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The temperature dependence of the mutual solubility of alcohol–hydrocarbon mixtures

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Abstract

Binary liquid–liquid equilibrium data for alcohol + saturated hydrocarbon mixtures over a wide temperature range have been well correlated with the UNIQUAC associated-solution model, whose energy parameters are assumed to be temperature dependent. The derived parameters lead to good prediction of the activity coefficients in miscible regions for the binary mixtures, and of liquid–liquid equilibria for ternary mixtures of methanol with two saturated hydrocarbons.

LIST OF SYMBOLS

a_{IJ}	binary interaction parameter for I–J pair
A, B	alcohol and saturated hydrocarbon
A_{IJ}, B_{IJ}, C_{IJ}	coefficients of eqns. (11) and (12)
h_A	molar enthalpy of a hydrogen bond
K_A	association constant of alcohol
q_I	molecular geometric area parameter of pure component I
r_I	molecular geometric volume parameter of pure component I
R	universal gas constant
T	absolute temperature
V	true molar volume of alcohol mixture
V_A°	true molar volume of pure alcohol
x_I	liquid phase mole fraction of component I
Z	lattice coordination number, here set as 10

Greek letters

γ_I	activity coefficient of component I
θ_I	area fraction of component I

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τ_{IJ}	binary parameter
ϕ_{I}	segment fraction of component I
ϕ_{A_1}	monomeric segment fraction of alcohol
$\phi^{\circ}_{\mathrm{A}_1}$	monomeric segment fraction of pure alcohol

Subscripts

A, B	alcohol and saturated hydrocarbon
$\mathrm{A}_1, \mathrm{B}_1$	monomers of alcohol and hydrocarbon
A_i	imer of alcohol
I, J, K	components

Superscripts

α, β	conjugated liquid phases
*	reference state of 50°C

INTRODUCTION

The thermodynamic properties of alcohol solutions have been extensively studied by means of the UNIQUAC associated-solution model [1–4]. In our recent papers we have shown that the UNIQUAC associated-solution model performs well in predicting ternary excess enthalpies of methanol-containing mixtures in which methanol + *n*-heptane shows phase separation [5], and in predicting and correlating total pressure vs. liquid composition data for ternary mixtures including two alcohols and one aliphatic hydrocarbon [6].

In this paper, we apply the UNIQUAC associated-solution model to describe the temperature dependence of the mutual solubility of mixtures of methanol or ethanol with saturated hydrocarbons, using temperature-dependent energy parameters. The parameters obtained are then used to predict the activity coefficients in binary miscible regions and ternary liquid–liquid equilibria for mixtures containing methanol and two saturated hydrocarbons.

SOLUTION MODEL

We assume that the alcohol (A) forms open chains and the association constant K_{A} is independent of the degree of association, as given by

$$\begin{aligned} K_{\mathrm{A}} &= \frac{\phi_{\mathrm{A}_{i+1}}}{\phi_{\mathrm{A}_i}\phi_{\mathrm{A}_1}}\frac{i}{i+1} \quad \text{for} \quad \mathrm{A}_i + \mathrm{A}_1 = \mathrm{A}_{i+1} \\ &= K_{\mathrm{A}}^{*} \exp\left[-\frac{h_{\mathrm{A}}}{R}\left(\frac{1}{T}-\frac{1}{T^{*}}\right)\right] \end{aligned} \tag{1}$$

The activity coefficients of the alcohol and saturated hydrocarbon (B) are given by eqns. (1) and (2) according to the UNIQUAC associated-solution model.

$$\ln \gamma_{\mathrm{A}} = \ln\left(\frac{\phi_{\mathrm{A}_1}}{\phi^{\circ}_{\mathrm{A}_1} x_{\mathrm{A}}}\right) + \frac{r_{\mathrm{A}}}{V^{\circ}_{\mathrm{A}}} - \frac{r_{\mathrm{A}}}{V} - \left(\frac{Z}{2}\right) q_{\mathrm{A}}\left(\ln\frac{\phi_{\mathrm{A}}}{\theta_{\mathrm{A}}} + 1 - \frac{\phi_{\mathrm{A}}}{\theta_{\mathrm{A}}}\right) + q_{\mathrm{A}}\left[1 - \ln\left(\sum_{\mathrm{J}} \theta_{\mathrm{A}} \tau_{\mathrm{JA}}\right) - \sum_{\mathrm{J}} \frac{\theta_{\mathrm{J}} \tau_{\mathrm{AJ}}}{\sum_{\mathrm{K}} \theta_{\mathrm{K}} \tau_{\mathrm{KJ}}}\right] \tag{2}$$

$$\ln \gamma_{\mathrm{B}} = \ln\left(\frac{\phi_{\mathrm{B}_1}}{x_{\mathrm{B}}}\right) + 1 - \frac{r_{\mathrm{B}}}{V} - \left(\frac{Z}{2}\right) q_{\mathrm{B}}\left(\ln\frac{\phi_{\mathrm{B}}}{\theta_{\mathrm{B}}} + 1 - \frac{\phi_{\mathrm{B}}}{\theta_{\mathrm{B}}}\right) + q_{\mathrm{B}}\left[1 - \ln\left(\sum_{\mathrm{J}} \theta_{\mathrm{B}} \tau_{\mathrm{JB}}\right) - \sum_{\mathrm{J}} \frac{\theta_{\mathrm{J}} \tau_{\mathrm{BJ}}}{\sum_{\mathrm{K}} \theta_{\mathrm{K}} \tau_{\mathrm{KJ}}}\right] \tag{3}$$

where Z is the lattice coordination number, here set as 10 and $\phi_{\mathrm{B}_1} = \phi_{\mathrm{B}}$. The monomer segment fraction of alcohol is obtained from the equilibrium constant K_{A} and the overall segment fraction of alcohol ϕ_{A} by

$$\phi_{\mathrm{A}_1} = \frac{1 + 2K_{\mathrm{A}}\phi_{\mathrm{A}} - (1 + 4K_{\mathrm{A}}\phi_{\mathrm{A}})^{0.5}}{2K_{\mathrm{A}}^2\phi_{\mathrm{A}}} \tag{4}$$

The segment fraction of alcohol monomer in pure alcohol reduces to

$$\phi^{\circ}_{\mathrm{A}_1} = \frac{1 + 2K_{\mathrm{A}} - (1 + 4K_{\mathrm{A}})^{0.5}}{2K_{\mathrm{A}}^2} \tag{5}$$

The true molar volume of the mixture and pure alcohol are given by

$$\frac{1}{V} = \frac{\phi_{\mathrm{A}_1}}{r_{\mathrm{A}}(1 - K_{\mathrm{A}}\phi_{\mathrm{A}_1})} + \frac{\phi_{\mathrm{B}}}{r_{\mathrm{B}}} \tag{6}$$

$$V^{\circ}_{\mathrm{A}} = \frac{r_{\mathrm{A}}}{(1 - K_{\mathrm{A}}\phi^{\circ}_{\mathrm{A}_1})} \tag{7}$$

The segment fractions ϕ_{A} and ϕ_{B}, the surface fractions θ_{A} and θ_{B} and the binary parameters τ_{AB} and τ_{BA} are defined as

$$\phi_{\mathrm{A}} = \frac{r_{\mathrm{A}}x_{\mathrm{A}}}{r_{\mathrm{A}}x_{\mathrm{A}} + r_{\mathrm{B}}x_{\mathrm{B}}} \qquad \phi_{\mathrm{B}} = \frac{r_{\mathrm{B}}x_{\mathrm{B}}}{r_{\mathrm{A}}x_{\mathrm{A}} + r_{\mathrm{B}}x_{\mathrm{B}}} \tag{8}$$

$$\theta_{\mathrm{A}} = \frac{q_{\mathrm{A}}x_{\mathrm{A}}}{q_{\mathrm{A}}x_{\mathrm{A}} + q_{\mathrm{B}}x_{\mathrm{B}}} \qquad \theta_{\mathrm{B}} = \frac{q_{\mathrm{B}}x_{\mathrm{B}}}{q_{\mathrm{A}}x_{\mathrm{A}} + q_{\mathrm{B}}x_{\mathrm{B}}} \tag{9}$$

$$\tau_{\mathrm{AB}} = \exp\left(-\frac{a_{\mathrm{AB}}}{T}\right) \qquad \tau_{\mathrm{BA}} = \exp\left(\frac{a_{\mathrm{BA}}}{T}\right) \tag{10}$$

where r and q are molecular parameters depending on the molecular sizes and shapes of the pure components.

In fitting the model to experimental mutual solubility data over a wide temperature range, we assume the temperature dependence of the energy parameters to be a quadratic function of temperature

$$a_{AB} = A_{AB} + B_{AB}T + C_{AB}T^2 \tag{11}$$

$$a_{BA} = A_{BA} + B_{BA}T + C_{BA}T^2 \tag{12}$$

The energy parameters are solved at any temperature from the thermodynamic relations of equality of activities of components in the equilibrated phases

$$a_A^\alpha = (x_A\gamma_A)^\alpha = a_A^\beta = (x_A\gamma_A)^\beta \tag{13}$$

$$a_B^\alpha = (x_B\gamma_B)^\alpha = a_B^\beta = (x_B\gamma_B)^\beta \tag{14}$$

CALCULATED RESULTS

Table 1 shows the values of the molecular structural parameters r and q calculated by the method of Vera et al. [7]. Two sets of the association parameters were used: case I, K_A^* at 50°C are 173.9 for methanol and 110.4 for ethanol [8] and $h_A = -23.2$ kJ mol^{-1} [9]; case II, K_A^* are 125.1 for methanol and 103.2 for ethanol and $h_A = -23.6$ kJ mol^{-1} [10].

Table 2 gives calculated results. Each experimental data set was reduced using two sets of the model parameters, which are assumed to be linearly or quadratically temperature dependent. The parameter set given in Table 2 provides a smaller deviation between the experimental and calculated liquid compositions than the other one. Figure 1 compares the calculated results derived from the UNIQUAC associated-solution model with the experimental results for some systems. The two sets of the association parameters give nearly the same results. The quality of correlation depends on the precision of the measurements in the systems

TABLE 1

Values of molecular structure parameters of pure components

Component	r	q
Methanol	1.15	1.12
Ethanol	1.69	1.55
Cyclohexane	3.18	2.55
n-Hexane	3.61	3.09
n-Heptane	4.15	3.52
n-Octane	4.69	3.95
n-Hexadecane	9.01	7.41

TABLE 2

Calculated results for mutual solubility data

System (1 + 2)	Temperature range (°C)	Case [a]	Average abs. dev. (mol%)		Parameters			Reference
			A [b]	B [c]	A_{12} A_{21}	B_{12} B_{21}	C_{12} C_{21}	
Methanol + cyclohexane	2.46–45.78	I	1.99	11.42	1006.900	−3.2941		11
					−694.659	2.5653		
		II	2.19	9.33	975.653	−3.2357		
					−696.210	2.6383		
	29.19–45.14	I	3.04	1.83	9883.796	−62.2191	0.0978	12
					−13248.120	85.3985	−0.1366	
		II	3.01	3.02	402.164	−1.3983		
					25.010	0.3273		
Methanol + *n*-hexane	−28.00–33.36	I	4.20	9.37	729.777	−2.4345		13
					−476.639	1.8537		
		II	4.30	9.83	738.030	−2.5422		
					−523.061	2.1110		
	−18.15–32.85	I	0.99	0.71	1742.377	−10.6850	0.0165	14
					−1722.514	11.6449	−0.0190	
		II	1.06	0.75	1814.559	−11.3343	0.0176	
					−1981.114	13.5285	−0.0221	
Methanol + *n*-heptane	−19.50–50.91	I	6.58	10.28	410.557	−1.3624		11
					−234.878	1.0658		
		II	7.39	6.60	414.823	−1.5824	0.0005	
					−661.649	4.1625	−0.0052	
	18.00–50.00	I	0.36	0.02	1383.038	−8.6864	0.0134	15
					−2232.451	15.3364	−0.0251	
		II	0.36	0.02	1352.504	−8.6397	0.0134	
					−2431.532	16.8789	−0.0277	
	−3.15–50.85	I	1.80	2.00	667.157	−2.1644		14
					−420.656	1.6471		
		II	4.33	1.37	348.156	−1.3236	0.0004	
					−841.982	5.6690	−0.0083	
	25.00–50.00	I	0.18	0.20	−111.316	0.4199		16
					336.969	−0.8663		
		II	0.18	0.20	−123.084	0.3808		
					380.620	−0.9071		
Methanol + *n*-octane	11.85–61.85	I	0.25	0.22	1315.858	−7.7970	0.0113	14
					−1329.350	8.8690	−0.0137	
		II	0.27	0.21	1269.672	−7.6763	0.0112	
					−1404.531	9.5797	−0.1480	
	25.00–60.00	I	0.11	0.07	4100.634	−25.3843	0.0390	16
					−4553.514	29.2454	−0.0458	
		II	0.12	0.07	3808.364	−23.7173	0.0365	
					−4638.904	30.0326	−0.0471	
Methanol + *n*-hexadecane	24.80–139.80	I	6.70	42.77	11.169	−0.3493		17
					198.246	0.1807		
		II	2.47	8.24	28.811	−0.3044		
					302.269	−0.1667		

TABLE 2 (continued)

System (1 + 2)	Temperature range (°C)	Case[a]	Average abs. dev. (mol%)		Parameters			Reference
			A[b]	B[c]	A_{12} A_{21}	B_{12} B_{21}	C_{12} C_{21}	
	26.85–136.85	I	6.03	7.11	53.919	−0.2761		14
					254.526	−0.2210		
		II	5.69	7.00	24.071	−0.2704		
					316.577	−0.2366		
Ethanol + *n*-hexadecane	25.00–52.10	I	4.98	0.77	17228.503	−110.1212	0.1760	18
					−18083.058	116.2929	−0.1865	
		II	4.01	0.48	17157.499	−109.6577	0.1753	
					−18344.907	117.9787	−0.1892	
	36.85–51.85	I	1.34	0.55	13461.351	−85.3064	0.1352	14
					−14258.894	91.0106	−0.1447	
		II	1.34	0.55	13387.645	−84.8418	0.1344	
					−14446.098	92.2065	−0.1466	

[a] I: K_A^* at 50°C is 173.9 for methanol and 110.4 for ethanol [8]; $h_A = -23.2$ kJ mol^{-1} [9]. II: K_A^* at 50°C is 125.1 for methanol and 103.2 for ethanol; $h_A = -23.6$ kJ mol^{-1} [10].

[b] A: linear temperature dependence of the energy parameters assumed.

[c] B: quadratic temperature dependence of the energy parameters assumed.

under investigation. For example, in the methanol + *n*-hexane system the UNIQUAC associated-solution model gives better reproduction of the experimental data of Skrzecz [14] than those of Hradetzky and Lempe [13]. The results of data reduction indicate that the linear temperature dependence of the energy parameters works quite well and sometimes the quadratic dependence gives worse results. The physical significance of the energy parameters listed in Table 2 is verified by comparing predicted activity coefficients with experimental ones in miscible regions. As shown in Figs. 2–5, the predicted values agree well the experimental ones. Hradetzky and Lempe [13] correlated the mutual solubility data of the methanol + *n*-hexane or +*n*-heptane systems by means of the NRTL model (whose energy parameters could be expressed as a linear function of temperature), calculated the total pressure of the systems in miscible regions at 30°C and stated that the absolute relative deviation in pressure ranged from 8% to 10% for the experimental data of Goral et al. [20]. In contrast, the UNIQUAC associated-solution model gives only 2.8–3.8%, as given in Table 3.

Ternary prediction of liquid–liquid equilibrium for mixtures of methanol with two saturated hydrocarbons were performed using the binary parameters of the three constituent binaries. The energy parameters of

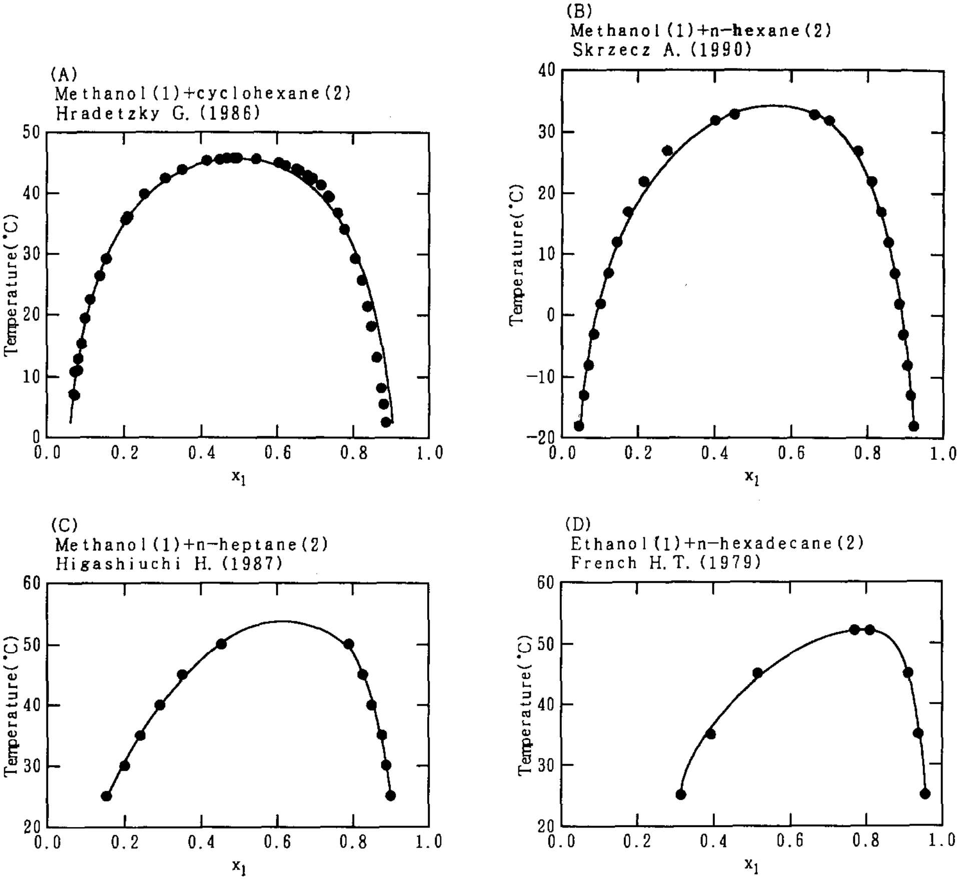


Fig. 1. Calculated liquid–liquid equilibrium curves for alcohol–saturated hydrocarbon systems: ●, experimental; ——, calculated. (A) Methanol + cyclohexane [11]; (B) methanol + *n*-hexane [14]; (C) methanol + *n*-heptane [16]; (D) ethanol + *n*-hexadecane [18].

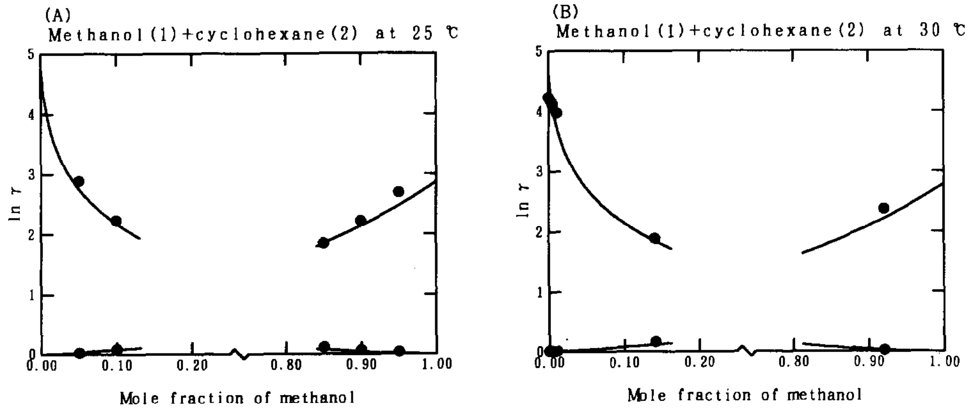


Fig. 2. Activity coefficients for methanol + cyclohexane. Experimental: (A) data of Hwang and Robinson [19] at 25°C; (B) data of Goral et al. [20] at 30°C.

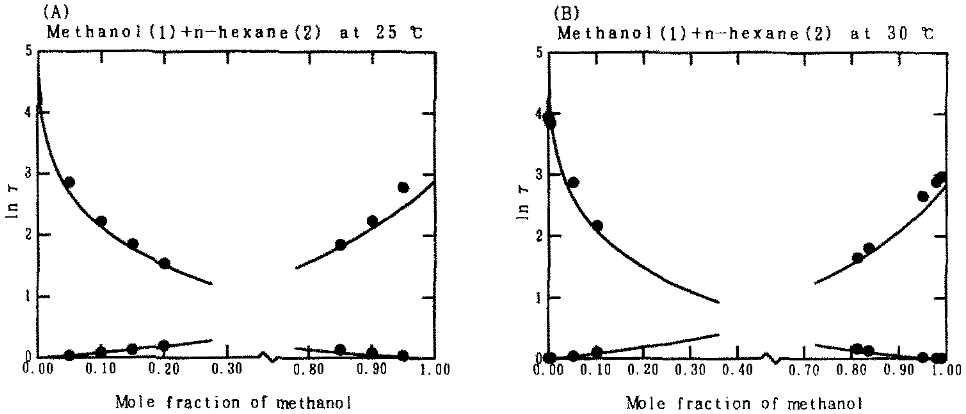


Fig. 3. Activity coefficients for methanol + *n*-hexane. Experimental: (A) data of Hwang and Robinson [19] at 25°C; (B) data of Goral et al. [20] at 30°C.

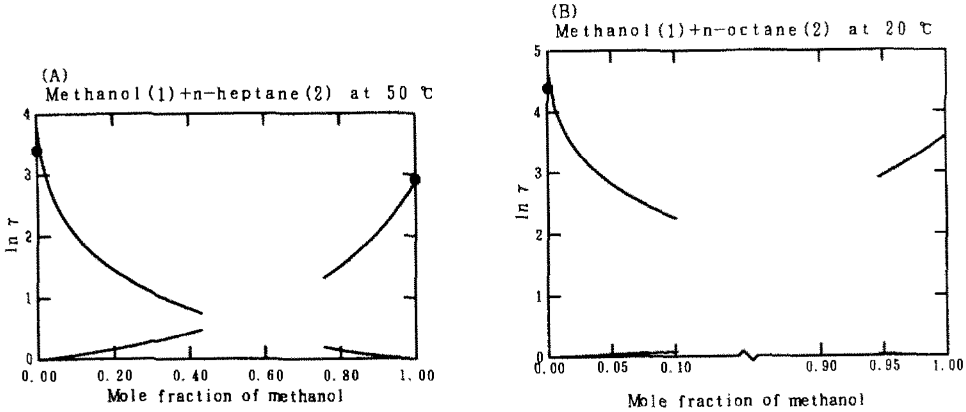


Fig. 4. Activity coefficients for (A) methanol + *n*-heptane and (B) methanol + *n*-octane. Experimental: (A) data of Tochigi and Kojima [21] at 50°C; (B) data of Thomas et al. [22] at 20°C.

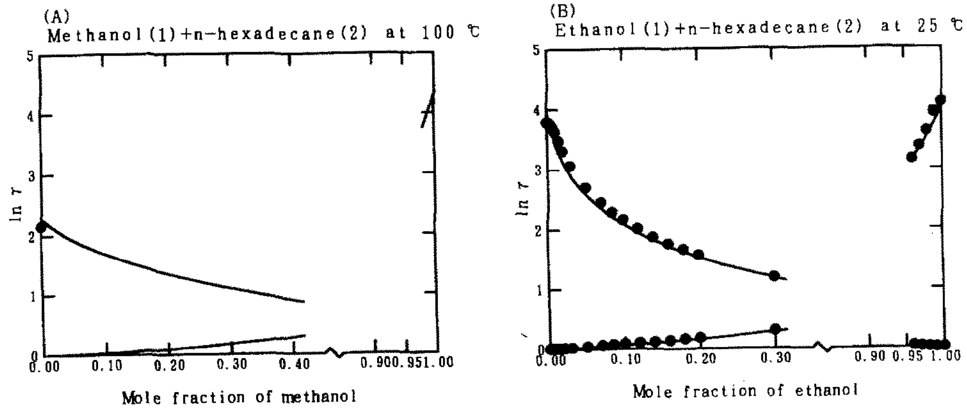


Fig. 5. Activity coefficients for (A) methanol + *n*-hexane and (B) ethanol + *n*-hexadecane. Experimental: (A) data of Comanita et al. [23] at 100°C; (B) data of French et al. [18] at 25°C.

TABLE 3

Results of vapour–liquid equilibrium data

System (1 + 2)	Temp. (°C)	Number of data points	Case[a]	Abs. relative mean dev.	Reference
				$\sigma P/P$ (%)	
Methanol + cyclohexane	30	9	I	3.0	20
			II	2.8	
Methanol + *n*-hexane	30	18	I	3.8	20
			II	3.7	

[a] I: association constant K_A^* at 50°C is 173.9 [8]; $h_A = -23.2$ kJ mol^{-1} [9]. II: association constant K_A^* at 50°C is 125.1; $h_A = -23.6$ kJ mol^{-1} [10].

TABLE 4

Results for vapour–liquid equilibrium data reduction for three binary hydrocarbon mixtures

System (1 + 2)	Temp. (°C)	Number of data points	Root-mean-square deviations				Parameters (K)		Reference
			δp (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{12}	a_{21}	
Cyclohexane + *n*-hexane	35	14	0.03	0.00	0.0		94.63	−74.04	25
Cyclohexane + *n*-heptane	25	30	0.07	0.00	0.1	0.7	43.08	−31.58	26
Cyclohexane + *n*-octane	25	26	0.05	0.00	0.1	0.4	73.66	−57.33	26

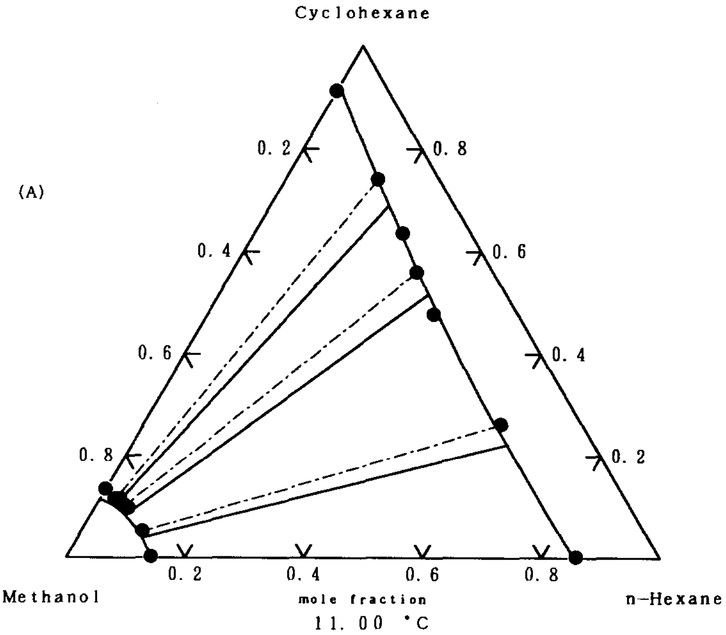
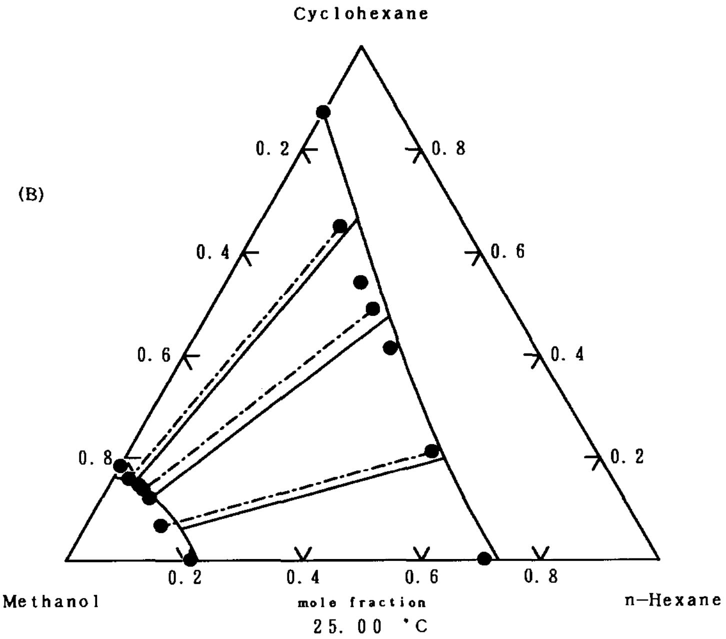


Fig. 6. Ternary liquid–liquid equilibria for mixtures of methanol with two saturated hydrocarbons: ●-----●, experimental tie line; ——, calculated. (A) Methanol + cyclohexane + *n*-hexane at 11°C [27]; (B) methanol + cyclohexane + *n*-hexane at 25°C [27]; (C) methanol + cyclohexane + *n*-hexane at 40°C [13]; (D) methanol + cyclohexane + *n*-heptane at 25°C [28]; (E) methanol + cyclohexane + *n*-octane at 25°C [29].

(B)



(C)

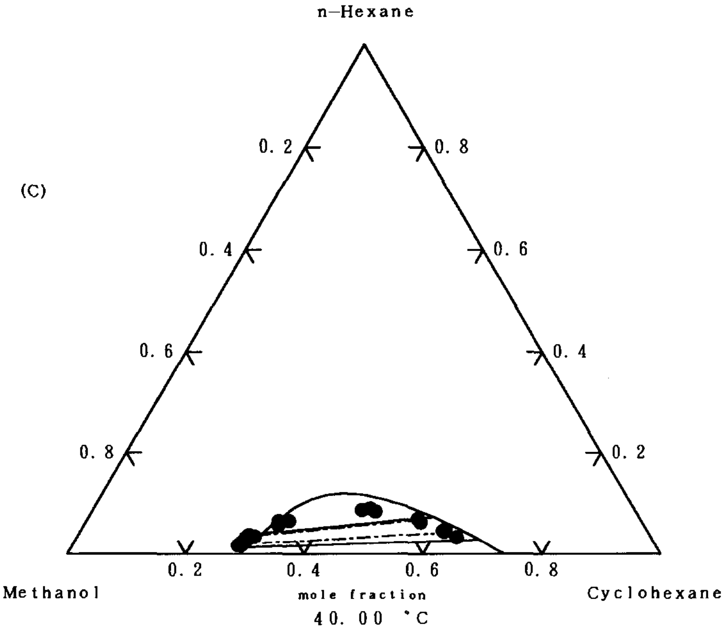
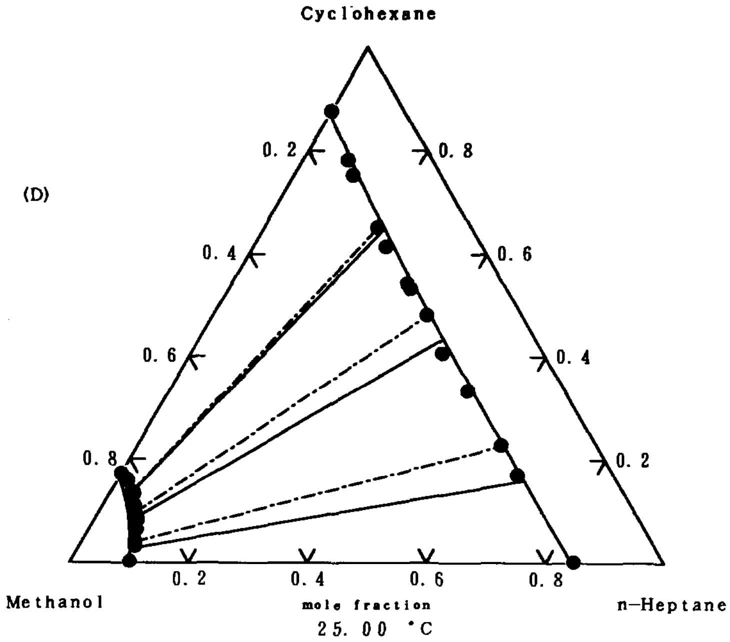


Fig. 6. (continued)

(D)



(E)

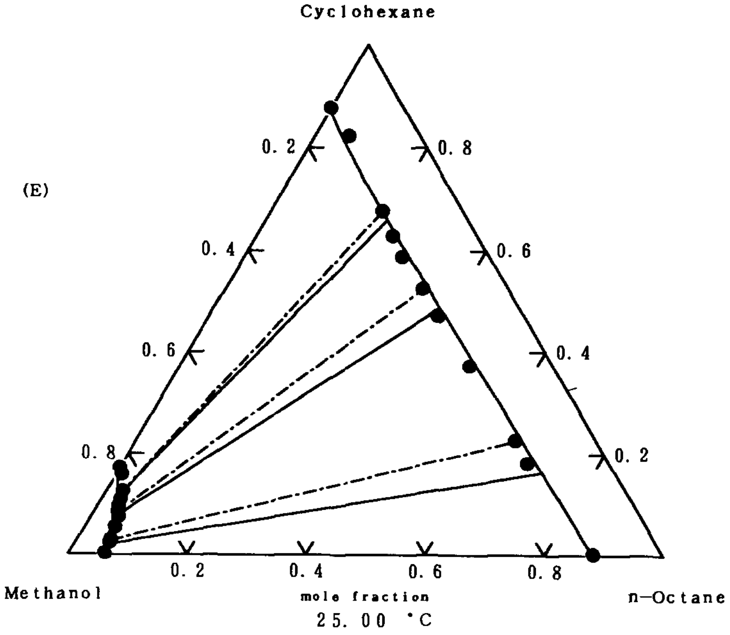


Fig. 6. (continued)

binary hydrocarbon mixtures were obtained from vapour–liquid equilibrium data reduction. For this purpose the computer program described by Prausnitz et al. [24] was used by taking account for vapour-phase non-ideality and the Poynting correction. Table 4 gives the results of data reduction for three binary hydrocarbon mixtures. Figure 6 shows the results predicted for ternary liquid–liquid equilibria. The accuracy of the predictions obtained is good.

CONCLUSIONS

The temperature dependence of the mutual solubility data for alcohol + saturated hydrocarbon is well reproduced by the UNIQUAC associated-solution model whose energy parameters are assumed to be temperature-dependent. The model also predicts binary activity coefficients in miscible regions and ternary liquid–liquid equilibria for methanol + two-hydrocarbon mixtures with good accuracy.

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