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# LIQUID–LIQUID EQUILIBRIA FOR THE ACETONITRILE–2-PROPANOL–SATURATED HYDROCARBON AND ACETONITRILE–ISOBUTANOL–SATURATED HYDROCARBON SYSTEMS

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## ABSTRACT

Tie-line data of (acetonitrile–2-propanol)–(cyclohexane or n-hexane or n-heptane) and of (acetonitrile–isobutanol)–(cyclohexane or n-hexane or n-heptane) at 25 ° C are presented. The experimental data for the ternary systems compare well with the values predicted by the extended UNIQUAC and UNIQUAC associated-solution models with binary parameters alone.

## LIST OF SYMBOLS

| | |
|---|---|
| A, B, C | acetonitrile, alcohol and saturated hydrocarbon |
| $a_{IJ}$ | binary interaction parameter |
| $B_{IJ}$ | second virial coefficient |
| $h_B$ | enthalpy of hydrogen-bond formation |
| $h_{BA}$ | enthalpy of formation of chemical complex $B_iA$ |
| $I$, $J$, $K$ | components |
| $i$ | alcohol $i$-mer |
| $K_B$ | association constant, $(\Phi_{B_{i+1}}/\Phi_{B_i}\Phi_{B_1})[i/(i+1)]$ |
| $K_{BA}$ | solvation constant, $(\Phi_{B_iA}/\Phi_{B_i}\Phi_{A_1})[i/(ir_B + r_A)]$ |
| $P$ | total pressure |
| $P_I^s$ | saturated vapour pressure of pure component $I$ |
| $q_I$ | molecular area parameter of pure component $I$ |
| $q_I'$ | molecular interaction area parameter of pure component $I$ |
| $R$ | universal gas constant |
| $r_I$ | molecular volume parameter of pure component $I$ |
| $T$ | absolute temperature |
| $V$ | true molar volume of alcohol mixture |
| $V_B^0$ | true molar volume of pure alcohol liquid |
| $v_I^L$ | molar volume of pure liquid $I$ |

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| | |
|---|---|
| $x_I$ | liquid-phase mole fraction of component $I$ |
| $y_I$ | vapour-phase mole fraction of component $I$ |
| $Z$ | coordination number equal to 10 |

*Greek letters*

| | |
|---|---|
| $\alpha$, $\beta$ | liquid phases |
| $\gamma_I$ | liquid-phase activity coefficient of component $I$ |
| $\theta_I$ | area fraction of component $I$ |
| $\tau_{IJ}$ | $\exp(-a_{IJ}/T)$ |
| $\Phi_I$ | segment fraction of component $I$ |
| $\Phi_{A_1}$ | segment fraction of acetonitrile monomer in alcohol mixture |
| $\Phi_{B_1}$ | segment fraction of alcohol monomer in alcohol mixture |
| $\Phi_{B_1}^0$ | segment fraction of alcohol monomer in pure alcohol solution |
| $\Phi_{C_1}$ | segment fraction of saturated hydrocarbon monomer in alcohol mixture |
| $\phi_I$ | vapour-phase fugacity coefficient of component $I$ at system pressure $P$ and system temperature $T$ |
| $\phi_I^s$ | vapour-phase fugacity coefficient of pure component $I$ at its saturated pressure $P_I^s$ and system temperature $T$ |

## INTRODUCTION

Experimental tie-line data for the ternary systems of (acetonitrile–saturated hydrocarbon)–(methanol or ethanol or 1-propanol or 1-butanol) have already been reported from this laboratory [1,2] This paper presents measured tie-line results for three acetonitrile–2-propanol–saturated hydrocarbon systems and three acetonitrile–isobutanol–saturated hydrocarbon systems at 25 °C The data observed have been used to test the predictive ability of the extended UNIQUAC [3] and UNIQUAC associated-solution models [4] The binary parameters of both models can be obtained from phase equilibrium data The vapour–liquid equilibrium data of eight component binary systems constituting the present ternary systems have been reported in the literature for 2-propanol–acetonitrile at 50 °C [5], for 2-propanol–cyclohexane at 50 °C [6], for 2-propanol–n-hexane at 55 06 °C [7], for 2-propanol–n-heptane at 30 °C [8], for isobutanol–acetonitrile at 60 °C [9], for isobutanol–cyclohexane at 25 °C [8], for isobutanol–n-hexane at 59 38 °C [10], for isobutanol–n-heptane at 60 °C [11] Mutual solubilities for acetonitrile–(cyclohexane or n-hexane or n-heptane) have been measured at 25 °C [1,12]

## EXPERIMENTAL

All chemicals (Wako Pure Chemical Industries Ltd , guaranteed reagent grade) were used directly for experimental work Densities and refractive indices of the chemicals were measured with an Anton Paar densimeter (DMA40) and a Shimadzu Pulfrich refractometer at 25 ° C and are compared with literature values in Table 1

All tie-line measurements were carried out in a glass cell equipped with a magnetic stirrer and thermostatted to within ±0 01° C In each run a two-phase mixture was stirred vigorously for 2 h and then left to settle for 2 h in order to ensure the phase separation of the mixture in equilibrium Samples of the two liquid phases were withdrawn with Hamilton syringes The compositions of the conjugate phases were analyzed using a Shimadzu gas chromatograph (GC-8C) connected with a Shimadzu Chromatopac (C-E1B) and the experimental error in the liquid-phase mole fraction measurements was within ±0 002

## RESULTS AND DISCUSSION

Tables 2 and 3 give observed liquid–liquid equilibrium data for the ternary systems acetonitrile–2-propanol–saturated hydrocarbon and acetonitrile–isobutanol–saturated hydrocarbon, respectively These experimental results are compared with those calculated from two solution models extended UNIQUAC, and UNIQUAC associated-solution

### *Extended UNIQUAC model*

The activity coefficient of any component $I$ in the ternary mixture is expressed by

$$\ln \gamma_I = \ln \frac{\Phi_I}{x_I} + 1 - \frac{\Phi_I}{x_I} - \left(\frac{Z}{2}\right) q_I \left(\ln \frac{\Phi_I}{\theta_I} + 1 - \frac{\Phi_I}{\theta_I}\right) - q_I' \ln\left(\sum_J \theta_J \tau_{JI}\right)$$
$$+ q_I \sum_J \left(\frac{q_J'}{q_J}\right) \theta_J - q_I \sum_J \frac{(q_J'/q_J)\theta_J \tau_{IJ}}{\sum_K \theta_K \tau_{KJ}} \qquad (1)$$

where $Z$ is the coordination number taken as 10 and the segment fraction $\Phi_I$, the surface fraction $\theta_I$ and the adjustable parameter $\tau_{IJ}$ related to an energy parameter $a_{IJ}$ are given by

$$\Phi_I = r_I x_I / \sum_J r_J x_J \qquad (2)$$

$$\theta_I = q_I x_I / \sum_J q_J x_J \qquad (3)$$

$$\tau_{IJ} = \exp(-a_{IJ}/T) \qquad (4)$$

TABLE 1

Densities and refractive indices of compounds at 25 °C

| Compound | Density (g cm$^{-3}$) | | Refractive index | |
|---|---|---|---|---|
| | Exptl | Lit [13] | Exptl | Lit [13] |
| Acetonitrile | 0 7766 | 0 7766 | 1 34161 | 1 34163 |
| Cyclohexane | 0 7738 | 0 77389 | 1 42324 | 1 42354 |
| n-Hexane | 0 6550 | 0 65481 | 1 37242 | 1 37226 |
| n-Heptane | 0 6794 | 0 67951 | 1 38487 | 1 38511 |
| Isobutanol | 0 7979 | 0 7978 | 1 39394 | 1 3939 |
| 2-Propanol | 0 7812 | 0 7813 | 1 37541 | 1 3752 |

TABLE 2

Tie-line data for acetonitrile–2-propanol–saturated hydrocarbon at 25 °C

| Phase I | | | Phase II | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| *Acetonitrile (1) – 2-propanol (2) – cyclohexane (3)* | | | | | |
| 0 9399 | 0 | 0 0601 | 0 0440 | 0 | 0 9560 [a] |
| 0 8375 | 0 0669 | 0 0956 | 0 0542 | 0 0142 | 0 9316 |
| 0 7889 | 0 1008 | 0 1103 | 0 0650 | 0 0258 | 0 9092 |
| 0 7304 | 0 1373 | 0 1323 | 0 0776 | 0 0443 | 0 8781 |
| 0 6818 | 0 1653 | 0 1529 | 0 0855 | 0 0629 | 0 8516 |
| 0 6273 | 0 1954 | 0 1773 | 0 1050 | 0 0888 | 0 8062 |
| 0 5305 | 0 2314 | 0 2381 | 0 1485 | 0 1370 | 0 7145 |
| 0 4797 | 0 2405 | 0 2798 | 0 1853 | 0 1639 | 0 6508 |
| 0 3914 | 0 2366 | 0 3720 | 0 2522 | 0 1979 | 0 5499 |
| *Acetonitrile (1) – 2-propanol (2) – n-hexane (3)* | | | | | |
| 0 9433 | 0 | 0 0567 | 0 0584 | 0 | 0 9416 [b] |
| 0 8542 | 0 0696 | 0 0762 | 0 0788 | 0 0181 | 0 9031 |
| 0 7706 | 0 1323 | 0 0971 | 0 0978 | 0 0482 | 0 8540 |
| 0 6751 | 0 1851 | 0 1398 | 0 1300 | 0 0943 | 0 7757 |
| 0 6278 | 0 2129 | 0 1593 | 0 1533 | 0 1235 | 0 7232 |
| 0 5691 | 0 2336 | 0 1973 | 0 1884 | 0 1554 | 0 6562 |
| 0 5059 | 0 2499 | 0 2442 | 0 2340 | 0 1905 | 0 5755 |
| 0 4484 | 0 2439 | 0 3077 | 0 2927 | 0 2117 | 0 4956 |
| *Acetonitrile (1) – 2-propanol (2) – n-heptane (3)* | | | | | |
| 0 9622 | 0 | 0 0378 | 0 0621 | 0 | 0 9379 [b] |
| 0 8880 | 0 0643 | 0 0477 | 0 0755 | 0 0157 | 0 9088 |
| 0 8076 | 0 1291 | 0 0633 | 0 0874 | 0 0429 | 0 8697 |
| 0 7614 | 0 1644 | 0 0742 | 0 0931 | 0 0643 | 0 8426 |
| 0 7080 | 0 2009 | 0 0911 | 0 1141 | 0 0951 | 0 7908 |
| 0 6734 | 0 2241 | 0 1025 | 0 1215 | 0 1162 | 0 7623 |
| 0 6287 | 0 2476 | 0 1237 | 0 1453 | 0 1455 | 0 7092 |
| 0 5563 | 0 2816 | 0 1621 | 0 1811 | 0 1921 | 0 6268 |
| 0 4721 | 0 3004 | 0 2275 | 0 2459 | 0 2433 | 0 5108 |

[a] Taken from ref 12 [b] Taken from ref 1

TABLE 3

Tie-line data for acetonitrile–isobutanol–saturated hydrocarbon at 25 °C

| Phase I | | | Phase II | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| *Acetonitrile (1) – isobutanol (2) – cyclohexane (3)* | | | | | |
| 0.9399 | 0 | 0.0601 | 0.0440 | 0 | 0.9560 [a] |
| 0.8145 | 0.0737 | 0.1118 | 0.0602 | 0.0239 | 0.9159 |
| 0.7621 | 0.1081 | 0.1298 | 0.0741 | 0.0405 | 0.8854 |
| 0.7164 | 0.1281 | 0.1555 | 0.0936 | 0.0601 | 0.8463 |
| 0.6632 | 0.1428 | 0.1940 | 0.1385 | 0.0872 | 0.7743 |
| 0.6150 | 0.1649 | 0.2201 | 0.1620 | 0.1114 | 0.7266 |
| 0.5436 | 0.1790 | 0.2774 | 0.1936 | 0.1283 | 0.6781 |
| 0.5104 | 0.1844 | 0.3052 | 0.2316 | 0.1446 | 0.6238 |
| *Acetonitrile (1) – isobutanol (2) – n-hexane (3)* | | | | | |
| 0.9433 | 0 | 0.0567 | 0.0584 | 0 | 0.9416 [b] |
| 0.8364 | 0.0757 | 0.0879 | 0.0797 | 0.0279 | 0.8924 |
| 0.7669 | 0.1160 | 0.1171 | 0.1013 | 0.0562 | 0.8425 |
| 0.6901 | 0.1491 | 0.1608 | 0.1558 | 0.0888 | 0.7554 |
| 0.6532 | 0.1635 | 0.1833 | 0.1887 | 0.1194 | 0.6919 |
| 0.5878 | 0.1860 | 0.2262 | 0.2139 | 0.1408 | 0.6453 |
| 0.5354 | 0.1859 | 0.2787 | 0.2838 | 0.1584 | 0.5578 |
| *Acetonitrile (1) – isobutanol (2) – n-heptane (3)* | | | | | |
| 0.9622 | 0 | 0.0378 | 0.0621 | 0 | 0.9379 [b] |
| 0.8171 | 0.1092 | 0.0737 | 0.0834 | 0.0440 | 0.8726 |
| 0.7501 | 0.1618 | 0.0881 | 0.1098 | 0.0900 | 0.8002 |
| 0.7041 | 0.1815 | 0.1144 | 0.1282 | 0.1168 | 0.7550 |
| 0.6589 | 0.2022 | 0.1389 | 0.1495 | 0.1467 | 0.7038 |
| 0.5736 | 0.2258 | 0.2006 | 0.2554 | 0.1913 | 0.5533 |
| 0.4992 | 0.2268 | 0.2740 | 0.3453 | 0.2170 | 0.4377 |

[a] Taken from ref. 12. [b] Taken from ref. 1.

The pure component molecular constants $r$, $q$ and $q'$ depend on the molecular volume and the external surface area.

### *UNIQUAC associated-solution model*

This model assumes that in the ternary mixture containing acetonitrile (A), the alcohol (B) and the saturated hydrocarbon (C) two types of chemical complexes exist as $B_i$ $(B_{i-1} + B_1 \rightarrow B_i)$ and $B_iA$ $(B_i + A_1 \rightarrow B_iA)$. Then the activity coefficients of acetonitrile and the alcohol are given by

$$\ln \gamma_A = \ln\frac{\Phi_{A_1}}{x_A} + 1 - \frac{r_A}{V} - \left(\frac{Z}{2}\right)q_A\left(\ln\frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right) + q_A\left[1 - \ln\left(\sum_J \theta_J \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right] \qquad (5)$$

$$\ln \gamma_{\mathrm{B}} = \ln \frac{\Phi_{\mathrm{B}_1}}{\Phi^0_{\mathrm{B}_1} x_{\mathrm{B}}} + \frac{r_{\mathrm{B}}}{V^0_{\mathrm{B}}} - \frac{r_{\mathrm{B}}}{V} - \left(\frac{Z}{2}\right) q_{\mathrm{B}} \left(\ln \frac{\Phi_{\mathrm{B}}}{\theta_{\mathrm{B}}} + 1 - \frac{\Phi_{\mathrm{B}}}{\theta_{\mathrm{B}}}\right)$$

$$+ q_{\mathrm{B}} \left[1 - \ln\left(\sum_J \theta_J \tau_{J\mathrm{B}}\right) - \sum_J \frac{\theta_J \tau_{\mathrm{B}J}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{6}$$

and that of the saturated hydrocarbon is given by changing the subscript A in eqn (5) with C

The monomer segment fractions of the components are simultaneously solved from the following mass balance equations

$$\Phi_{\mathrm{A}} = \Phi_{\mathrm{A}_1} \left[1 + \frac{r_{\mathrm{A}} K_{\mathrm{BA}} \Phi_{\mathrm{B}_1}}{\left(1 - K_{\mathrm{B}} \Phi_{\mathrm{B}_1}\right)}\right] \tag{7}$$

$$\Phi_{\mathrm{B}} = \frac{\Phi_{\mathrm{B}_1}}{\left(1 - K_{\mathrm{B}} \Phi_{\mathrm{B}_1}\right)^2} \left(1 + r_{\mathrm{B}} K_{\mathrm{BA}} \Phi_{\mathrm{A}_1}\right) \tag{8}$$

$$\Phi_{\mathrm{C}} = \Phi_{\mathrm{C}_1} \tag{9}$$

Then the true molar volume of the ternary mixture is given by

$$\frac{1}{V} = \frac{\Phi_{\mathrm{A}_1}}{r_{\mathrm{A}}} \left[1 + \frac{K_{\mathrm{BA}} r_{\mathrm{A}} \Phi_{\mathrm{B}_1}}{\left(1 - K_{\mathrm{B}} \Phi_{\mathrm{B}_1}\right)}\right] + \frac{\Phi_{\mathrm{B}_1}}{r_{\mathrm{B}}\left(1 - K_{\mathrm{B}} \Phi_{\mathrm{B}_1}\right)} + \frac{\Phi_{\mathrm{C}_1}}{r_{\mathrm{C}}} \tag{10}$$

$\Phi^{\ominus}_{\mathrm{B}_1}$ and $V^{\ominus}_{\mathrm{B}}$ at pure alcohol state are derived from eqns (8) and (10) respectively

$$\Phi^{\ominus}_{\mathrm{B}_1} = \frac{2K_{\mathrm{B}} + 1 - \left(1 + 4K_{\mathrm{B}}\right)^{0\ 5}}{2K^2_{\mathrm{B}}} \tag{11}$$

$$\frac{1}{V^{\ominus}_{\mathrm{B}}} = \frac{\left(1 - K_{\mathrm{B}} \Phi^{\ominus}_{\mathrm{B}_1}\right)}{r_{\mathrm{B}}} \tag{12}$$

The values of $r$ and $q$ used in the model were calculated by the method of Vera et al [14] These values differ from those for the extended UNIQUAC model Table 4 gives the values of the structural constants for both models

The association constant of the alcohol, the enthalpy of hydrogen bond, the solvation constant between the alcohol and acetonitrile and the enthalpy of solvation are as follows $K_{\mathrm{B}}$ at 50 °C is 49 1 for 2-propanol and 50 6 for isobutanol [15], a value of $h_{\mathrm{A}}$ of $-23\ 2$ kJ mol$^{-1}$ is used for the alcohol [16], which is the same as given in a previous paper [2], $K_{\mathrm{BA}}$ at 50 °C is 23 for 2-propanol–acetonitrile [2] and 30 for isobutanol–acetonitrile [9], $h_{\mathrm{BA}}$ is $-17$ kJ mol$^{-1}$ for these alcohol–acetonitrile mixtures [2,9] These values of

TABLE 4

Pure component structural parameters for two models

| Component | Extended UNIQUAC model | | | UNIQUAC associated-solution model | |
|---|---|---|---|---|---|
| | $r$ | $q$ | $q'$ | $r$ | $q$ |
| Acetonitrile | 1 87 | 1 72 | $q^{0\,2}$ | 1 50 | 1 40 |
| Cyclohexane | 3 97 | 3 01 | $q^{0\,2}$ | 3 18 | 2 55 |
| n-Hexane | 4 50 | 3 86 | $q^{0\,2}$ | 3 61 | 3 09 |
| n-Heptane | 5 17 | 4 40 | $q^{0\,2}$ | 4 15 | 3 52 |
| Isobutanol | 3 45 | 3 05 | 0 88 | 2 77 | 2 42 |
| 2-Propanol | 2 78 | 2 51 | 0 89 | 2 23 | 1 98 |

$h_B$ and $h_{BA}$ were assumed to be temperature-independent and fix the temperature dependence of the equilibrium constants according to

$$\frac{\partial \ln K_B}{\partial(1/T)} = -\frac{h_B}{R} \qquad \frac{\partial \ln K_{BA}}{\partial(1/T)} = -\frac{h_{BA}}{R} \tag{13}$$

TABLE 5

Binary parameters and root-mean-square deviations

| System | Temp (°C) | No of data points | Model[a] | Root-mean-square deviations | | | | Parameters (K) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\delta P$ (torr) | $\delta T$ (K) | $\delta x$ ($\times 10^3$) | $\delta y$ ($\times 10^3$) | $a_{AB}$ | $a_{BA}$ |
| 2-Propanol (A)–acetonitrile (B) | 50 | 12 | I | 0 82 | 0 02 | 0 5 | 3 3 | 356 68 | 70 27 |
| | | | II | 0 53 | 0 01 | 0 5 | 3 7 | 538 50 | 84 11 |
| 2-Propanol (A)–cyclohexane (B) | 50 | 9 | I | 1 27 | 0 04 | 0 6 | 5 6 | 123 14 | 869 10 |
| | | | II | 1 10 | 0 04 | 0 4 | 3 8 | 155 98 | −84 76 |
| 2-Propanol (A)–n-hexane (B) | 55 06 | 24 | I | 0 94 | 0 00 | 0 4 | 2 2 | 155 14 | 888 33 |
| | | | II | 1 08 | 0 00 | 0 4 | 1 4 | 175 93 | −97 83 |
| 2-Propanol (A)–n-heptane (B) | 30 | 11 | I | 0 80 | 0 00 | 0 3 | | 162 55 | 1098 10 |
| | | | II | 0 44 | 0 00 | 0 3 | | 135 54 | −76 81 |
| Isobutanol (A)–acetonitrile (B) | 60 | 14 | I | 1 21 | 0 00 | 0 6 | 3 4 | 420 34 | 8 40 |
| | | | II | 2 02 | 0 00 | 1 5 | 5 3 | 638 85 | 104 83 |
| Isobutanol (A)–cyclohexane (B) | 25 | 10 | I | 4 02 | 0 00 | 0 9 | 11 5 | 92 98 | 648 96 |
| | | | II | 4 23 | 0 00 | 0 5 | 11 2 | 300 82 | −181 15 |
| Isobutanol (A)–n-hexane (B) | 59 38 | 21 | I | 1 47 | 0 00 | 0 5 | 1 5 | 139 19 | 830 82 |
| | | | II | 2 60 | 0 00 | 0 9 | 2 3 | 216 42 | −127 32 |
| Isobutanol (A)–n-heptane (B) | 60 | 16 | I | 0 68 | 0 00 | 0 3 | 8 0 | 137 30 | 854 66 |
| | | | II | 0 84 | 0 00 | 0 3 | 7 1 | 231 10 | −139 37 |
| Acetonitrile (A)–cyclohexane (B) | 25 | MS[b] | I | | | | | 432 81 | 948 66 |
| | | | II | | | | | 142 38 | 689 58 |
| Acetonitrile (A)–n-hexane (B) | 25 | MS | I | | | | | 414 68 | 983 15 |
| | | | II | | | | | 100 74 | 692 54 |
| Acetonitrile (A)–n-heptane (B) | 25 | MS | I | | | | | 439 86 | 990 57 |
| | | | II | | | | | 99 25 | 692 34 |

[a] I, extended UNIQUAC model, II, UNIQUAC associated-solution model [b] MS, mutual solubilities

The thermodynamic relations used to reduce the vapour–liquid equilibrium data of the eight binary systems are

$$P y_I \phi_I = \gamma_I x_I \phi_I^s P_I^s \exp\left[v_I^L (P - P_I^s)/RT\right] \tag{14}$$

$$\ln \phi_I = \left(2\sum_J y_J B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ}\right)\frac{P}{RT} \tag{15}$$

where $P$ is the total pressure, $y$ is the vapour-phase mole fraction, $\phi$ is the vapour-phase fugacity coefficient, $v^L$ is the pure liquid molar volume calculated from the Rackett equation as modified by Spencer and Danner [17], $P^s$ is the pure component vapour pressure taken from original refer-

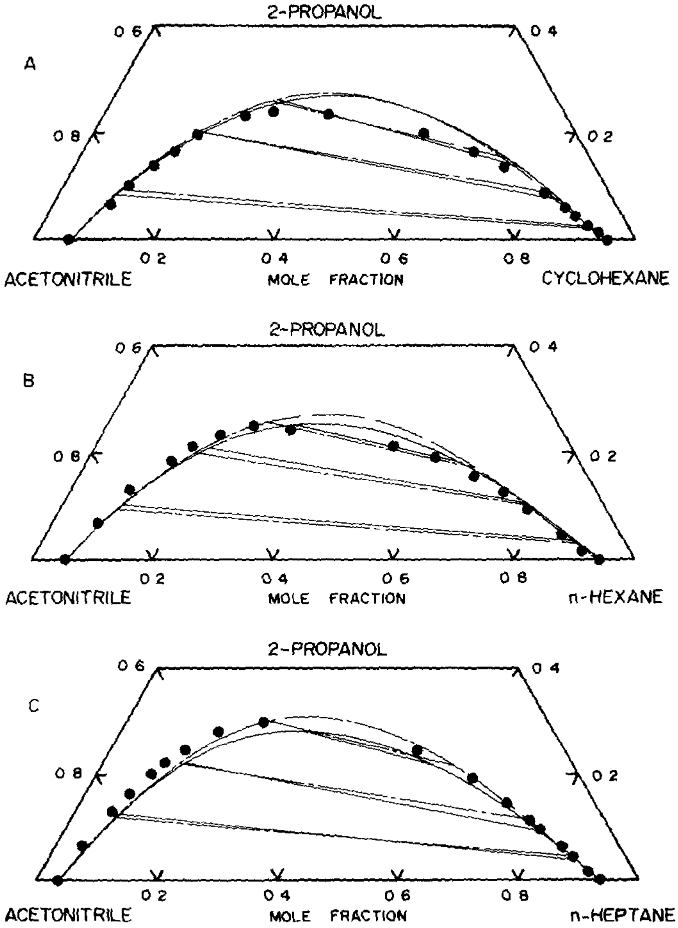

Fig 1 Experimental tie-lines and binodal curves predicted from the extended UNIQUAC and UNIQUAC associated-solution models at 25 °C (A acetonitrile–2-propanol–cyclohexane, B, acetonitrile–2-propanol–n-hexane, C, acetonitrile–2-propanol–n-heptane) Experimental, ● Calculated ——, extended UNIQUAC model, – – –, UNIQUAC associated-solution model

ences of vapour-liquid equilibrium data or calculated from the Antoine equation [13], $B_{ij}$ is the second virial coefficient estimated by using the general correlation of Hayden and O'Connell [18] and $R$ is the universal gas constant

The computer program used to obtain the optimum parameters of the models was similar to that developed by Prausnitz et al. [19], based on the maximum-likelihood principle The standard deviations for the measured variables used in data reduction were 1 torr for pressure, 0 05 K for temperature, 0 001 for liquid-phase mole fraction and 0 003 for vapour-phase mole fraction

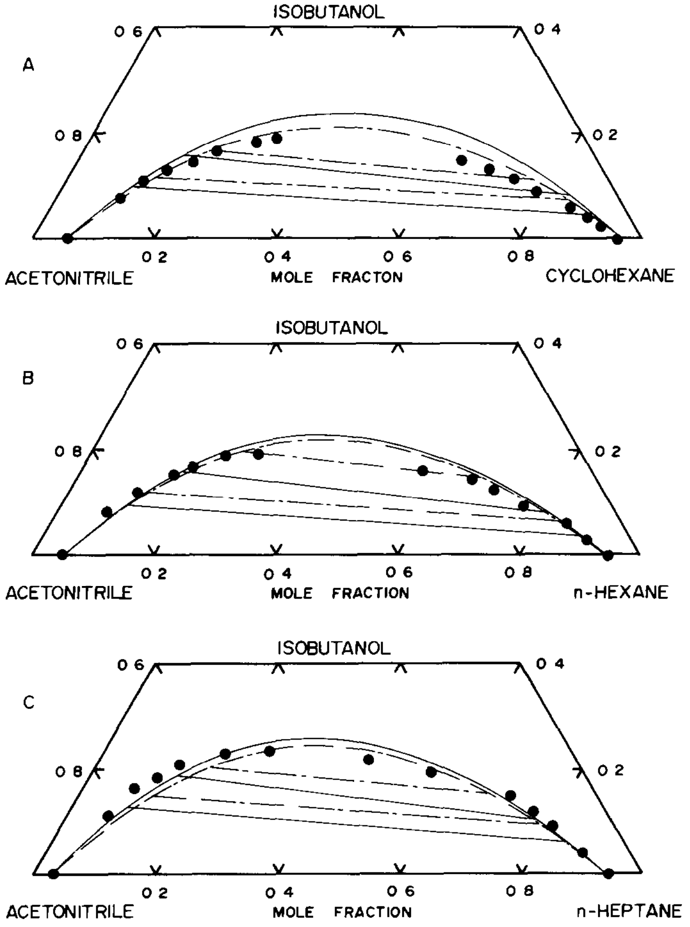

Fig 2 Experimental tie-lines and binodal curves predicted from the extended UNIQUAC and UNIQUAC associated-solution models at 25 °C (A, acetonitrile–isobutanol–cyclohexane, B, acetonitrile–isobutanol–n-hexane, C, acetonitrile–isobutanol–n-heptane) Experimental, ● Calculated ———, extended UNIQUAC model, — - —, UNIQUAC associated-solution model

Mutual solubility data provide the binary parameters of the models for a partially miscible system by solving eqn (16) based on the isoactivity criterion for each component

$$(x_I\gamma_I)^{\alpha} = (x_I\gamma_I)^{\beta} \tag{16}$$

where the superscripts $\alpha$ and $\beta$ represent two equilibrium liquid phases

Table 5 shows the resulting parameters of the extended UNIQUAC and UNIQUAC associated-solution models and the root-mean-square deviations between experimental and calculated results for the eight completely miscible and three partially miscible binary systems These parameters were used to calculate the ternary liquid-liquid equilibria of the six systems Figures 1 and 2 compare the experimental results with the calculated values The calculated results derived from the two models do not differ significantly from each other and the UNIQUAC associated-solution model gives slightly better results than the extended UNIQUAC model for the five systems except for the acetonitrile–isobutanol–n-heptane system

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