ln\left(\frac{\phi_{OB}}{x_2}\right) + 1 - \frac{r_2}{V} + \left(\frac{Z}{2}\right) q_2 \ln\left(\frac{\theta_2}{\phi_2}\right) + (1 - l_2)\phi_2 + (1 - l_3)\phi_3 \frac{r_2}{r_3} + (1 - l_1)\phi_1 \frac{r_2}{r_1} + l_2 - 1 \tag{6}$$

$$\ln(\gamma_3)_{\mathrm{chem}} = \ln\left(\frac{\phi_{OC}}{x_3}\right) + 1 - \frac{r_3}{V} + \left(\frac{Z}{2}\right) q_3 \ln\left(\frac{\theta_3}{\phi_3}\right) + (1 - l_3)\phi_3 + (1 - l_1)\phi_1 \frac{r_3}{r_1} + (1 - l_2)\phi_2 \frac{r_3}{r_2} + l_3 - 1 \tag{7}$$

$$\ln(\gamma_i)_{\mathrm{phys}} = -q_i \ln\left(\sum_{j=1}^{3} \theta_j \tau_{ji}\right) + q_i - q_i \sum_{j=1}^{3} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{3} \theta_k \tau_{kj}} \tag{8}$$

$$\tau_{ji} = \exp[-(u_{ji} - u_{ii})/RT] \tag{9}$$

where the binary parameters $(u_{ji} - u_{ii})$ can be obtained from experimental data and V is the segment number of one true mole of the alcohol solution.

$$\frac{1}{V^0} = \sum_{i=1}^{\infty} \frac{\phi_{A_i}}{r_{A_i}} + \sum_{i=0}^{\infty} \frac{\phi_{A_iB}}{r_{A_iB}} + \sum_{i=0}^{\infty} \frac{\phi_{A_iC}}{r_{A_iC}} \tag{10}$$

V^0 is V at pure alcohol state.

$$\frac{1}{V} = \sum_{i=1}^{\infty} \frac{\phi^0_{A_i}}{r_{A_i}} \tag{11}$$

θ is the surface fraction, ϕ is the volume fraction, the coordination number Z is equal to 10 and l is the bulk factor.

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{3} q_j x_j} \tag{12}$$

$$\phi_i = \frac{r_i x_i}{\sum_{j=1}^{3} r_j x_j} \tag{13}$$

$$l_i = \left(\frac{Z}{2}\right)(r_i - q_i) - (r_i - 1) \tag{14}$$

$$g^E = g^E_{\text{chem}} + g^E_{\text{phys}} \tag{15}$$

$$\frac{g^E_{\text{chem}}}{RT} = x_1 \ln\left(\frac{\phi_{A_1}}{\phi^0_{A_1} x_1}\right) + x_2 \ln\left(\frac{\phi_{OB}}{x_2}\right) + x_3 \ln\left(\frac{\phi_{OC}}{x_3}\right) + \frac{r_1 x_1}{V^0} + x_2 + x_3$$

$$- \frac{\sum_{i=1}^{3} r_i x_i}{V} + \left(\frac{Z}{2}\right)\sum_{i=1}^{3} q_i x_i \ln\left(\frac{\theta_i}{\phi_i}\right) \tag{16}$$

$$\frac{g^E_{\text{phys}}}{RT} = -\sum_{i=1}^{3} q_i x_i \ln\left(\sum_{j=1}^{3} \theta_j \tau_{ji}\right) \tag{17}$$

For the associated mixtures of the Mecke—Kempter type, we may define the chemical equilibrium constants for eqns. (1—3) as follows.

$$K_A = \frac{\phi_{A_{i+1}}}{\phi_{A_i}\phi_{A_1}} \tag{18}$$

$$K_{AB} = \frac{\phi_{A_iB}}{\phi_{A_i}\phi_{OB}} \tag{19}$$

$$K_{AC} = \frac{\phi_{A_iC}}{\phi_{A_i}\phi_{OC}} \tag{20}$$

Then, the monomer volume fractions of the components, ϕ_{A_1}, ϕ_{OB}, and ϕ_{OC} are given by solving the following material balance equations between the nominal components and the chemical complexes.

$$\phi_1 = \sum_{i=1}^{\infty} \phi_{A_i} + \sum_{i=1}^{\infty} \frac{n_{A_iB} r_{A_i}}{V} + \sum_{i=1}^{\infty} \frac{n_{A_iC} r_{A_i}}{V} \tag{21}$$

$$= \frac{\phi_{A_1}}{1 - K_A\phi_{A_1}} + K_{AB}\phi_{OB}\phi_{A_1}\left(\frac{1}{1 - K_A\phi_{A_1}} - \frac{\rho_{AB} f_{AB}}{K_A\phi_{A_1}}\right)$$

$$+ K_{AC}\phi_{OC}\phi_{A_1}\left(\frac{1}{1 - K_A\phi_{A_1}} - \frac{\rho_{AC} f_{AC}}{K_A\phi_{A_1}}\right) \tag{21}$$

$$\phi_2 = \sum_{i=0}^{\infty} \frac{n_{A_iB} r_2}{V} = \phi_{OB}\left(1 + \frac{K_{AB}\rho_{AB} f_{AB}}{K_A}\right) \tag{22}$$

$$\phi_3 = \sum_{i=0}^{\infty} \frac{n_{A_iC} r_3}{V} = \phi_{OC}\left(1 + \frac{K_{AC}\rho_{AC} f_{AC}}{K_A}\right) \tag{23}$$

where ρ_{AB} is the ratio of r_2 to r_1 and $\rho_{AC} = r_3/r_1$. f_{AB} and f_{AC} are expressed by

$$f_{AB} = \sum_{i=1}^{\infty} \frac{(K_A\phi_{A_1})^i}{i + \rho_{AB}} \tag{24}$$

$$f_{AC} = \sum_{i=1}^{\infty} \frac{(K_A\phi_{A_1})^i}{i + \rho_{AC}} \tag{25}$$

$\phi^0_{A_1}$, V, and V^0 are given by

$$\phi^0_{A_1} = (1 + K_A)^{-1} \tag{26}$$

$$\frac{1}{V} = -\frac{\ln(1 - K_A\phi_{A_1})}{K_A r_1} + \frac{\phi_{OB}}{r_2}\left(1 + \frac{K_{AB}\rho_{AB}f_{AB}}{K_A}\right) + \frac{\phi_{OC}}{r_3}\left(1 + \frac{K_{AC}\rho_{AC}f_{AC}}{K_A}\right) \tag{27}$$

$$\frac{1}{V^0} = -\frac{\ln(1 - K_A\phi^0_{A_1})}{K_A r_1} \tag{28}$$

The ternary excess enthalpy is also represented as the sum of the chemical and physical contribution terms.

$$h^E = h^E_{chem} + h^E_{phys} \tag{29}$$

The enthalpy of formation of the complexes is expressed by

$$h_f = h_A \sum_{i=1}^{\infty} (i - 1)(n_{A_i} + n_{A_iB} + n_{A_iC}) + h_{AB} \sum_{i=1}^{\infty} n_{A_iB} + h_{AC} \sum_{i=1}^{\infty} n_{A_iC} \tag{30}$$

The definition of the excess enthalpy gives

$$\begin{aligned} h^E_{chem} &= h_f - x_1 h^0_f \\ &= \frac{h_A}{K_A}[x_1 \ln(1 + K_A) + (x_1 + \rho_{AB}x_2 + \rho_{AC}x_3)\ln(1 - K_A\phi_{A_1})] \\ &\quad + (h_{AB} - h_A)\frac{K_{AB}\rho_{AB}f_{AB}x_2}{K_A + K_{AB}\rho_{AB}f_{AB}} + (h_{AC} - h_A)\frac{K_{AC}\rho_{AC}f_{AC}x_3}{K_A + K_{AC}\rho_{AC}f_{AC}} \end{aligned} \tag{31}$$

where h_A is the enthalpy of formation of an alcohol hydrogen bond, h_{AB} is the enthalpy of complex formation of an alcohol-interacting component B bond and h_{AC} is similar to h_{AB}.

TABLE 1

Values of the pure component structural parameters

Component	r	q	l	Component	r	q	l
Methanol	1.15	1.12	0	Tetrachloromethane	2.71	2.37	0
Ethanol	1.65	1.55	0	Methyl ethanoate	2.25	2.00	0
1-Propanol	2.23	1.98	0	Ethyl ethanoate	2.79	2.43	0
2-Propanol	2.23	1.98	0	Ethyl methanoate	2.26	2.01	0
1-Butanol	2.77	2.42	0	2-Propanone	2.06	1.85	0
Cyclopentanol	2.88	2.30	1	2-Butanone	2.60	2.28	0
Cyclohexanol	3.45	2.74	1	Triethylamine	4.02	3.41	0
n-Hexane	3.61	3.09	0	Diethyl ether	2.72	2.38	0
Cyclohexane	3.18	2.55	1	Tetrahydrofuran	2.36	1.89	1
Methylcyclohexane	3.72	2.98	1	Piperidine	3.15	2.52	1
Benzene	2.56	2.05	1	Pyridine	2.40	1.92	1
Toluene	3.10	2.48	1	*N*,*N*-Dimethylacetamide	3.01	2.61	0
Dichloromethane	1.83	1.67	0	Ethanenitrile	1.50	1.40	0
Trichloromethane	2.30	2.04	0				

TABLE 2

Values of h_{AB} and K_{AB} for binary alcohol solutions

System	$-h_{AB}$ (kcal mole^{-1})	K_{AB} [T°C]	Ref.
Methanol—benzene	2.2	9	25
Ethanol—benzene	2.2	8	25
1-Propanol—benzene	2.2	7	25
2-Propanol—benzene	2.2	7	25
1-Butanol—benzene	2.2	7	25
Methanol—toluene	2.6	9	25
Ethanol—toluene	2.6	8	25
1-Propanol—toluene	2.6	7	25
2-Propanol—toluene	2.6	7	25
1-Butanol—toluene	2.6	7	25
Methanol—dichloromethane	5.0	230	50
Methanol—trichloromethane	5.9	185	50
Ethanol—trichloromethane	5.9	85	50
1-Propanol—trichloromethane	5.9	55	50
2-Propanol—trichloromethane	5.9	45	50
1-Butanol—trichloromethane	5.9	50	50
Methanol—tetrachloromethane	3.8	2.2	25
Ethanol—tetrachloromethane	3.8	2	25
1-Propanol—tetrachloromethane	3.8	2	25
2-Propanol—tetrachloromethane	3.8	2	25
1-Butanol—tetrachloromethane	3.8	2	25
Methanol—ester	4.8	190	25
Ethanol—ester	4.8	120	25
1-Propanol—ester	4.8	85	25
2-Propanol—ester	4.8	70	25
1-Butanol—ester	4.8	75	25
Methanol—ketone, amine	5.5	190	50
Ethanol—ketone, amine	5.5	90	50
1-Propanol—ketone	5.5	60	50
2-Propanol—ketone	5.5	45	50
1-Butanol—ketone	5.5	50	50
Cyclopentanol—2-propanone	5.5	30	50
Cyclohexanol—2-propanone	5.5	20	50
Methanol—diethyl ether, tetrahydrofuran	5.5	150	50
Ethanol—diethyl ether	5.5	95	50
Methanol—piperidine	5.5	200	50
Ethanol—pyridine	5.5	150	50
1-Propanol—pyridine	5.5	60	50
1-Butanol—pyridine	5.5	50	50
Methanol—*N*,*N*-dimethylacetamide	5.9	185	50
Ethanol—*N*,*N*-dimethylacetamide	5.9	85	50
1-Propanol—*N*,*N*-dimethylacetamide	5.9	55	50
1-Butanol—*N*,*N*-dimethylacetamide	5.9	50	50
Ethanol—ethanenitrile	5.0	100	50

TABLE 3

Correlation for binary excess Gibbs free energy and excess enthalpy data

System (1–2)	Temp. (°C)	No. of data points	Abs. arith. mean dev. (cal mole^{-1})	C_1	C_2	D_1	D_2	Ref.
				(cal mole^{-1})		(cal mole^{-1} K^{-1})		
g^E								
Methanol–dichloromethane	35	9	1.9	1101.13	−307.74			13
Methanol–trichloromethane	35	9	2.6	1276.55	−351.56			13
Methanol–tetrachloromethane	35	9	1.8	−89.41	143.97			13
Methanol–triethylamine	39.95	9	1.2	618.16	−386.02			14
Methanol–piperidine	25	9	4.5	18.16	−552.31			15
Ethanol–triethylamine	64.85	9	0.8	245.20	−73.16			14
Ethanol–pyridine	65	11	0.5	−380.43	584.41			16
1-Propanol–triethylamine	69.95	9	0.3	213.60	−93.05			14
1-Propanol–pyridine	70	11	0.4	261.94	−322.09			16
1-Butanol–pyridine	70	11	0.4	−82.06	192.70			16
Cyclopentanol–2-propanone	25	13	1.6	−249.06	667.41			17
Cyclohexanol–2-propanone	25	23	1.8	−245.13	704.16			18
h^E								
Methanol–benzene	25	10	0.8	1511.02	−1074.36	1.1707	−3.6771	19
Methanol–toluene	25	10	0.6	1897.92	−1530.53	−2.4375	−5.2449	19
Methanol–2-propanone	25.05	8	1.7	254.11	6.18	0.0554	−0.1009	20
Methanol–2-butanone	25	13	3.9	520.94	−146.00	0.1604	−0.2517	21
Methanol–methyl ethanoate	25	16	3.4	351.33	37.31	0.1117	0.3090	22
Methanol–tetrahydrofuran	25	19	1.3	−186.12	−138.42	−0.1511	−1.3391	23

Methanol—dichloromethane	35	11	2.5	1840.10	131.08	−2.8695	2.6548	13
Methanol—trichloromethane	35	10	3.6	1608.01	−105.03	−4.2761	2.4088	13
Methanol—tetrachloromethane	35	13	3.0	1454.84	−590.23	1.6492	−1.7091	24
Methanol—triethylamine	25	9	3.8	83.80	89.77	5.3277	0.5320	25
Methanol—*N*,*N*-dimethylacetamide	25	20	1.2	206.24	265.24	3.7255	−0.0610	26
Methanol—piperidine	25	23	4.0	−716.86	983.73	22.2856	−25.6210	15
Ethanol—cyclohexane	25	21	0.6	117.60	318.24	0.1162	0.6302	27
Ethanol—toluene	25	10	2.1	999.28	−478.04	1.8251	−1.4188	19
Ethanol—2-propanone	25.12	9	0.8	313.22	986.02	−0.5292	1.8476	20
Ethanol—ethyl methanoate	25	9	1.5	−165.01	252.38	−0.3473	0.4172	28
Ethanol—diethyl ether	25.15	8	4.1	996.42	−912.16	−0.0744	−2.9948	20
Ethanol—trichloromethane	25	29	4.4	1106.00	260.53	−1.3943	4.1065	29
Ethanol—triethylamine	25	9	2.5	71.25	147.33	3.0062	0.8245	25
Ethanol—*N*,*N*-dimethylacetamide	25	21	0.9	56.40	379.93	1.5028	−0.3210	26
Ethanol—pyridine	25	11	2.0	−266.28	87.38	−4.2153	7.0120	30
1-Propanol—2-butanone	35	12	1.4	288.37	731.69	−0.2395	0.8473	31
1-Propanol—*N*,*N*-dimethylacetamide	25	21	0.8	56.45	502.87	0.9089	0.1125	26
2-Propanol—cyclohexane	25	18	4.2	21.56	50.85	0.0630	−0.4868	32
2-Propanol—methylcyclohexane	25	19	4.0	41.50	110.80	0.0334	0.0337	33
2-Propanol—benzene	25	17	1.8	30.13	−66.05	−0.1538	−0.5854	33
1-Butanol—*N*,*N*-dimethylacetamide	25	20	0.5	313.03	803.09	1.2145	1.2976	26
Cyclopentanol—2-propanone	25	16	0.6	−10.61	870.03	−1.6458	0.6419	17
Cyclohexanol—2-propanone	25	19	1.1	94.21	824.42	−1.2876	−0.1438	18
Toluene—cyclohexane	25	12	0.8	172.02	45.64	−0.1602	−0.0424	34
Benzene—methylcyclohexane	25	17	0.2	227.46	157.73	0.1340	−0.0684	33
Benzene—cyclohexane	25	24	0.3	256.40	129.84	0.1914	−0.2396	27

TABLE 4

Correlation for binary vapor—liquid equilibrium data

System (1—2)	Temp. (°C)	No. of data points	Abs. arith. mean dev.		$u_{21} - u_{11}$	$u_{12} - u_{22}$	Ref.
			Vapor mole fraction (×1000)	Pressure (Torr)	(cal mole^{-1})	(cal mole^{-1})	
Methanol—benzene	55	9	16.4	12.0	101.42	−101.82	36
Methanol—2-propanone	50	35	11.4	4.4	−230.05	380.36	37
Methanol—2-butanone	50	13	5.4	1.3	−150.76	351.51	21
Methanol—methyl ethanoate	50	15	11.9	6.0	−374.52	621.64	37
Methanol—ethyl ethanoate	55	11	6.0	1.9	−353.14	568.88	38
Methanol—ethyl methanoate	45	12	3.3	1.8	−197.11	414.78	28
Methanol—diethyl ether	25	19		4.7	493.51	−152.96	39
Methanol—tetrahydrofuran	25	19		1.5	−270.55	466.81	23
Methanol—trichloromethane	50	25	8.0	4.2	1398.98	−406.46	37
Methanol—tetrachloromethane	25	11	6.2		−165.90	233.90	40
Ethanol—n-hexane	40	16	7.5	4.5	−263.73	447.67	41
Ethanol—benzene	45	12	8.9	1.5	−42.34	89.41	42
Ethanol—2-propanone	32	14	6.1	1.4	−251.08	627.82	43
Ethanol—2-butanone	55	14	5.2	1.1	−193.58	443.38	21
Ethanol—methyl ethanoate	45	11	4.2	3.7	−211.69	529.68	22

Ethanol—ethyl ethanoate	55	11	2.1	1.5	−139.65	313.93	38
Ethanol—ethyl methanoate	45	12	6.3	3.8	14.77	237.78	28
Ethanol—trichloromethane	35	15	6.2	1.9	1127.40	−393.26	44
Ethanol—tetrachloromethane	60	12	8.3	4.0	144.34	−113.88	45
Ethanol—ethanenitrile	40	14	3.7	0.8	−12.14	719.47	41
Ethanol—diethyl ether	0	19	3.7	2.8	338.51	−72.51	46
1-Propanol—benzene	45	11	3.0	0.9	−147.63	268.83	47
1-Propanol—methyl ethanoate	45	11	6.3	6.2	−326.94	847.98	21
1-Propanol—ethyl ethanoate	55	12	5.7	2.7	−228.70	488.42	38
1-Propanol—ethyl methanoate	45	11	6.1	9.5	−121.55	439.07	28
1-Propanol—tetrachloromethane	70	11	6.1	2.1	5.35	18.44	48
2-Propanol—benzene	70	10	7.3	3.2	−112.71	227.23	49
2-Propanol—2-butanone	55	9	10.7	2.0	−1.22	122.31	21
2-Propanol—methyl ethanoate	45	11	3.8	3.5	−264.42	606.79	21
2-Propanol—ethyl ethanoate	55	12	7.2	1.4	−63.60	177.85	38
2-Propanol—ethyl methanoate	45	11	7.8	3.6	−111.61	420.18	28
1-Butanol—benzene	45	9	2.2	1.3	−275.53	524.46	47
1-Butanol—tetrachloromethane	35	21	2.1	1.4	−334.54	537.60	50
Tetrahydrofuran—cyclohexane	25	19		0.9	512.75	−201.63	51
2-Propanone—trichloromethane	50	29	4.6	2.1	109.79	−309.53	37
2-Propanone—methyl ethanoate	50	35	3.4	3.1	173.99	−126.49	37
Ethanenitrile—n-hexane	40 [a]				1302.67	167.65	41
Methanol—cyclohexane	25 [a]				−196.81	446.44	40

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[a] Solubility data.

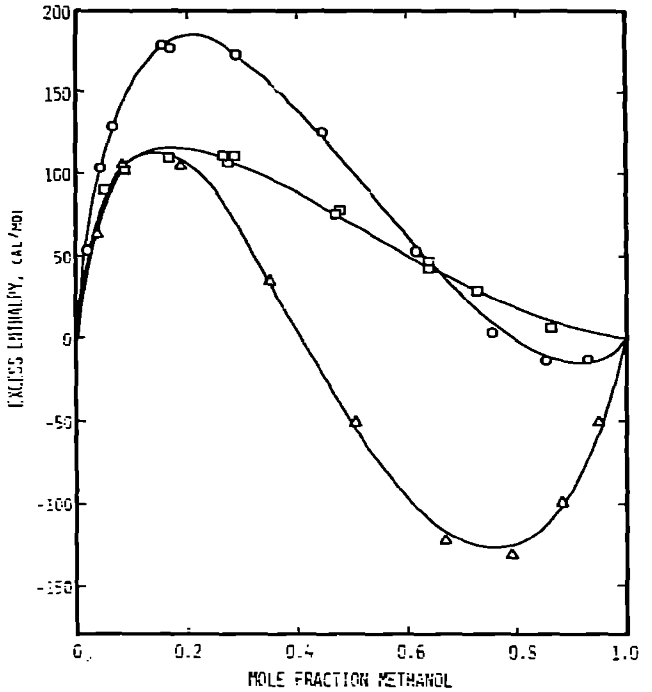

Fig. 1. Excess enthalpies for methanol—chloromethane at 35°C: (———) calculated; experimental data: (○) methanol—dichloromethane, Moelwyn-Hughes and Missen [13]; (△) methanol—trichloromethane, Moelwyn-Hughes and Missen [13]; (□) methanol—tetrachloromethane, Otterstedt and Missen [24].

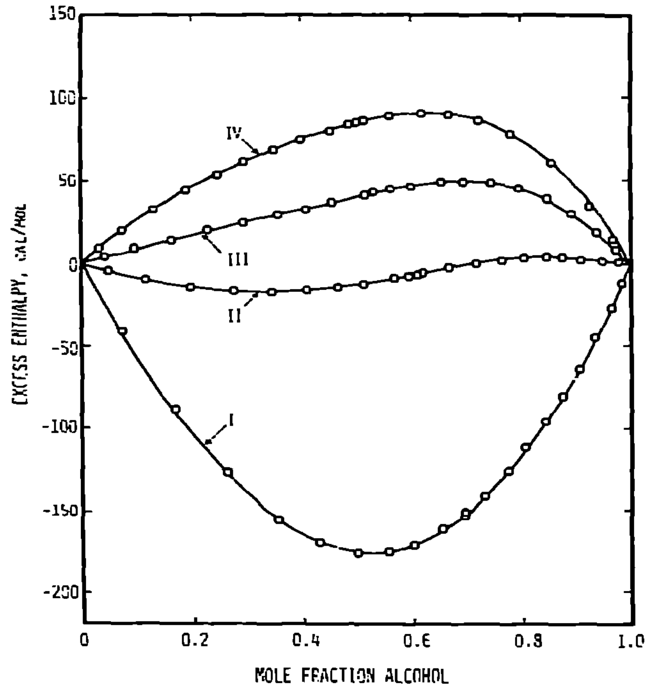

Fig. 2. Excess enthalpies for n-alcohols—*N,N*-dimethylacetamide at 25°C: (———) calculated; (○) experimental data of Oba et al. [26]: (I) methanol—*N,N*-dimethylacetamide; (II) ethanol—*N,N*-dimethylacetamide; (III) 1-propanol—*N,N*-dimethylacetamide; (IV) 1-butanol—*N,N*-dimethylacetamide.

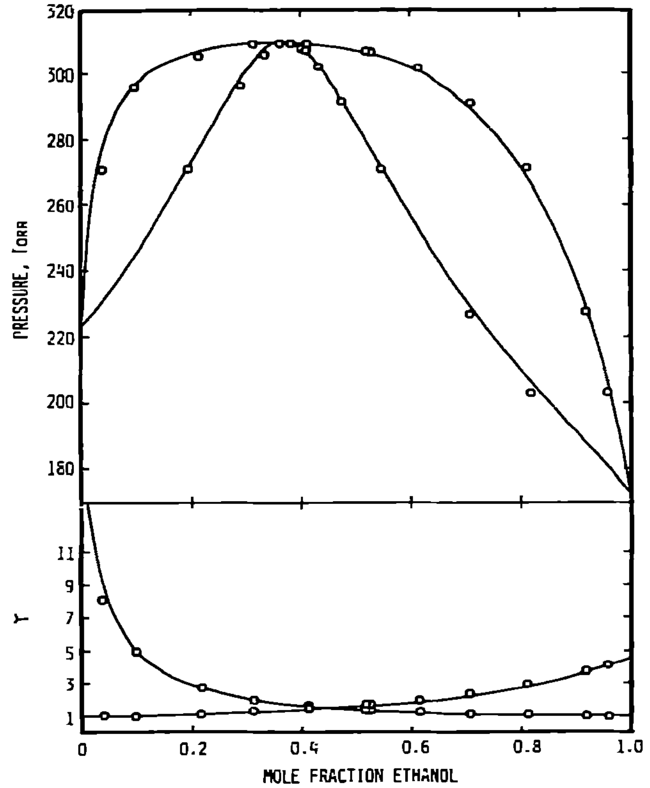

Fig. 3. Vapor—liquid equilibria for ethanol—benzene at 45°C: (———) calculated; (o) experimental data of Brown and Smith [42].

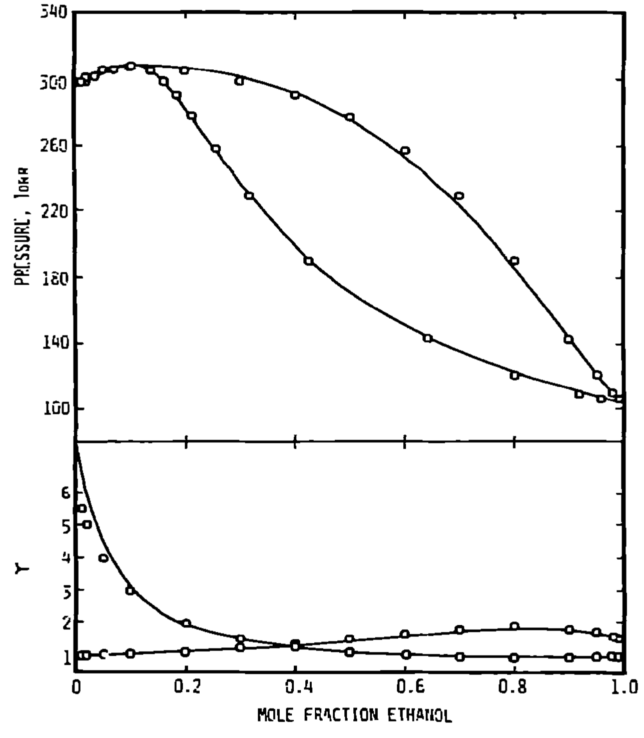

Fig. 4. Vapor—liquid equilibria for ethanol—trichloromethane at 35°C: (———) calculated; (o) experimental data of Scatchard and Raymond [44].

Combining use of eqn. (17) and the Gibbs—Helmholtz equation gives the physical contribution term of the excess enthalpy.

$$h^{E}_{\text{phys}} = \frac{\partial(g^{E}_{\text{phys}}/T)}{\partial(1/T)} = -R\sum_{i=1}^{3} q_i x_i \frac{\sum_{j=1}^{3} \theta_j \frac{\partial \tau_{ji}}{\partial(1/T)}}{\sum_{j=1}^{3} \theta_j \tau_{ji}} \tag{32}$$

CALCULATED RESULTS

The pure component structural parameters were estimated according to the method suggested by Vera et al. [10]. Table 1 gives r and q for pure components. These values seem to be consistent with the restraints imposed on the quasi-lattice theory of liquids [10,11]: $l = 0$ for straight or branched open-chain molecules; $l = 1$ for cyclic molecules (aromatics, cycloalkanes, etc.).

The equilibrium constant K_A at 50°C is 350 for methanol, 170 for ethanol, 110 for 1-propanol, 85 for 2-propanol, 95 for 1-butanol, 80 for cyclopentanol, and 70 for cyclohexanol [8]. We have used one value for h_A, —6 kcal mole^{-1} [12]. The van't Hoff equation fixes the temperature dependence of the equilibrium constant by

$$\frac{\partial \ln K}{\partial(1/T)} = -\frac{h}{R} \tag{33}$$

The value of K_{AB} and h_{AB} listed in Table 2 are selected which best reproduce all experimental data available to us. In excess enthalpy data reduction, we have assumed that the energy parameters could be expressed by linear functions of temperature

$$u_{ji} - u_{ii} = C_i + D_i(T - 273.15) \tag{34}$$

The coefficients C_i and D_i were obtained using the simplex method described by Nelder and Mead [35].

The condition for vapor—liquid equilibrium at normal pressures is given by

$$\psi_i y_i P = x_i \gamma_i \psi_i^s P_i^s \exp \frac{(P - P_i^s) v_i^L}{RT} \tag{35}$$

where y_i is the vapor mole fraction, P is the total pressure, P_i^s is the saturated pressure, and v_i^L is the molar liquid volume for pure component i at temperature T. ψ_i, the fugacity coefficient of component i at P, and ψ_i^s, that at saturation, can be calculated from second virial coefficients in accordance with the methods described by Prausnitz et al. [53].

The condition for liquid—liquid equilibrium between liquid phase I and liquid phase II becomes

$$x_i^{I} \gamma_i^{I} = x_i^{II} \gamma_i^{II} \tag{36}$$

Some typical results are shown in Tables 3 and 4 and in Figs. 1—4. Figures

1 and 2 illustrate a good ability of the associated solution theory in the correlation of excess enthalpy data. Figure 3 shows experimental and calculated phase equilibria for the ethanol—benzene system at 45°C. The good quality data of Brown and Smith [42] are well represented by the present model. Figure 4 shows a good fit of the model to the excellent data of Scatchard and Raymond [44] for ethanol—trichloromethane. This system exhibits extrema in the activity coefficients. Such extrema are usually not

TABLE 5

Calculation of ternary excess enthalpy data at 25°C

System	No. of data points	Abs. arith. mean dev. (cal mole^{-1})	Ref.
Ethanol—toluene—cyclohexane	8	5.4	52
2-Propanol—benzene—methylcyclohexane	53	3.4	33
2-Propanol—benzene—cyclohexane	67	5.4	32

TABLE 6

Calculation of ternary vapor—liquid equilibrium data at 50°C

System	No. of data points	Abs. arith. mean dev.		Ref.
		Vapor mole fraction (×1000)	Pressure (Torr)	
2-Propanone Trichloromethane Methanol	30	7 9 14	12.2	37
2-Propanone Methanol Methyl ethanoate	35	7 16 12	6.9	37

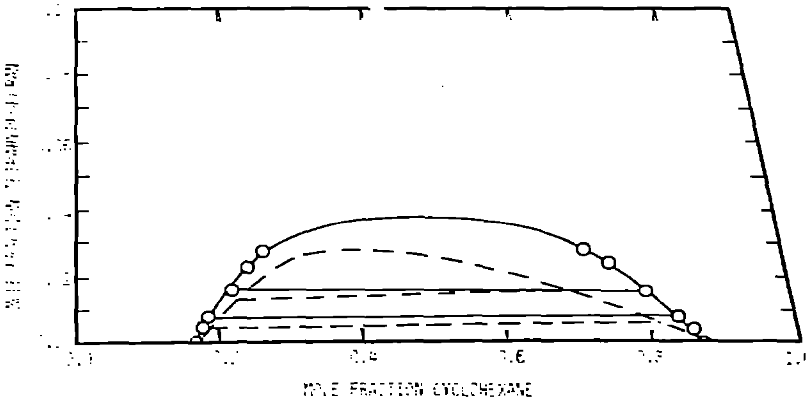

Fig. 5. Liquid—liquid equilibria for methanol—tetrahydrofuran—cyclohexane at 25°C: (— — —) calculated; (o———o) experimental data of Sugi et al. [54]

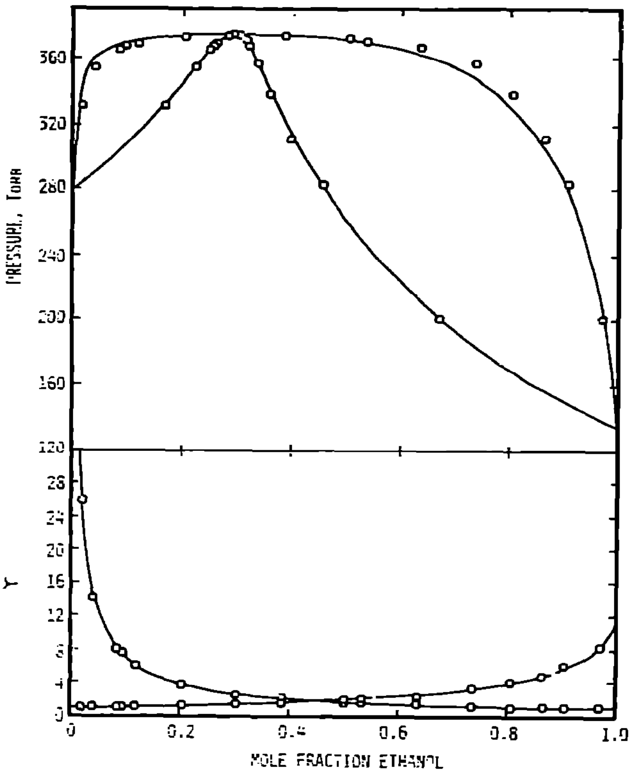

Fig. 6. Vapor—liquid equilibria for ethanol—n-hexane at 40°C: (———) calculated; (o) experimental data of Sugi and Katayama [41].

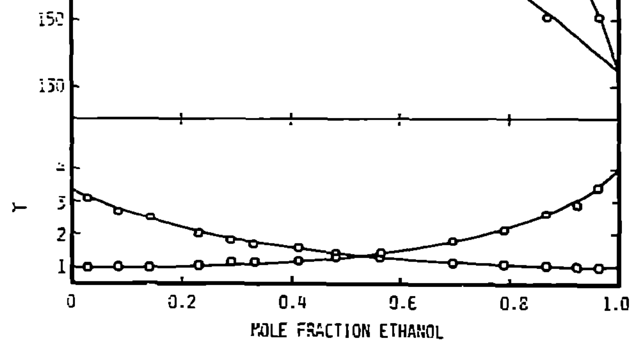

Fig. 7. Vapor—liquid equilibria for ethanol—ethanenitrile at 40°C: (———) calculated; (o) experimental data of Sugi and Katayama [41].

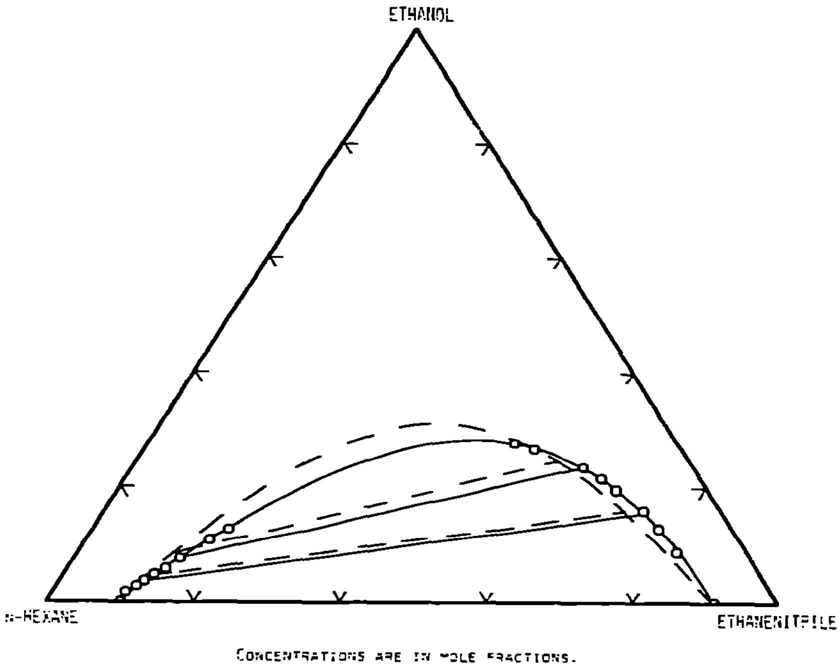

Fig. 8. Liquid—liquid equilibria for ethanol—ethanenitrile—n-hexane at 40°C: (— — —) calculated; (o———o) experimental data of Sugi and Katayama [41].

well correlated by the UNIQUAC equation.

Ternary calculations of excess enthalpy and vapor—liquid equilibrium data from the binary parameters given in Tables 3 and 4 were carried out; the results are presented in Tables 5 and 6. The agreement between ternary calculated and experimental liquid—liquid solubility curves was not satisfactory for methanol-containing systems in which the two-phase region is extremely small (Fig. 5). Figures 6 and 7 show observed and calculated vapor—liquid equilibria for the two miscible binaries of the ternary ethanol—ethanenitrile—n-hexane system. The calculations agree substantially with the experimental values of this ternary (Fig. 8). Ternary predictions by the UNIQUAC equation gave too large immiscible range, because the UNIQUAC equation does not fit adequately the binary vapor—liquid equilibria for alcohol—hydrocarbon systems.

CONCLUSION

The UNIQUAC associated solution theory of the Mecke—Kempter type is useful in the correlation of the excess thermodynamic functions of concentrated alcohol solutions involving various kinds of unassociated components in binary as well as ternary systems. However, the calculated ternary liquid—liquid equilibria did not agree well with the experimental values of those systems having a small two-phase region.

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