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# TERNARY LIQUID—LIQUID EQUILIBRIA AND THEIR REPRESENTATION BY MODIFIED NRTL EQUATIONS

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## ABSTRACT

Experimental liquid—liquid equilibrium data are reported for the systems acetonitrile—acetone—cyclohexane at 318.15 K and acetonitrile—methyl acetate—cyclohexane at 313.15 K. Two modified forms of the NRTL equation proposed by Renon are presented by substituting local surface fractions for local mole fractions and further by including Guggenheim's combinatorial entropy for athermal mixtures whose molecules differ in size and shape. The resultant equations involve three adjustable parameters and are extended to multicomponent systems without adding ternary (or higher) parameters. Calculated results of vapor—liquid and liquid—liquid equilibria for typical binary and ternary mixtures are presented.

## NOTATION

| | |
|---|---|
| $a^E$ | excess Helmholtz free energy |
| $a_{ji}$ | binary interaction parameter defined as $\Delta u_{ji}/R$ |
| $g^E$ | excess Gibbs free energy |
| $l_i$ | bulk factor of pure component i as defined by $l_i = (Z/2)(r_i - q_i) - (r_i - 1)$ |
| $q_i$ | surface parameter of pure component i |
| $r_i$ | size parameter of pure component i |
| $R$ | gas constant |
| $s^E$ | excess entropy of mixing |
| $T$ | absolute temperature |
| $\Delta u_{ji}$ | binary interaction parameter |
| $x_i$ | liquid-phase mole fraction of component i |
| $Z$ | lattice coordination number, a constant set to 10 |
| $\alpha_{ij}$ | proportionality constant similar to the nonrandomness constant of the NRTL equation |
| $\gamma$ | activity coefficient |
| $\theta_{ij}$ | local surface fraction as defined in eqn. (18) |
| $\theta_i$ | surface fraction of component i |
| $\tau_{ji}$ | coefficient defined as $\Delta u_{ji}/RT$ |
| $\phi_i$ | size fraction of component i |

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## INTRODUCTION

For estimating ternary liquid—liquid equilibria from binary data, a thermodynamic procedure, which uses a solution model for excess Gibbs energy, is sound and is more useful than empirical and/or graphical methods, provided that isothermal vapor—liquid equilibrium data of good quality for miscible binaries and mutual solubility data for partially miscible binary pairs are used and a selected model represents well these phase equilibrium relationships. Many solution models based on the concept of local composition have been proposed and are not perfect. Model refinements need to obtain more reliable results.

In this work we discuss the abilities of newly modified NRTL equations especially in the correlation of ternary liquid—liquid equilibria for several systems with a plait point. Ternary liquid—liquid equilibria are reported here for two systems: acetonitrile—acetone—cyclohexane at 318.15 K and acetonitrile—methyl acetate—cyclohexane at 313.15 K. Isothermal vapor—liquid equilibrium data have been given in the literature for the miscible binary systems which constitute these ternaries: acetonitrile—acetone at 45°C [1]; acetone—cyclohexane at 45°C [2]; acetonitrile—methyl acetate at 50°C [3]; methyl acetate—cyclohexane at 40°C [4]. Results of data reduction obtained with the original NRTL equation [5] are also presented for comparison.

## EXPERIMENTAL

The experimental apparatus and procedure are the same as described in a previous paper [6]. All reagent grade chemicals (acetone, acetonitrile and cyclohexane) were directly used. $1 \times 10^{-3}$ $m^3$ of chemically pure methyl acetate was refluxed for 6 h with 85 $cm^3$ of acetic anhydride and then distilled through a glass column packed with McMahon packings. The distillate was shaken with 20 g of anhydrous potassium carbonate and redistilled. Refractive indices of the compounds used for experimental work are compared with literature values in Table 1. Tables 2 and 3 list experimental solubility data and tie-lines for the two ternary systems, respectively.

TABLE 1

Refractive indices of compounds at 298.15 K

| Compound | Exptl. | Ref. 7 |
|---|---|---|
| Acetone | 1.35603 | 1.35596 |
| Acetonitrile | 1.34170 | 1.34163 |
| Cyclohexane | 1.42352 | 1.42354 |
| Methyl acetate | 1.35877 | 1.3588 * |

* Ref. 4.

TABLE 2

Ternary solubility data

| $x_1$ | $x_2$ | $x_1$ | $x_2$ | $x_1$ | $x_2$ |
|---|---|---|---|---|---|
| *Acetonitrile(1)—acetone(2)—cyclohexane(3) at 318.15 K* | | | | | |
| 0.0935 | 0.0000 | 0.3275 | 0.1669 | 0.6200 | 0.1606 |
| 0.1788 | 0.1026 | 0.3667 | 0.1790 | 0.6551 | 0.1464 |
| 0.1970 | 0.1146 | 0.3959 | 0.1857 | 0.7816 | 0.0749 |
| 0.2171 | 0.1250 | 0.4856 | 0.1946 | 0.8196 | 0.0497 |
| 0.2380 | 0.1354 | 0.5052 | 0.1944 | 0.8615 | 0.0210 |
| 0.2847 | 0.1524 | 0.5776 | 0.1774 | 0.8883 | 0.0000 |
| *Acetonitrile(1)—methyl acetate(2)—cyclohexane(3) at 313.15 K* | | | | | |
| 0.8961 | 0.0000 | 0.5928 | 0.1847 | 0.2104 | 0.1267 |
| 0.8501 | 0.0366 | 0.4851 | 0.1988 | 0.1805 | 0.1084 |
| 0.8077 | 0.0691 | 0.3860 | 0.1797 | 0.1538 | 0.0883 |
| 0.7151 | 0.1209 | 0.3131 | 0.1627 | 0.1278 | 0.0659 |
| 0.6395 | 0.1621 | 0.2660 | 0.1494 | 0.0787 | 0.0000 |

TABLE 3

Ternary tie-line data

| Acetonitrile-rich phase | | Cyclohexane-rich phase | |
|---|---|---|---|
| $x_1^{\mathrm{I}}$ | $x_2^{\mathrm{I}}$ | $x_1^{\mathrm{II}}$ | $x_2^{\mathrm{II}}$ |
| *Acetonitrile(1)—acetone(2)—cyclohexane(3) at 318.15 K* | | | |
| 0.8223 | 0.0449 | 0.0988 | 0.0140 |
| 0.7853 | 0.0708 | 0.1020 | 0.0224 |
| 0.7584 | 0.0862 | 0.1083 | 0.0297 |
| 0.6929 | 0.1233 | 0.1292 | 0.0453 |
| 0.6665 | 0.1381 | 0.1347 | 0.0551 |
| 0.6288 | 0.1539 | 0.1508 | 0.0677 |
| *Acetonitrile(1)—methyl acetate(2)—cyclohexane at 313.15 K* | | | |
| 0.8580 | 0.0281 | 0.0868 | 0.0113 |
| 0.7835 | 0.0797 | 0.0890 | 0.0337 |
| 0.7317 | 0.1090 | 0.1094 | 0.0521 |
| 0.6802 | 0.1399 | 0.1371 | 0.0719 |
| 0.6578 | 0.1488 | 0.1459 | 0.0800 |
| 0.6301 | 0.1633 | 0.1533 | 0.0871 |
| 0.4481 | 0.1864 | 0.2907 | 0.1544 |

## EXCESS GIBBS ENERGY EQUATIONS

### *Binary systems*

The energy of mixing, $u^{\mathrm{E}}$, for a binary mixture of components 1 and 2 is derived by using Scott's two liquids theory and the local composition concept.

$$u^{\mathrm{E}} = x_1\theta_{21}\Delta u_{21} + x_2\theta_{12}\Delta u_{12} \tag{1}$$

For $\theta_{21}$ and $\theta_{12}$ Renon and Prausnitz [5] used the local mole fractions to derive their NRTL equation and Bruin and Prausnitz [8] chose the local volume fractions. In this work we adopt the local surface fractions.

$$\theta_{21} = \theta_2 \exp(-\Delta u_{21}\alpha_{12}/RT)/[\theta_1 + \theta_2 \exp(-\Delta u_{21}\alpha_{12}/RT)] \tag{2}$$

$$\theta_{12} = \theta_1 \exp(-\Delta u_{12}\alpha_{12}/RT)/[\theta_2 + \theta_1 \exp(-\Delta u_{12}\alpha_{12}/RT)] \tag{3}$$

where $\theta_1$ and $\theta_2$ are the surface fractions defined by surface area parameter $q$, $\Delta u_{ji}$ is a parameter related to the difference between the potential energies of the pairs j—i and i—i, and $\alpha_{12}$ is a constant of proportionality similar to the nonrandomness constant of the NRTL equation ($\alpha_{ij} = \alpha_{ji}$).

$$\theta_1 = x_1q_1/(x_1q_1 + x_2q_2)\colon\ \theta_2 = x_2q_2/(x_1q_1 + x_2q_2) \tag{4}$$

An expression for the molar excess Helmholtz energy is obtained as follows

$$a^{\mathrm{E}} = u^{\mathrm{E}} - Ts^{\mathrm{E}} \tag{5}$$

For $(-s^{\mathrm{E}}/R)$ we use the equation of Guggenheim [9] for athermal mixtures whose molecules differ in size and shape.

$$-(s^{\mathrm{E}}/R)_{\mathrm{athermal}} = x_1 \ln\frac{\phi_1}{x_1} + x_2 \ln\frac{\phi_2}{x_2} + \left(\frac{Z}{2}\right)\left(q_1x_1 \ln\frac{\theta_1}{\phi_1} + q_2x_2 \ln\frac{\theta_2}{\phi_2}\right) \tag{6}$$

where $\phi$ is the size fraction defined by size parameter $r$.

$$\phi_1 = x_1r_1/(x_1r_1 + x_2r_2)\colon\ \phi_2 = x_2r_2/(x_1r_1 + x_2r_2) \tag{7}$$

At low pressure we may assume that [10]

$$(a^{\mathrm{E}})_{T,V} = (g^{\mathrm{E}})_{T,P} \tag{8}$$

where $g^{\mathrm{E}}$ is the molar excess Gibbs energy. Then we obtain

$$\frac{g^{\mathrm{E}}}{RT} = x_1 \ln\frac{\phi_1}{x_1} + x_2 \ln\frac{\phi_2}{x_2} + \left(\frac{Z}{2}\right)\left(q_1x_1 \ln\frac{\theta_1}{\phi_1} + q_2x_2 \ln\frac{\theta_2}{\phi_2}\right) + x_1\theta_{21}\frac{\Delta u_{21}}{RT} + x_2\theta_{12}\frac{\Delta u_{12}}{RT} \tag{9}$$

which is called the modified NRTL1 equation.

Equations for activity coefficients are derived by differentiation of eqn. (9).

$$\ln\gamma_1 = \ln\frac{\phi_1}{x_1} + \left(\frac{Z}{2}\right) q_1 \ln\frac{\theta_1}{\phi_1} + \phi_2\left(l_1 - \frac{r_1}{r_2}\, l_2\right) + \theta_{21}^2\frac{\Delta u_{21}}{RT} + \frac{x_2}{x_1}\,\theta_{12}(1-\theta_{12})\frac{\Delta u_{12}}{RT} \tag{10}$$

$$\ln\gamma_2 = \ln\frac{\phi_2}{x_2} + \left(\frac{Z}{2}\right) q_2 \ln\frac{\theta_2}{\phi_2} + \phi_1\left(l_2 - \frac{r_2}{r_1}\, l_1\right) + \theta_{12}^2\frac{\Delta u_{12}}{RT} + \frac{x_1}{x_2}\,\theta_{21}(1-\theta_{21})\frac{\Delta u_{21}}{RT} \tag{11}$$

where $l_i$ is defined by

$$l_i = (Z/2)(r_i - q_i) - (r_i - 1) \tag{12}$$

Maurer and Prausnitz [11] derived the following equation for $u^E$

$$u^E = x_1 q_1 \theta_{21}\, \Delta u_{21} + x_2 q_2 \theta_{12}\, \Delta u_{12} \tag{13}$$

Then, the final $g^E$ expression including eqns. (6) and (13) is

$$\frac{g^E}{RT} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \left(\frac{Z}{2}\right)\left(q_1 x_1 \ln \frac{\theta_1}{\phi_1} + q_2 x_2 \ln \frac{\theta_2}{\phi_2}\right) + x_1 q_1 \theta_{21} \frac{\Delta u_{21}}{RT} + x_2 q_2 \theta_{12} \frac{\Delta u_{12}}{RT} \tag{14}$$

This is called the modified NRTL2 equation. From eqn. (14) $\gamma_1$ is given by

$$\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + \left(\frac{Z}{2}\right) q_1 \ln \frac{\theta_1}{\phi_1} + \phi_2\left(l_1 - \frac{r_1}{r_2}\, l_2\right) + q_1 \theta_{21}^2 \frac{\Delta u_{21}}{RT} + q_2 \frac{x_2}{x_1}\, \theta_{12}(1 - \theta_{12}) \frac{\Delta u_{12}}{RT} \tag{15}$$

and $\gamma_2$ can be obtained by interchanging subscripts 1 and 2.

## *Multicomponent systems*

The equations for binary mixtures are easily extended to multicomponent mixtures without including additional parameters, because only two-body interactions should be taken into account in both binary and multicomponent systems.

The modified NRTL1 equation gives

$$\frac{g^E}{RT} = \sum_i x_i \ln \frac{\phi_i}{x_i} + \left(\frac{Z}{2}\right) \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} + \sum_i \sum_j (x_i \theta_{ji} \tau_{ji} + x_j \theta_{ij} \tau_{ij}) \tag{16}$$

and the activity coefficient of component i becomes

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \left(\frac{Z}{2}\right) q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j + \sum_j \theta_{ji} \tau_{ji} + \sum_j \frac{x_j \theta_{ij}}{x_i} \left(\tau_{ij} - \sum_k \theta_{ki} \tau_{kj}\right) \tag{17}$$

where $\theta_{ij}$ and $\tau_{ij}$ are given by

$$\theta_{ij} = \frac{\theta_i \exp(-\tau_{ij} \alpha_{ij})}{\sum_k \theta_k \exp(-\tau_{kj} \alpha_{kj})} \tag{18}$$

$$\tau_{ij} = \frac{\Delta u_{ij}}{RT} \equiv \frac{a_{ij}}{T} \tag{19}$$

TABLE 4

Correlation of binary vapor—liquid equilibrium data

| System, 1—2 | Temp. or pressure | No. of data points | | Energy parameters (K) | | $\alpha_{12}$ | Relative pressure * (×1000) | | | Vapor mole * fraction (×1000) | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $a_{21}$ | $a_{12}$ | | N ** | I *** | II † | N | I | II | |
| Acetonitrile—benzene | 45°C | 11 | I | 381.06 | −57.42 | 0.40 | 4 | 7 | 7 | 6 | 10 | 10 | 16 |
| | | | II | 296.81 | −92.45 | 0.40 | | | | | | | |
| Benzene—*n*—heptane | 45°C | 15 | I | 65.89 | 117.25 | 0.40 | 6 | 5 | 5 | 4 | 3 | 3 | 16 |
| | | | II | 16.30 | 35.59 | 0.40 | | | | | | | |
| Ethyl acetate—ethanol | 40°C | 14 | I | −20.86 | 378.50 | 0.40 | 4 | 4 | 4 | 4 | 4 | 5 | 17 |
| | | | II | −83.90 | 276.72 | 0.40 | | | | | | | |
| | 55°C | 14 | I | −31.60 | 356.89 | 0.40 | 5 | 4 | 4 | 5 | 6 | 6 | 17 |
| | | | II | −85.32 | 264.06 | 0.40 | | | | | | | |
| | 70°C | 15 | I | −49.22 | 339.85 | 0.40 | 8 | 7 | 7 | 5 | 5 | 5 | 17 |
| | | | II | −91.47 | 257.08 | 0.40 | | | | | | | |
| Ethanol—water | 40°C | 13 | I | 53.83 | 131.84 | 0.40 | 33 | 34 | 34 | 6 | 9 | 9 | 17 |
| | | | II | 13.80 | 103.22 | 0.40 | | | | | | | |
| | 55°C | 13 | I | 268.03 | 15.68 | 0.40 | 8 | 8 | 8 | 9 | 9 | 9 | 17 |
| | | | II | 190.03 | −44.71 | 0.40 | | | | | | | |
| | 70°C | 13 | I | 344.70 | −15.13 | 0.40 | 8 | 9 | 9 | 9 | 9 | 9 | 17 |
| | | | II | 255.44 | −86.98 | 0.40 | | | | | | | |
| Chloroform—acetone | 20°C | 9 | I | −545.18 | 804.63 | 0.40 | 5 | 2 | 8 | 4 | 4 | 9 | 18 |
| | | | II | 606.09 | −399.44 | 0.40 | | | | | | | |
| | 25°C | 7 | I | −536.84 | 739.14 | 0.40 | 8 | 5 | 11 | 8 | 11 | 8 | 19 |
| | | | II | 617.97 | −401.63 | 0.40 | | | | | | | |
| | 30°C | 9 | I | −512.14 | 784.12 | 0.40 | 6 | 3 | 7 | 5 | 3 | 8 | 18 |
| | | | II | 583.63 | −394.90 | 0.40 | | | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acetone—water | 25°C | 13 | I | −163.12 | 574.86 | 0.40 | 18 | 31 | 28 | 14 | 17 | 17 | 20 |
| | | | II | −131.48 | 469.07 | 0.40 | | | | | | | |
| Methyl acetate—methanol | 760 mm Hg | 14 | I | −78.89 | 385.87 | 0.40 | 6 | 8 | 7 | 8 | 11 | 11 | 21 |
| | | | II | −82.92 | 325.42 | 0.40 | | | | | | | |
| Methyl acetate—benzene | 760 mm Hg | 12 | I | 285.99 | −186.11 | 0.40 | 4 | 4 | 4 | 9 | 11 | 12 | 22 |
| | | | II | 207.14 | −160.51 | 0.40 | | | | | | | |
| Methanol—benzene | 760 mm Hg | 18 | I | 705.54 | 75.52 | 0.40 | 7 | 7 | 10 | 9 | 13 | 16 | 21 |
| | | | II | 567.55 | −55.03 | 0.40 | | | | | | | |
| Nitromethane—carbon tetrachloride | 45°C | 12 | I | 675.67 | 314.99 | 0.47 | 12 | 6 | 19 | 10 | 4 | 12 | 23 |
| | | | II | 402.05 | −5.25 | 0.47 | | | | | | | |
| Carbon tetrachloride—acetonitrile | 45°C | 13 | I | 171.13 | 655.75 | 0.47 | 6 | 9 | 15 | 8 | 9 | 15 | 24 |
| | | | II | −42.11 | 449.50 | 0.47 | | | | | | | |
| Ethanol—benzene | 45°C | 12 | I | 604.48 | 111.41 | 0.47 | 5 | 7 | 11 | 7 | 6 | 10 | 25 |
| | | | II | 387.96 | −55.45 | 0.47 | | | | | | | |
| 1-Propanol—benzene | 45°C | 11 | I | 503.40 | 113.33 | 0.47 | 6 | 6 | 9 | 4 | 4 | 6 | 26 |
| | | | II | 281.89 | −48.77 | 0.47 | | | | | | | |
| 2-Propanol—benzene | 45°C | 12 | I | 457.53 | 134.86 | 0.47 | 6 | 5 | 8 | 8 | 6 | 8 | 27 |
| | | | II | 248.55 | −28.35 | 0.47 | | | | | | | |
| Acetone-acetonitrile | 45°C | 10 | I | 87.52 | −37.03 | 0.40 | 4 | 4 | 4 | 2 | 2 | 2 | 1 |
| | | | II | 81.67 | −61.79 | 0.40 | | | | | | | |
| Acetone—cyclohexane | 45°C | 9 | I | 459.43 | 126.63 | 0.40 | 16 | 16 | 17 | 3 | 3 | 3 | 2 |
| | | | II | 279.68 | −52.53 | 0.40 | | | | | | | |
| Methyl acetate—acetonitrile | 50°C | 14 | I | −101.31 | 162.75 | 0.40 | 1 | 1 | 1 | | | | 3 |
| | | | II | −70.32 | 126.72 | 0.40 | | | | | | | |
| Methyl acetate—cyclohexane | 40°C | 9 | I | 330.62 | 166.97 | 0.40 | 10 | 10 | 10 | 8 | 7 | 8 | 4 |
| | | | II | 175.08 | −7.19 | 0.40 | | | | | | | |

* Root mean square deviation.

** N = NRTL equation.

*** I = Modified NRTL1 equation.

† II = Modified NRTL2 equation.

The modified NRTL2 equation provides

$$\frac{g^E}{RT} = \sum_i x_i \ln \frac{\phi_i}{x_i} + \left(\frac{Z}{2}\right) \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} + \sum_i \sum_j \left(x_i q_i \theta_{ji} \tau_{ji} + x_j q_j \theta_{ij} \tau_{ij}\right) \tag{20}$$

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \left(\frac{Z}{2}\right) q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j + q_i \sum_j \theta_{ji} \tau_{ji} + \sum_j \frac{x_j \theta_{ij} q_j}{x_i} \left(\tau_{ij} - \sum_k \theta_{kj} \tau_{kj}\right) \tag{21}$$

## CALCULATED RESULTS

### *Vapor—liquid equilibria*

The pure component structural parameters $r$ and $q$ were obtained in accordance with the methods suggested by Abrams and Prausnitz [12]. Vapor-phase nonideality corrections were calculated from the method of Hayden and O'Connell [13] for the second virial coefficients. Parameter-determining procedures were described by Prausnitz et al. [14]. The simplex method of Nelder and Mead [15] was used for this purpose. Renon and Prausnitz [5] showed that a proper value of $\alpha_{12}$ can be specified a priori, its value depending on the binary system and varying from 0.2 to 0.47. If $\alpha_{12}$ is assigned, the present modified NRTL equations have two adjustable parameters per binary: $\Delta u_{21}$ ($a_{21} = \Delta u_{21}/R$) and $\Delta u_{12}$ ($a_{12} = \Delta u_{12}/R$). In this work, for alcohols—alkanes, alcohols—aromatics, alcohols—carbon tetrachloride, carbon tetrachloride—acetonitrile and carbon tetrachloride—nitromethane,

TABLE 5

Prediction of ternary vapor—liquid equilibrium data

| System | Temp. or pressure | No. of data points | Absolute arith. dev. | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | | Vapor mole fraction (× 1000) | | | Press (mm Hg) | | | |
| | | | N * | I ** | II *** | N | I | II | |
| Acetonitrile—<br>benzene—<br>*n*-heptane | 45°C | 51 | 11<br>4<br>9 | 8<br>5<br>7 | 19<br>7<br>16 | 6 | 5 | 10 | 16 |
| Ethyl acetate—<br>ethanol—<br>water | 40°C | 9 | 9<br>9<br>14 | 8<br>10<br>13 | 9<br>9<br>14 | 7 | 7 | 7 | 17 |
| Methyl acetate—<br>methanol—<br>benzene | 760 mm Hg | 18 | 5<br>5<br>3 | 5<br>6<br>4 | 5<br>7<br>6 | 6 | 10 | 10 | 28 |

* N = NRTL equation.

** I = Modified NRTL1 equation.

*** II = Modified NRTL2 equation.

TABLE 6

Parameters from binary liquid—liquid equilibrium data

| System, 1—2 | Temp. (°C) | Energy parameters (K) | | $\alpha_{12}$ | Ref. |
|---|---|---|---|---|---|
| | | $a_{21}$ | $a_{12}$ | | |
| Acetonitrile—$n$-heptane | 45 I * | 920.80 | 736.88 | 0.40 | 16 |
| | II ** | 566.23 | −5.64 | 0.40 | |
| Ethyl acetate—water | 40 I | 614.63 | 641.51 | 0.54 | 17 |
| | II | 102.51 | 352.37 | 0.40 | |
| | 55 I | 669.78 | 641.51 | 0.54 | 17 |
| | II | 144.93 | 299.90 | 0.40 | |
| Chloroform—water | 25 I | 615.32 | 961.32 | 0.20 | 29 |
| | II | 342.03 | 641.62 | 0.40 | |
| Acetonitrile—cyclohexane | 40 I | 886.71 | 584.30 | 0.40 | This work |
| | II | 553.65 | 9.50 | 0.40 | |
| | 45 I | 844.84 | 402.40 | 0.36 | This work |
| | II | 538.90 | 9.13 | 0.40 | |
| Benzene—water | 25 I | 1151.13 | 1374.28 | 0.38 | 7 |
| | II | 376.53 | 856.11 | 0.40 | |

* I = Modified NRTL1 equation.

** II = Modified NRTL2 equation.

$\alpha_{12} = 0.47$, and for other systems including aqueous systems, $\alpha_{12} = 0.4$. Table 4 shows typical results comparable to those obtained with the NRTL equation. Ternary results predicted from binary parameters indicate that all the three equations have a similar predictive ability, as shown in Table 5.

### *Liquid—liquid equilibria*

Table 6 lists binary parameters for heterogeneous systems. These parameters for fixed values of $\alpha_{12}$ were obtained by solving simultaneously two equations which express the equality of activities of each component in two liquid phases. The capabilities of the modified NRTL equations in correlating ternary liquid—liquid equilibria for systems having a plait point are compared with those of the NRTL equation in Figs. 1—6. The values of $\alpha_{13}$ of the original and modified NRTL equations for a partially miscible system were fitted to each individual ternary diagram. For the five systems as shown in Figs. 1—5, the results obtained from the modified NRTL1 equation are similar to those derived from the original NRTL equation. De Fré and Verhoeye [31] pointed out that the sets of parameters of the NRTL equation related to the homogeneous binary systems have only a small influence on the position of the binodal curve of ternary liquid—liquid equilibria, but the set related to the heterogeneous binary system has an important influence: increasing the value of $\alpha$ decreases the total surface of the heterogeneous area and the parameter set obtained at a higher value of $\alpha$ causes a deflection in the binodal curve. Such a deflection was found in the calculated results

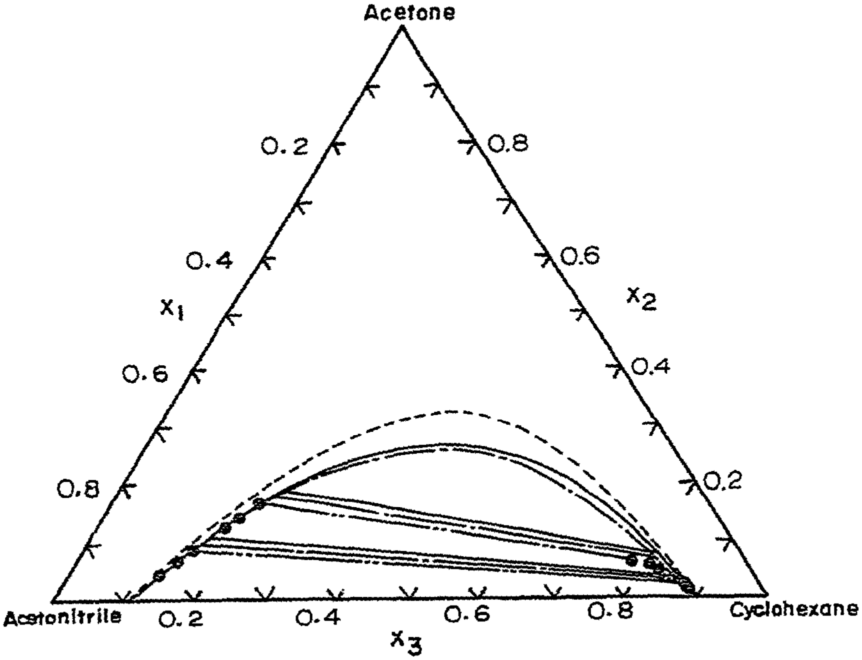

Fig. 1. Liquid—liquid equilibria for the acetonitrile(1)—acetone(2)—cyclohexane(3) system at 45°C. Experimental data of this work (●— - - —●). Calculated: modified NRTL1 eqn. ($\alpha_{12} = \alpha_{23} = 0.4, \alpha_{13} = 0.36$) (———); modified NRTL2 eqn. ($\alpha_{12} = \alpha_{23} = \alpha_{13} = 0.4$) (- - - - - -); NRTL eqn. ($\alpha_{12} = 0.3, \alpha_{23} = 0.2, \alpha_{13} = 0.32$) (— · — · —). Concentrations are in mole fractions.

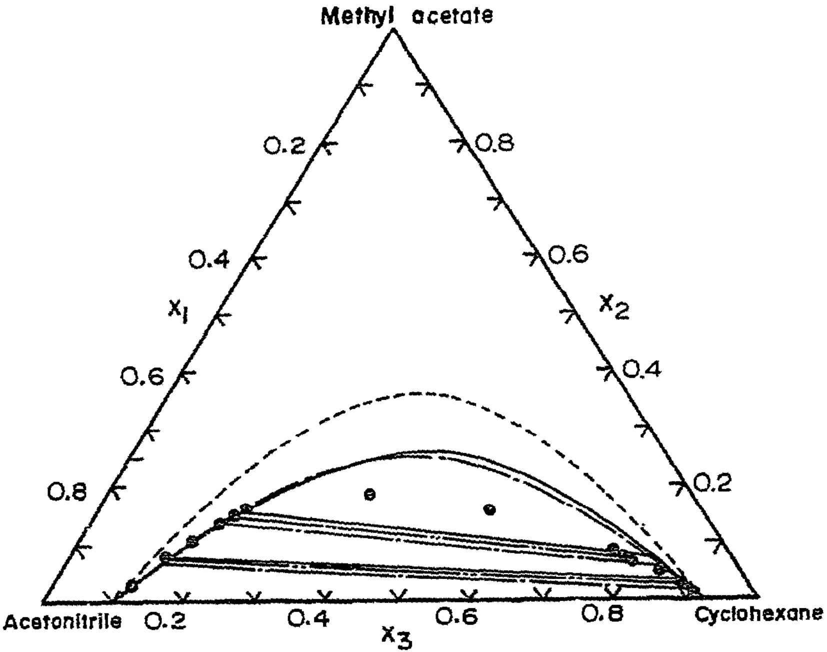

Fig. 2. Liquid—liquid equilibria for the acetonitrile(1)—methyl acetate(2)—cyclohexane(3) system at 40°C. Experimental data of this work (●— - - —●). Calculated: modified NRTL1 eqn. ($\alpha_{12} = \alpha_{23} = \alpha_{13} = 0.4$) (———); modified NRTL2 eqn. ($\alpha_{12} = \alpha_{23} = \alpha_{13} = 0.4$) (- - - - - -); NRTL eqn. ($\alpha_{12} = 0.3, \alpha_{23} = 0.2, \alpha_{13} = 0.36$) (· — · — ·). Concentrations are in mole fractions.

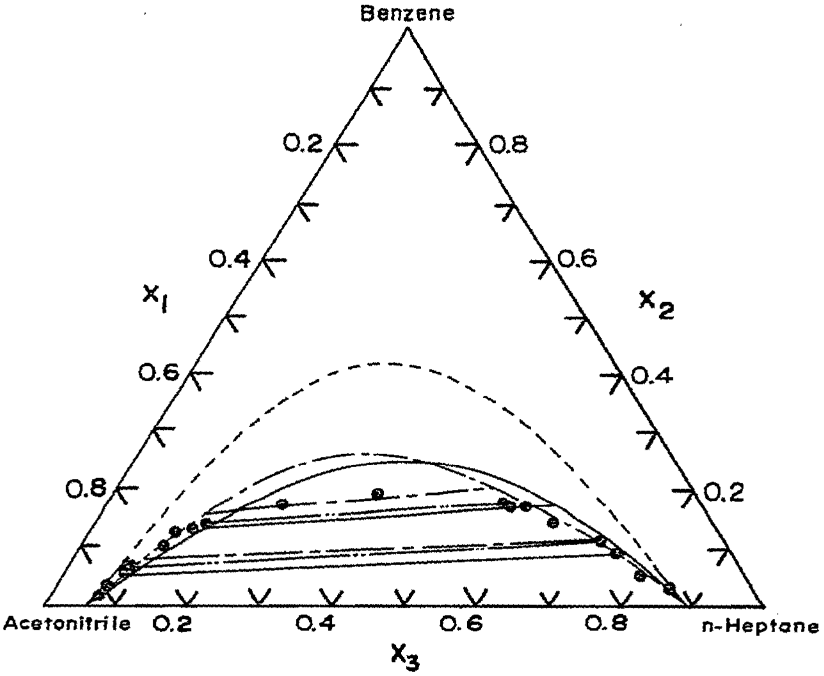

Fig. 3. Liquid–liquid equilibria for the acetonitrile(1)–benzene(2)-*n*-heptane(3) system at 45°C. Experimental data of ref. 16 (●– – – –●). Calculated: modified NRTL1 eqn. ($\alpha_{12} = \alpha_{13} = \alpha_{23} = 0.4$) (————); modified NRTL2 eqn. ($\alpha_{12} = \alpha_{13} = \alpha_{23} = 0.4$) (- - - - - -); NRTL eqn. ($\alpha_{12} = \alpha_{23} = 0.3, \alpha_{13} = 0.4$) (· — · — ·). Concentrations are in mole fractions.

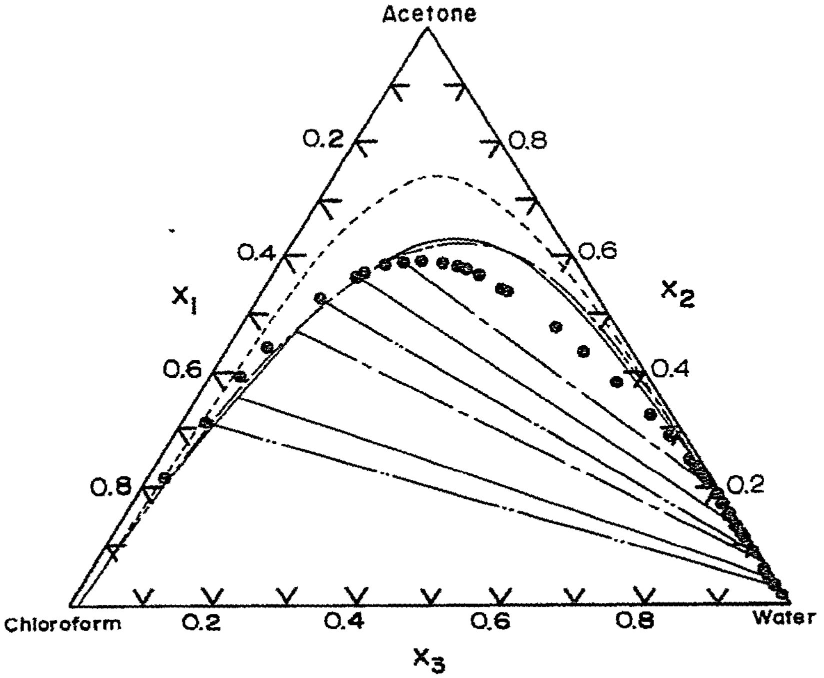

Fig. 4. Liquid–liquid equilibria for the chloroform(1)–acetone(2)–water(3) system at 25°C. Experimental data of ref. 29 (●– – – –●). Calculated: modified NRTL1 eqn. ($\alpha_{12} = \alpha_{23} = 0.4$, $\alpha_{13} = 0.2$) (————); modified NRTL2 eqn. ($\alpha_{12} = \alpha_{23} = \alpha_{13} = 0.4$) (- - - - - -); NRTL eqn. ($\alpha_{12} = \alpha_{23} = 0.3$, $\alpha_{13} = 0.2$) (· — · — ·). Concentrations are in mole fractions.

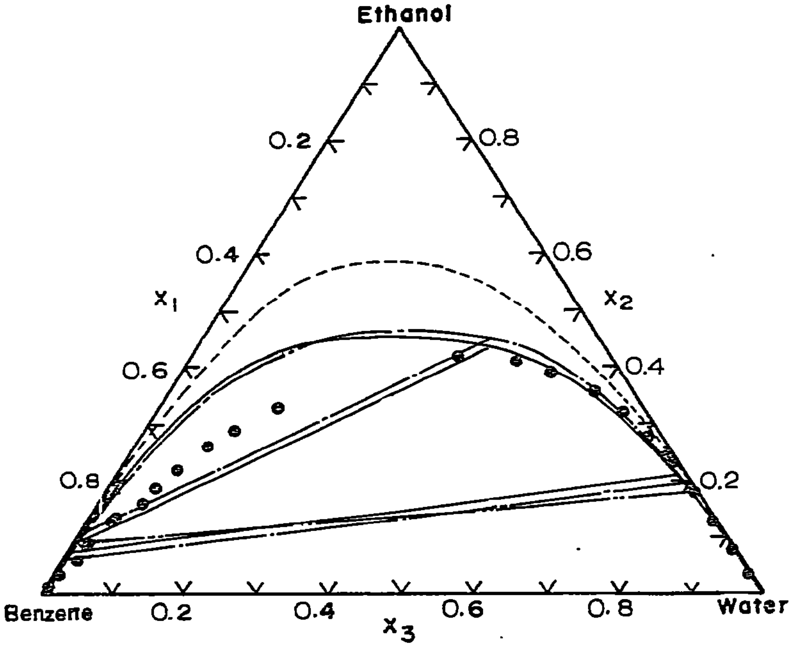

Fig. 5. Liquid—liquid equilibria for the benzene(1)—ethanol(2)—water(3) system at 25°C. Experimental data of ref. 30 (●— · · —●). Calculated: modified NRTL1 eqn. ($\alpha_{12} = 0.47$, $\alpha_{23} = 0.4$, $\alpha_{13} = 0.38$) (———); modified NRTL2 eqn. ($\alpha_{12} = 0.47$, $\alpha_{23} = \alpha_{13} = 0.4$) (- - - - -); NRTL eqn. ($\alpha_{12} = 0.47$, $\alpha_{23} = 0.3$, $\alpha_{13} = 0.26$) (· — · — ·). Concentrations are in mole fractions.

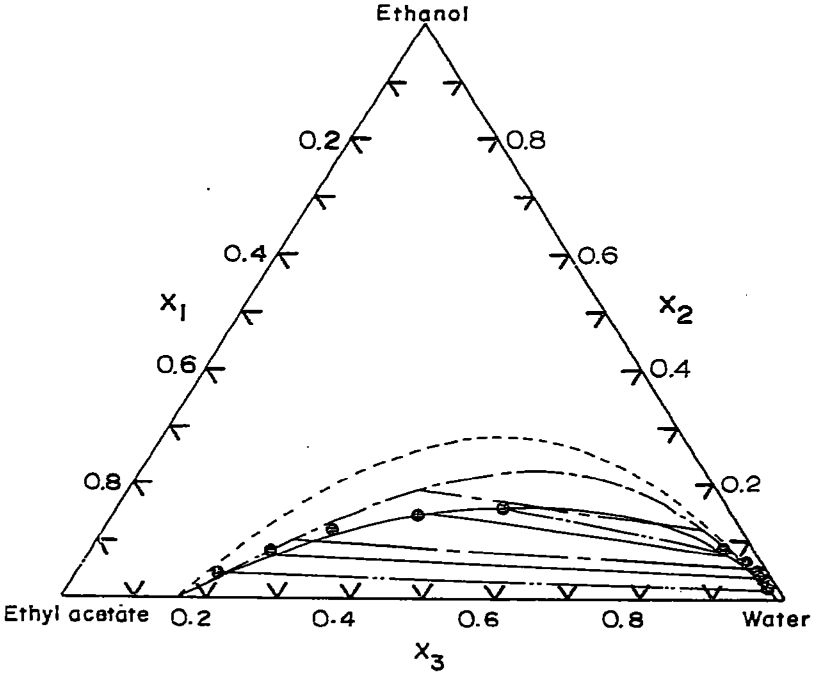

Fig. 6. Liquid—liquid equilibria for the ethyl acetate(1)—ethanol(2)—water(3) system at 40°C. Experimental data of ref. 17 (●— · · —●). Calculated: modified NRTL1 eqn. ($\alpha_{12} = \alpha_{23} = 0.4$, $\alpha_{13} = 0.54$) (———); modified NRTL2 eqn. ($\alpha_{12} = \alpha_{23} = \alpha_{13} = 0.4$) (- - - - -); NRTL eqn. ($\alpha_{12} = \alpha_{23} = 0.3$, $\alpha_{13} = 0.36$) (· — · — ·). Concentrations are in mole fractions.

obtained by the NRTL equation with the value of $\alpha_{13}$ higher than 0.36 for the ethyl acetate(1)—ethanol(2)—water(3) system. Hence, in Fig. 6 we used the NRTL equation having $\alpha_{13} = 0.36$, and the modified NRTL1 equation with $\alpha_{13} = 0.54$ gives the calculated results in good agreement with the experimental data. The results obtained by the modified NRTL2 equation for six ternary systems studied in this work show that the calculated immiscible region was too large and the $\alpha$ value of a partially miscible system has little influence on the binodal curve. This is an important difference between the modified NRTL1 and NRTL2 equations concerning their performance in ternary liquid—liquid equilibrium calculations.

In conclusion, the modified NRTL1 equation and the original NRTL equation are essentially similar in prediction accuracy of vapor—liquid equilibria, although the modified NRTL1 equation is sometimes better than the NRTL equation in the correlation of ternary liquid—liquid equilibria. As an expression of $u^E$ eqn. (1) is better than eqn. (13).

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