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PREDICTION OF THERMODYNAMIC EQUILIBRIUM PROPERTIES FROM MUTUAL SOLUBILITY DATA *

ISAMU NAGATA and KAORU MIYAMOTO

Department of Chemical Engineering, Kanazawa University, Kanazawa 920 (Japan)

PAOLO ALESSI and IRENEO KIKIC

Istituto di Chimica Applicata e Industriale, Universita di Trieste, 34127 Trieste (Italy)

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ABSTRACT

The ability of four existing activity coefficient models to extrapolate mutual solubility data to completely miscible regions is studied. The UNIQUAC associated-solution, extended UNIQUAC, UNIQUAC and NRTL models are used to predict the behaviour of alcohol + saturated hydrocarbon systems. Only experimental mutual solubility data are used to obtain parameters for the four models. The results obtained using these models are compared. In addition, the ability of these models to calculate ternary liquid–liquid equilibria using only binary parameters is studied. The calculated results indicate that the UNIQUAC associated-solution model has the best overall performance.

INTRODUCTION

Activity coefficient models, based on the local composition concept, have been widely used for the description of solution non-ideality. The models have two or three adjustable parameters per binary system. These parameters must be estimated from binary experimental phase equilibrium data: vapour–liquid equilibrium (VLE) data (P, x, y) at constant temperature or pressure and total pressure data (P, x or y) at constant temperature. A full set of these data is not always available. Sometimes only a limited number of experimental data such as activity coefficients at infinite dilution, mutual solubilities and azeotropic data exist, from which it is possible to obtain only two parameters. If a three-parameter model is used, the third parameter must be set as a constant. In a previous paper [1] the ability of existing models to extrapolate properties from infinite dilution to regions far from infinite dilution was investigated.

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In this work, we study the possibilities of extrapolating experimental information obtained from mutual solubilities to finite concentration. The models to be studied are the UNIQUAC associated-solution [2,3], extended UNIQUAC [4], UNIQUAC [5] and NRTL [6] models.

SOLUTION MODELS

The symbol A stands for the alcohol and B for the saturated hydrocarbon. The liquid phase activity coefficients of the components are given below.

UNIQUAC associated-solution model

The model assumes the linear successive polymerization of alcohol molecules ($A_i + A_1 = A_{i+1}$) and that the self-association constant is independent of the degree of association:

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{\Phi^0_{A_1} x_A}\right) + r_A\left(\frac{1}{V^0_A} - \frac{1}{V}\right) - \left(\frac{Z}{2}\right) q_A\left(\ln\frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right)$$
$$+ q_A\left[-\ln(\theta_A + \theta_B\tau_{BA}) + \theta_B\left(\frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}} - \frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}}\right)\right] \quad (1)$$

$$\ln \gamma_B = \ln\left(\frac{\Phi_{B_1}}{x_B}\right) + 1 - \frac{r_B}{V} - \left(\frac{Z}{2}\right) q_B\left(\ln\frac{\Phi_B}{\theta_B} + 1 - \frac{\Phi_B}{\theta_B}\right)$$
$$+ q_B\left[-\ln(\theta_B + \theta_A\tau_{AB}) + \theta_A\left(\frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}} - \frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}}\right)\right] \quad (2)$$

with

$$\Phi_A = x_A r_A/(x_A r_A + x_B r_B) \qquad \Phi_B = x_B r_B/(x_A r_A + x_B r_B) \quad (3)$$

$$\theta_A = x_A q_A/(x_A q_A + x_B q_B) \qquad \theta_B = x_B q_B/(x_A q_A + x_B q_B) \quad (4)$$

$$\tau_{AB} = \exp(-a_{AB}/T) \qquad \tau_{BA} = \exp(-a_{BA}/T) \quad (5)$$

and Z is the coordination number taken as 10.

The segment fraction of alcohol monomer Φ_{A_1} and the true molar volume of an alcohol + saturated hydrocarbon mixture are given by the following equations:

$$\Phi_{A_1} = \left(2K_A\Phi_A + 1 - \sqrt{1 + 4K_A\Phi_A}\right)/2K_A^2\Phi_A \quad (6)$$

$$1/V = \Phi_{A_1}/\left[r_A(1 - K_A\Phi_{A_1})\right] + \Phi_B/r_B \quad (7)$$

In the pure alcohol state, Φ_{A_1} and V reduce to $\Phi^0_{A_1}$ and V^0_A respectively:

$$\Phi^0_{A_1} = \left(2K_A + 1 - \sqrt{1 + 4K_A}\right)/2K_A^2 \quad (8)$$

$$1/V^0_A = \left(1 - K_A\Phi^0_{A_1}\right)/r_A \quad (9)$$

The temperature dependence of the alcohol association constant K_A is expressed by the van't Hoff relation:

$$\partial \ln K_A/\partial(1/T) = -h_A/R \tag{10}$$

The values of K_A at 50 °C were taken from Brandani [7]: for methanol, $K_A = 173.9$; for ethanol, $K_A = 110.4$. The value of h_A is -23.2 kJ mol^{-1}, which is the enthalpy of dilution of ethanol in *n*-hexane at 25 ° C [8] and was assumed to be temperature independent. The molecular structural parameters of the pure components r and q were calculated in accordance with the method of Vera et al. [9].

Extended UNIQUAC model

$$\ln \gamma_A = \ln \frac{\Phi_A}{x_A} + 1 - \frac{\Phi_A}{x_A} - \left(\frac{Z}{2}\right) q_A \left(\ln \frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right) - q_A^* \ln(\theta_A + \theta_B \tau_{BA})$$
$$+ q_A \theta_B \left[\left(\frac{q_A^*}{q_A}\right)\left(\frac{\tau_{BA}}{\theta_A + \theta_B \tau_{BA}} - 1\right) - \left(\frac{q_B^*}{q_B}\right)\left(\frac{\tau_{AB}}{\theta_B + \theta_A \tau_{AB}} - 1\right)\right] \tag{11}$$

$$\ln \gamma_B = \ln \frac{\Phi_B}{x_B} + 1 - \frac{\Phi_B}{x_B} - \left(\frac{Z}{2}\right) q_B \left(\ln \frac{\Phi_B}{\theta_B} + 1 - \frac{\Phi_B}{\theta_B}\right) - q_B^* \ln(\theta_B + \theta_A \tau_{AB})$$
$$+ q_B \theta_A \left[\left(\frac{q_B^*}{q_B}\right)\left(\frac{\tau_{AB}}{\theta_B + \theta_A \tau_{AB}} - 1\right) - \left(\frac{q_A^*}{q_A}\right)\left(\frac{\tau_{BA}}{\theta_A + \theta_B \tau_{BA}} - 1\right)\right] \tag{12}$$

q^* is set as 1.00 for methanol and ethanol, because previously assigned values for these two alcohols did not give a phase separation for binary mixtures of methanol or ethanol with *n*-alkanes. For 2-propanol, $q^* = 0.89$ and for other pure components studied in this work, $q^* = q^{0.2}$ [4]. The values of r and q are given by Prausnitz et al. [10].

UNIQUAC model

$$\ln \gamma_A = \ln \frac{\Phi_A}{x_A} + 1 - \frac{\Phi_A}{x_A} - \left(\frac{Z}{2}\right) q_A \left(\ln \frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right) - q'_A \ln(\theta'_A + \theta'_B \tau_{BA})$$
$$+ q'_A \theta'_B \left(\frac{\tau_{BA}}{\theta'_A + \theta'_B \tau_{BA}} - \frac{\tau_{AB}}{\theta'_B + \theta'_A \tau_{AB}}\right) \tag{13}$$

$$\ln \gamma_B = \ln \frac{\Phi_B}{x_B} + 1 - \frac{\Phi_B}{x_B} - \left(\frac{Z}{2}\right) q_B \left(\ln \frac{\Phi_B}{\theta_B} + 1 - \frac{\Phi_B}{\theta_B}\right) - q'_B \ln(\theta'_B + \theta'_A \tau_{AB})$$
$$+ q'_B \theta'_A \left(\frac{\tau_{AB}}{\theta'_B + \theta'_A \tau_{AB}} - \frac{\tau_{BA}}{\theta'_A + \theta'_B \tau_{BA}}\right) \tag{14}$$

For alcohols, the following values of q' are given: for methanol, $q' = 0.96$;

for ethanol, $q' = 0.92$; for 2-propanol, $q' = 0.89$ [5,10]. For acetonitrile, $q' = 0.95$ and for other components, $q' = q$.

NRTL model

$$\ln \gamma_A = x_B^2\left[\tau_{BA}G_{BA}^2/(x_A + x_BG_{BA})^2 + \tau_{AB}G_{AB}/(x_B + x_AG_{AB})^2\right] \tag{15}$$

$$\ln \gamma_B = x_A^2\left[\tau_{AB}G_{AB}^2/(x_B + x_AG_{AB})^2 + \tau_{BA}G_{BA}/(x_A + x_BG_{BA})^2\right] \tag{16}$$

with

$$\tau_{AB} = a_{AB}/T \qquad \tau_{BA} = a_{BA}/T \tag{17}$$

$$G_{AB} = \exp(-\alpha_{AB}\tau_{AB}) \qquad G_{BA} = \exp(-\alpha_{BA}\tau_{BA}) \tag{18}$$

where $\alpha_{AB}(=\alpha_{BA})$ is the non-randomness parameter, here set as 0.2 for partially miscible mixtures.

RESULTS AND DISCUSSION

Binary mixtures

A literature search showed that experimental information on a full set of liquid–liquid equilibrium (LLE) and VLE data and activity coefficient data at infinite dilution is available for only a limited number of binary alcohol + saturated hydrocarbon mixtures as shown in Table 1, which gives the binary parameters of the four models together with experimental data.

The binary parameters of each model are determined solving numerically the equation of LLE for every component I:

$$(\gamma_I x_I)^{\mathrm{I}} = (\gamma_I x_I)^{\mathrm{II}} \tag{19}$$

where the superscripts I and II represent equilibrium liquid phases.

Figures 1–7 show calculated and experimental activity coefficients. In the methanol + saturated hydrocarbon systems mutual solubilities are approximately symmetric. This may be the main reason why the NRTL model gives nearly symmetric curves for the activity coefficient vs. composition relation. Moreover, this model gives smaller slopes near the dilute regions. The other three models are capable of showing unsymmetric behaviour and of giving values closer to the experimental results for all the systems investigated. In the alcohol-diluted region the experimental activity coefficient of the alcohol changes rapidly and these three models are able to reproduce this behaviour very well and in the meantime are able to reproduce also the behaviour in the hydrocarbon-diluted region where this variation is not so sharp. Table 1 indicates that the solubilities of methanol in a saturated hydrocarbon-rich phase reported in refs. 11, 13 and 14 are

TABLE 1

Calculated results for mutual solubility data

Mixture (A + B)	Temp. (°C)	Solubility		Parameter (K)								Ref.
		Mole fraction of A in B	Mole fraction of B in A	I [a]		II [b]		III [c]		IV [d]		
				a_{AB}	a_{BA}	a_{AB}	a_{BA}	a_{AB}	a_{BA}	a_{AB}	a_{BA}	
Methanol + cyclohexane	25	0.1244	0.1715	7.86	86.15	280.74	1122.7	11.00	1352.6	349.01	523.63	11
	25	0.1110	0.1750	−16.64	114.11	276.55	1164.3	9.80	1434.9	321.12	565.85	12
	30	0.1410	0.1970	−19.13	113.63	269.52	1130.2	5.78	1395.8	332.04	523.93	12
	40	0.2570	0.2700	−9.06	93.68	254.07	1030.7	−3.02	1266.3	374.96	409.26	12
	40	0.2371	0.2652	−22.43	109.80	253.56	1056.5	−3.00	1312.4	358.65	434.92	13
Methanol + *n*-hexane	25	0.2550	0.2005	25.89	57.89	376.05	1230.9	3.68	1503.9	463.04	313.11	14
	25	0.2100	0.2020	−13.29	100.01	372.60	1305.3	2.84	3111.9	408.07	384.67	12
	30	0.2690	0.2420	−19.72	104.17	367.64	1282.9	−0.44	2408.6	417.66	347.42	12
	5	0.1036	0.1136	48.03	45.73	393.62	1325.3	17.21	1604.4	419.87	463.40	15
	25	0.2323	0.1984	9.71	74.99	375.47	1263.6	3.79	1501.3	440.83	344.36	15
Methanol + *n*-heptane	25	0.1582	0.1074	1.96	89.43	409.70	1357.8	4.19	1565.0	553.38	348.79	14
	25	0.1370	0.1040	−14.07	110.67	411.90	1400.8	4.91	1693.7	532.70	390.26	12
Ethanol + *n*-hexadecane	45	0.5160	0.0870	4.97	46.03	360.05	1101.7	−110.35	2592.8	1107.3	−158.44	16
Acetonitrile + cyclohexane	25	0.0440	0.0601	142.38	689.58	432.81	948.65	56.93	1376.1	520.13	656.91	17
	40	0.0787	0.1039	109.44	654.45	362.87	889.55	26.44	1365.7	454.06	595.95	11
Acetonitrile + *n*-hexane	25	0.0584	0.0567	100.74	692.54	414.68	983.15	19.73	1500.6	575.39	562.18	14
Acetonitrile + *n*-heptane	25	0.0621	0.0378	99.25	692.34	439.86	990.57	13.81	1461.4	708.00	492.38	14

[a] I, UNIQUAC associated-solution model.

[b] II, extended UNIQUAC model.

[c] III, UNIQUAC model ($q' = 0.95$ for acetonitrile).

[d] IV, NRTL model ($\alpha_{AB} = 0.20$).

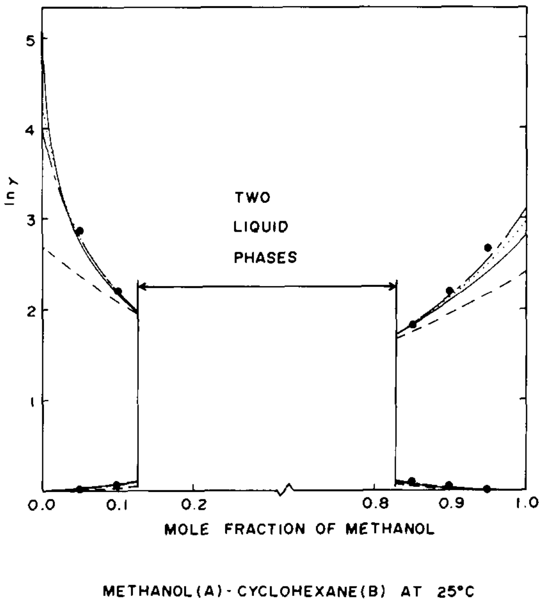

Fig. 1. Activity coefficients for methanol + cyclohexane at 25 °C. Experimental values (●) were obtained from $P-x$ data of ref. 18. Two-liquid phase region was taken from ref. 12. Calculated: ——, UNIQUAC associated-solution model; ·—·—·, extended UNIQUAC model; - - - - - - , UNIQUAC model; — — —, NRTL model.

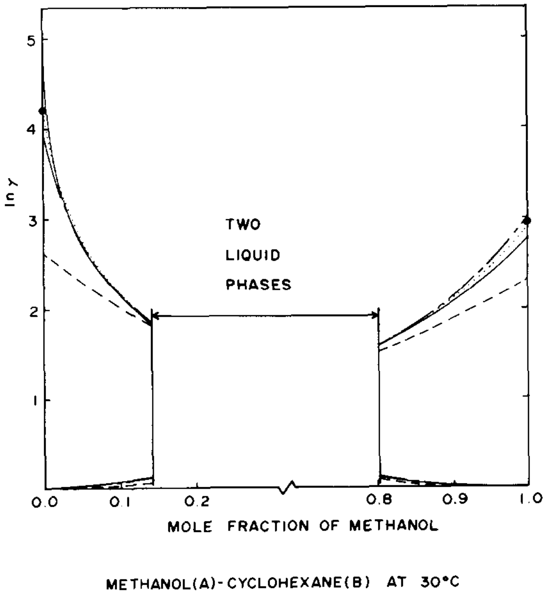

Fig. 2. Activity coefficients for methanol + cyclohexane at 30 °C. Experimental activity coefficients at infinite dilution (●) were interpolated from original data of ref. 19. Calculated: ——, UNIQUAC associated-solution model; ·—·—·, extended UNIQUAC model; - - - - - -, UNIQUAC model; — — —, NRTL model.

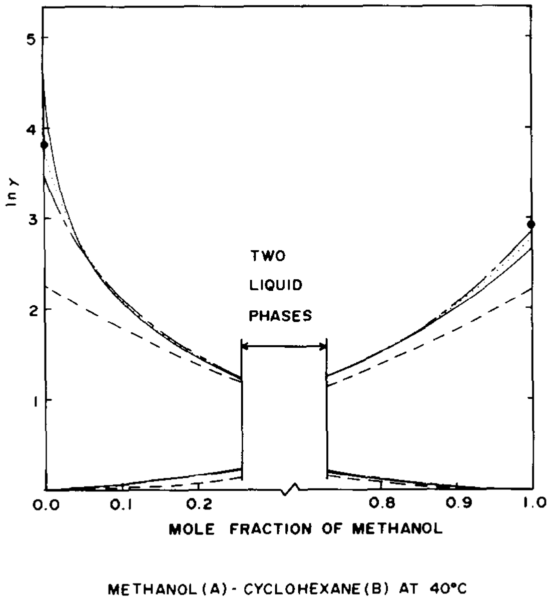

Fig. 3. Activity coefficients for methanol + cyclohexane at 40 °C. Experimental activity coefficients at infinite dilution (●) were interpolated from original data of ref. 19. Two-liquid phase region was taken from ref. 12. Calculated: ———, UNIQUAC associated-solution model; ·—·—·, extended UNIQUAC model; ------, UNIQUAC model; — — —, NRTL model.

markedly different from those given in ref. 12. However, different sets of solubilities for each mixture lead to nearly the same results as shown typically for the UNIQUAC associated-solution model in Fig. 4.

In the ethanol + *n*-hexadecane system a comparison of the models can be made on the basis of predictions of the limiting activity coefficients. Again, the activity coefficients calculated by means of the association model and the extended UNIQUAC model are in excellent agreement with the activity coefficients obtained from VLE, while the activity coefficients given by the NRTL equation are rather lower.

Ternary mixtures

Ternary LLE calculations provide further rather severe tests of the models and were carried out for five type I systems, where only one binary is partially miscible and the other two binaries are completely miscible, and for three type II systems, where two binaries are partially miscible and the third binary is completely miscible. Table 2 gives binary parameters derived for the models from VLE data.

The parameters were estimated using a computer program similar to that described by Prausnitz et al. [10], based on the maximum likelihood princi-

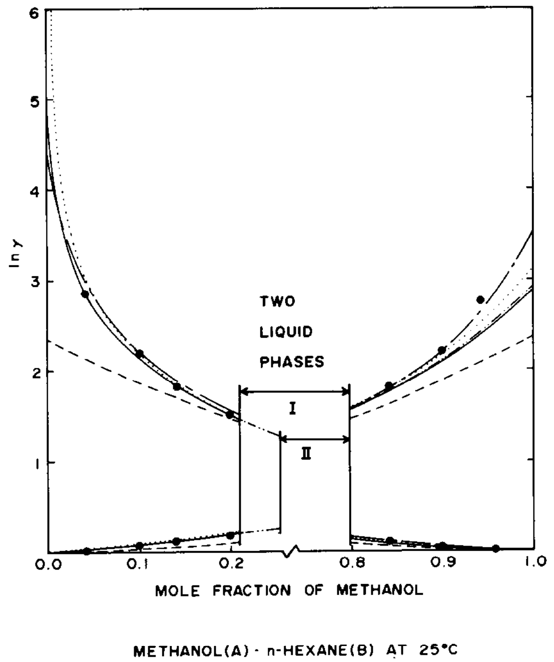

Fig. 4. Activity coefficients for methanol + *n*-hexane at 25 °C. Experimental values (●) were obtained from $P-x$ data of ref. 18. Two-liquid phase region I was taken from ref. 12 and II from ref. 11. Calculated activity coefficients based on solubilities of ref. 11 are shown for only those from the UNIQUAC associated-solution model to avoid overlap. Calculated: ——— and —··—, UNIQUAC associated-solution model; ·–·–·, extended UNIQUAC model; - - - - - -, UNIQUAC model; — — —, NRTL model.

ple, and the following thermodynamic relations for component I:

$$Py_I\phi_I = \gamma_I x_I P_I^s \phi_I^s \exp\left[v_I^L(P-P_I^s)/RT\right] \tag{20}$$

$$\ln \phi_I = \left(2\sum_J y_J B_{IJ} - \sum_I \sum_J B_{IJ} y_I y_J\right)\frac{P}{RT} \tag{21}$$

where P, y and ϕ are the total pressure, vapour phase mole fraction and vapour phase fugacity coefficient respectively. The second virial coefficients B_{IJ} were calculated from the correlation of Hayden–O'Connell [22]. The modified Rackett equation [23] was used to estimate the pure component liquid molar volume v^L. The pure component vapour pressure P^s was obtained from the Antoine equation [24,25]. The standard deviations in the measured variables were taken as $\sigma_P = 1$ Torr, $\sigma_T = 0.05$ K, $\sigma_x = 0.001$ and $\sigma_y = 0.003$.

The UNIQUAC associated-solution model assumes that two alcohols, A and B, solvate linearly to yield the multisolvated chemical complexes $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$ and $B_i(A_jB_k)_l$, where the subscripts i, j, k and l have values from unity to infinity and that alcohol A and an active non-associat-

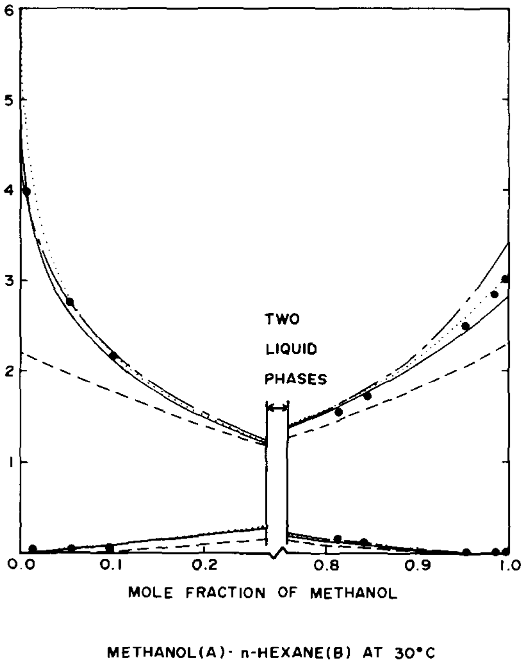

Fig. 5. Activity coefficients for methanol + *n*-hexane at 30 ° C. Experimental values (●) were obtained from $P-x$ data of ref. 20. Calculated: ——, UNIQUAC associated-solution model; -·-·-, extended UNIQUAC model; ------, UNIQUAC model; — — —, NRTL model.

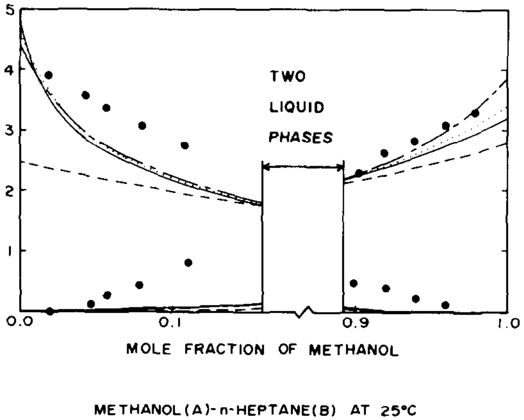

Fig. 6. Activity coefficients for methanol + *n*-heptane at 25 ° C. Experimental values (●) were obtained from $x-y$ data of ref. 21. Two-liquid phase region was taken from ref. 12. Calculated: ——, UNIQUAC associated-solution model; -·-·-, extended UNIQUAC model; ------, UNIQUAC model; — — —, NRTL model.

TABLE 2

Calculated results for binary vapour–liquid equilibrium data

Mixture (A + B)	Temp. (° C)	No. of data points	Model	Root-mean-square deviation				Parameter (K)		Ref.
				δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}	
Methanol + ethanol	25	12	I [a]	0.51	0.00	0.2	1.5	−17.19	150.68	27
			II [b]	0.32	0.00	0.1	1.0	73.61	−40.11	
			III [c]	0.32	0.00	0.1	1.0	144.27	−107.11	
			IV [d]	0.29	0.00	0.1	1.1	−62.61	59.24	
Methanol + 2-propanol	55	20	I	1.78	0.07	0.9	3.8	−87.96	208.01	28
			II	1.79	0.07	0.9	3.9	28.43	46.02	
			III	1.79	0.07	0.9	3.9	242.98	−109.58	
			IV [d]	1.79	0.07	0.9	3.9	264.04	−195.63	
Methanol + acetonitrile	25	10	I	0.80	0.01	1.3	7.8	454.35	−93.34	14
			II	1.28	0.02	0.5	5.1	102.76	259.27	
			III	1.26	0.02	0.6	5.1	188.54	216.36	
			IV [d]	1.37	0.02	0.5	5.2	148.56	201.82	
	55	14	I	1.00	0.04	1.0	5.3	480.47	−113.06	29
			II	1.83	0.00	0.3	2.7	131.95	207.67	
			III	1.76	0.00	0.3	2.5	225.11	159.88	
			IV [d]	2.00	0.00	0.4	3.0	211.96	126.50	
Methanol + benzene	25	26	I	3.05	0.00	1.2		−122.62	294.54	18
			II	1.77	0.00	0.6		58.46	993.58	
			III	1.57	0.00	0.5		−59.90	1175.16	
			IV [e]	2.21	0.00	1.2		362.85	709.25	

Methanol + tetrachloromethane	35	9	I	0.78	0.02	1.3	3.5	−110.87	233.50	28
			II	0.81	0.03	0.3	3.0	114.83	1143.87	
			III	0.46	0.02	0.3	2.0	−41.46	1330.40	
			IV [e]	2.47	0.09	1.9	8.8	425.03	803.03	
Ethanol + cyclohexane	20	7	I	0.77	0.01	0.3	3.3	103.02	−29.63	28
			II	0.45	0.01	0.6	4.5	153.31	956.89	
			III	0.69	0.01	0.4	2.8	−81.56	1413.81	
			IV [e]	0.95	0.01	0.3	7.1	467.54	733.99	
2-Propanol + cyclohexane	50	9	I	1.10	0.04	0.4	3.8	155.98	−84.76	30
			II	1.27	0.04	0.6	5.6	123.14	869.13	
			III	1.39	0.05	0.8	6.3	−160.91	1181.70	
			IV [e]	2.07	0.07	1.0	9.2	275.06	631.89	
2-Propanol + *n*-hexane	55.06	24	I	1.08	0.00	0.4	1.4	175.93	−97.83	31
			II	0.94	0.00	0.4	2.2	155.15	888.28	
			III	1.61	0.00	1.0	3.4	−164.18	1195.29	
			IV [e]	2.56	0.00	1.3	5.7	317.04	564.83	
Benzene + cyclohexane	25	11	I	0.23	0.00	0.1	0.9	10.21	56.92	32
			II	0.23	0.00	0.1	0.9	37.77	85.90	
			III	0.23	0.00	0.1	0.9	2.85	54.35	
			IV [d]	0.23	0.00	0.1	0.9	145.50	4.96	
Tetrachloromethane + cyclohexane	40	9	I	0.11	0.00	0.1	0.6	−57.24	72.58	32
			II	0.11	0.00	0.1	0.6	−115.70	142.65	
			III	0.11	0.00	0.1	0.6	−83.77	100.24	
			IV [d]	0.11	0.00	0.1	0.6	−23.40	56.73	

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[a] I, UNIQUAC associated-solution model.

[b] II, extended UNIQUAC model.

[c] III, UNIQUAC model ($q' = 0.95$ for acetonitrile).

[d] IV, NRTL model ($\alpha_{AB} = 0.30$).

[e] IV, NRTL model ($\alpha_{AB} = 0.47$).

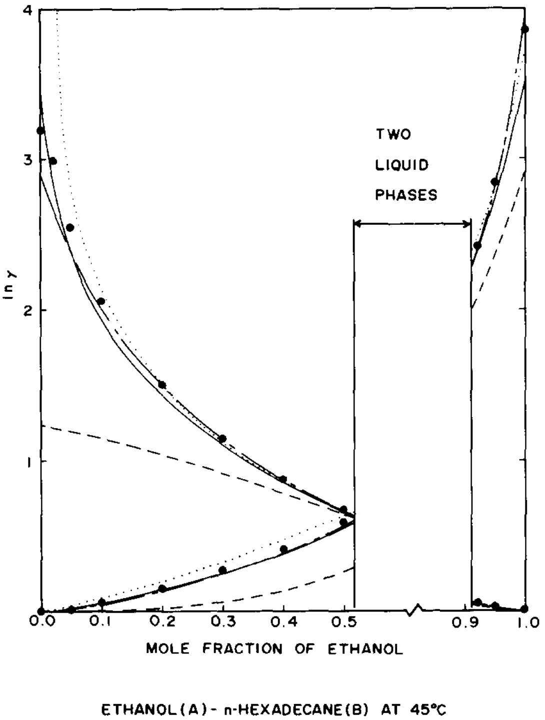

Fig. 7. Activity coefficients for ethanol + *n*-hexadecane at 45 °C. Experimental values (●) were obtained from $P-x$ data of ref. 16. Calculated: ———, UNIQUAC associated-solution model; ·–·–·, extended UNIQUAC model; ------; UNIQUAC model; — — —, NRTL model.

ing component B form A_iB. The solvation equilibrium constants at 50 °C and the enthalpies of complex formation are as follows: for methanol + 2-propanol, $K_{AB} = 70$ and $h_{AB} = -23.2$ kJ mol^{-1} [26]; for methanol + benzene, $K_{AB} = 4$ and $h_{AB} = -8.3$ kJ mol^{-1} [3]; for methanol + tetrachloromethane, $K_{AB} = 1$ and $h_{AB} = -5.5$ kJ mol^{-1} [3]. h_{AB} was assumed to be temperature independent and the temperature dependence of the solvation constant is fixed by the van't Hoff relation (eqn. (10)).

The binary parameters listed in Tables 1 and 2 were used to calculate the ternary LLE. Anderson and Prausnitz [33] stated that for systems of type II, if the mutual binary solubility data are known for the two partially miscible pairs, and if reasonable VLE data are known for the miscible pair, it is relatively simple to predict the ternary equilibria as shown previously by several researchers. This statement holds for systems whose solubility envelopes are nearly straight lines. However, this is not the case for the systems studied here, as shown in Fig. 8. Only the UNIQUAC associated-solution model is able to reproduce the skewed solubility envelopes of the acetonitrile + methanol + cyclohexane and acetonitrile + methanol + *n*-hexane systems

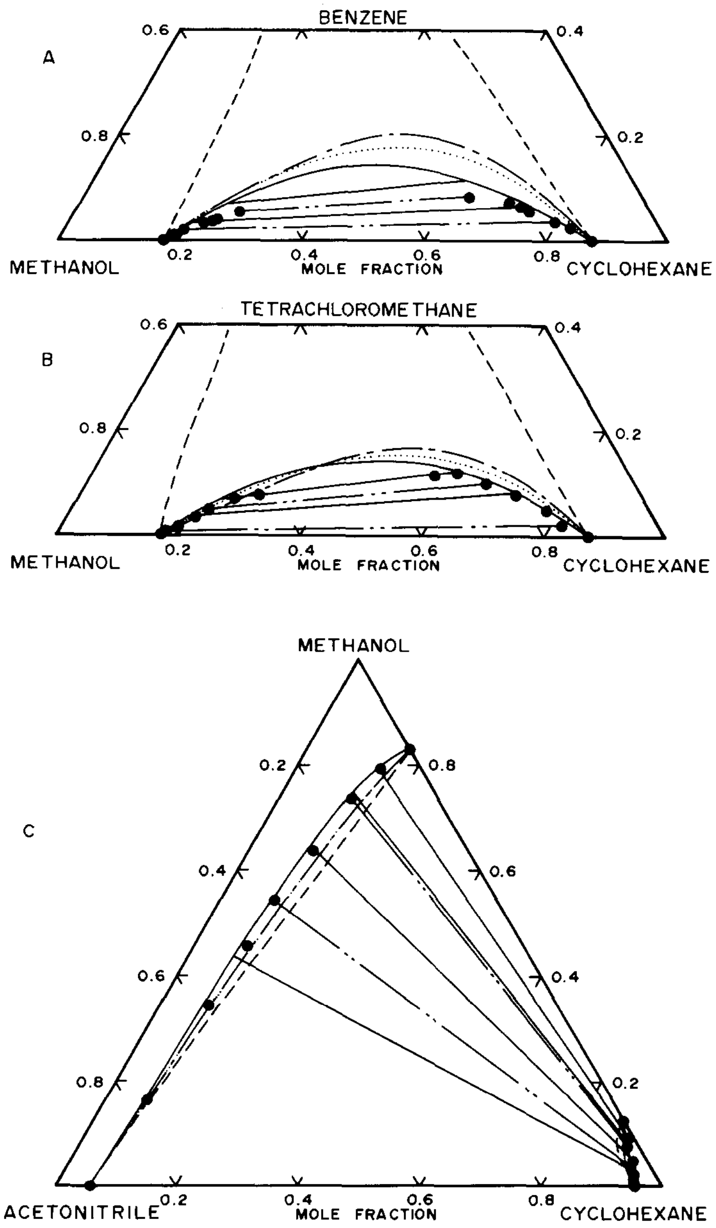

Fig. 8. Ternary liquid–liquid equilibria for mixtures containing one alcohol: (A) methanol + benzene + cyclohexane at 25 °C [34]; (B) methanol + tetrachloromethane + cyclohexane at 25 °C [21]; (C) acetonitrile + methanol + cyclohexane at 25 °C [14]; (D) acetonitrile + methanol + cyclohexane at 40 °C [13]; (E) acetonitrile + methanol + *n*-hexane at 25 °C [14] (○— · · —○, ref. 35). Experimental tie-line (●— · · —●). Calculated: ———, UNIQUAC associated-solution model; ·—·—·, extended UNIQUAC model; - - - - - -, UNIQUAC model; — — —, NRTL model.

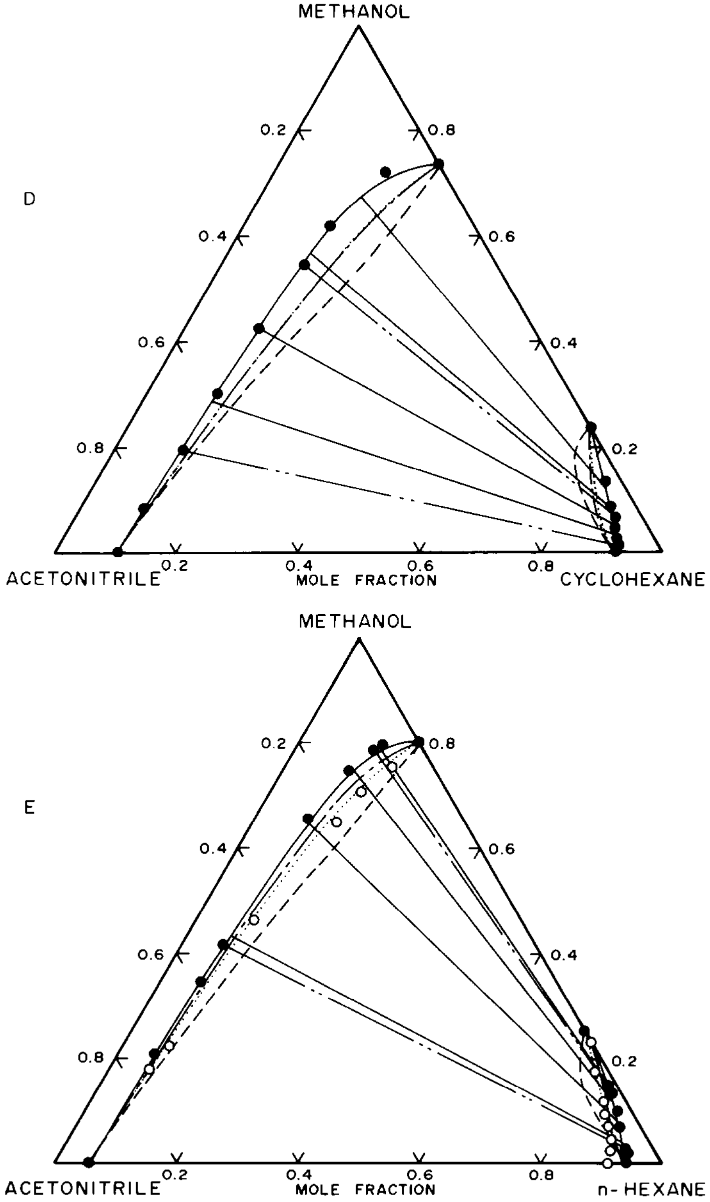

Fig. 8 (continued).

very well. For systems of type I, the association model also gives calculated results close to the experimental values and those derived from the NRTL equation show too large envelopes (Figs. 8 and 9). For systems containing two alcohols the extended UNIQUAC model works better than the UNIQUAC model.

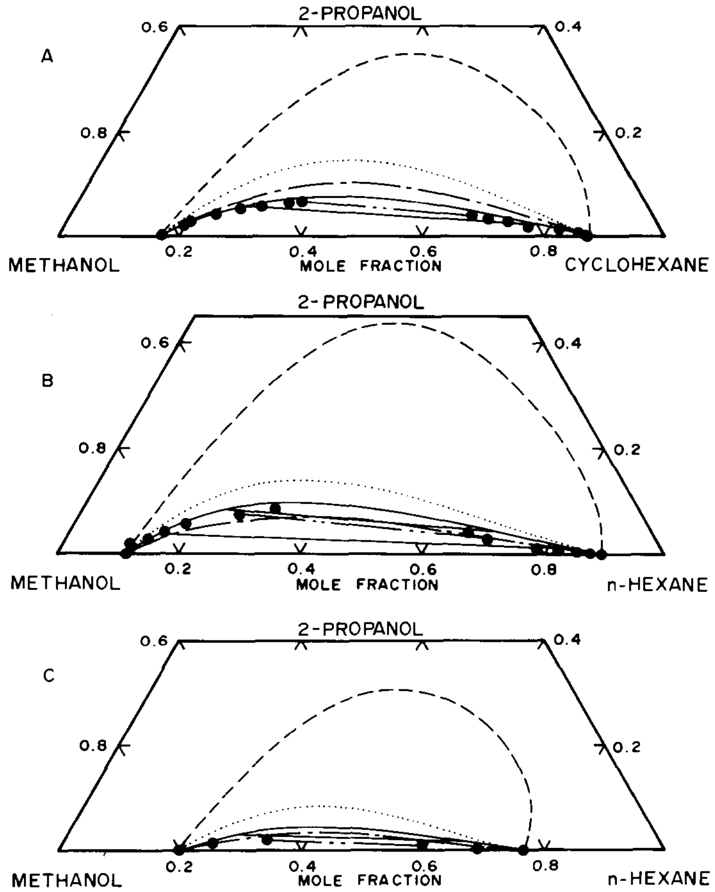

Fig. 9. Ternary liquid–liquid equilibria for mixtures containing two alcohols: (A) methanol + 2-propanol + cyclohexane at 25 °C [34]; (B) methanol + 2-propanol + *n*-hexane at 5 °C [15]; (C) methanol + 2-propanol + *n*-hexane at 25 °C [15]. Experimental tie-line, (●- - - -●). Calculated: ———, UNIQUAC associated-solution model; -·-·-, extended UNIQUAC model; ------, UNIQUAC model; — — —, NRTL model.

CONCLUSIONS

More experimental data are needed for partially miscible alcohol + hydrocarbon systems in order to test the UNIQUAC associated-solution model in the interpolation of thermodynamic information derived from mutual solubilities to miscible and infinitely diluted regions. The binary and ternary calculated LLE results may confirm the flexibility of the UNIQUAC associated-solution model, although the association model involves additionally the equilibrium constants, in contrast with the other commonly used local composition models.

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LIST OF SYMBOLS

A, B	components
a_{IJ}	binary interaction parameter related to τ_{IJ}
B_{IJ}	second virial coefficient
G_{IJ}	coefficient as defined by $\exp(-\alpha_{IJ}\tau_{IJ})$ in the NRTL model
h_{A}	enthalpy of hydrogen-bond formation
h_{AB}	enthalpy of chemical complex formation
K_{A}	alcohol association constant
K_{AB}	solvation constant between unlike molecules
P	total pressure
P_I^{s}	vapour pressure of pure component I
q_I	molecular geometric area parameter of pure component I
q_I^*	molecular interaction area parameter of pure component I in the extended UNIQUAC model
q_I'	molecular interaction parameter of pure component I in the UNIQUAC model
R	universal gas constant
r_I	molecular geometric volume parameter of pure component I
T	absolute temperature
V	true molar volume of alcohol mixture
V_{A}^0	true molar volume of pure alcohol solution
v_I^{L}	molar liquid volume of pure component I
x_I	liquid phase mole fraction of component I
y_I	vapour phase mole fraction of component I
Z	coordination number, here equal to 10

Greek letters

α_{IJ}	non-randomness parameter of the NRTL model
γ_I	activity coefficient of component I
θ_I	area fraction of component I
θ_I'	area fraction of component I in residual contribution to the activity coefficient of the UNIQUAC model
σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquid phase and vapour phase mole fraction respectively

τ_{IJ}	binary parameter
Φ_I	segment fraction of component I
Φ_{A_1}, Φ_{B_1}	monomer segment fractions of components A and B
ϕ_I	vapour phase fugacity coefficient of component I
ϕ_I^s	vapour phase fugacity coefficient of pure component I at P_I^s and T

Subscripts

A, B	components
A_1, B_1	monomers of components A and B
AB	binary complex
I, J	components
i, j, k, l	degree of association

Superscripts

0	pure liquid reference state
I, II	equilibrium liquid phases

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