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H. N. Solimo<sup>a</sup>; J. L. Zurita<sup>a</sup>

<sup>a</sup> Institute de Fisica, Universidad Nacional de Tucumán, San Miguel de Tucumán, Argentina

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# LIQUID-LIQUID EQUILIBRIA FOR THE WATER-ETHANOL-METHYL ETHYL KETONE TERNARY SYSTEM AT 298.15 AND 318.15 K

H. N. SOLIMO\* and J. L. ZURITA

*Instituto de Física, Universidad Nacional de Tucumán, Av. Independencia 1800,  
4000 San Miguel de Tucumán, Argentina.*

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Ternary liquid-liquid equilibrium data for the system water-ethanol-methyl ethyl ketone were obtained at 298.15 and 318.15 K. Data for the binodal curves have been determined by the cloud-point method and conjugate points on tie-lines were determined by gas-chromatographic analysis. Tie-line data at each temperature were satisfactorily correlated by the Othmer and Tobias' method and the plait points coordinates were estimated. The experimental data were also fitted with the UNIFAC group contribution method for the activity coefficients using the isoactivity conditions as restraint equations and with the NRTL and UNIQUAC models.

**KEY WORDS:** Liquid-liquid equilibrium; water-ethanol-methyl ethyl ketone system; NRTL, UNIQUAC and UNIFAC estimation.

## 1 INTRODUCTION

The methyl ethyl ketone (MEK)-water binary system is a well known example of partial miscibility: two equilibrium layers are formed in certain regions of concentration<sup>1-3</sup>.

The aim of this work was to investigate a ternary liquid-liquid system where the above cited binary is a part of it. Increases of the mutual solubilities with temperature is usually observed, but ternary systems containing the MEK-water binary has an opposite behaviour<sup>1-3</sup>. Keeping this in mind, we report the experimental results of liquid-liquid equilibrium (LLE) studies of ternary mixtures of water-ethanol-MEK at 298.15 and 318.15 K and the experimental values were compared with those estimated by means of the UNIFAC group contribution method<sup>4</sup> using the LLE interaction parameters reported by Magnussen *et al.*<sup>5</sup> The experimental data were also correlated by using the NRTL and UNIQUAC models fitted to the experimental results.

Binodal curves and several tie-lines at 298.15 and 318.15 K were obtained and the correlation of mutual solubility with tie-line data (Othmer and Tobias' method) permitted the estimation of the plait point (PP) coordinates<sup>6</sup>.

This paper is a continuation of our investigation on ternary liquid-liquid systems containing water-ethanol-solvents at several temperatures<sup>7,8</sup>.

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\* Author to whom correspondence should be addressed.

## 2 EXPERIMENTAL SECTION

Anhydrous ethanol (Merck, reagent grade) was dried with magnesium activated with iodine under reflux<sup>9</sup>. The product was then fractionally distilled and the middle fraction was collected. The last traces of water can be removed passing the ethanol through a glass column (3 × 200 cm) packed with 0.3 nm molecular sieves.

Methyl ethyl ketone (Douglas, commercial grade) was washed several times with saturated potassium carbonate solution to remove acid impurities and distilled to remove most of the water. The ketone was then dried for several days over sodium sulfate/anhydrous potassium carbonate and fractionally distilled thrice. In all distillations the middle fractions were collected<sup>9</sup>.

The purity of all the chemicals checked by gas chromatography showed to be greater than 99.8 wt% after purification.

The purified chemicals were stored over activated molecular sieves to prevent water absorption.

Water was bidistilled in an all-glass apparatus.

Data for the solubility curves were determined by using the cloud-point method<sup>10</sup> as described earlier<sup>7,8</sup> using a cell equipped with a magnetic stirrer and a jacket for circulating of the isothermal water at the desired temperature ( $\pm 0.05^\circ\text{C}$ ). The third component was added from a microburet until the transition point was reached. The contents of the three components were determined by weight to obtain a complete binodal curves. The uncertainty through the whole curve was less than 0.05 weight fraction % ethanol at each temperature.

Composition defining tie-lines were determined in the same cell. In each experiment different weighted ternary mixtures with composition within heterogeneous region were shaken vigorously for at least 2 hours at constant temperature. Preliminary assays indicated that this period was sufficient to reach equilibrium. Samples of the extract and raffinate phases were collected using Hamilton syringes.

The compositions of the conjugate phases were analyzed using a Perkin-Elmer Sigma 300 gas chromatograph with a thermal conductivity detector, a Perkin-Elmer LCI 100 Laboratory computing integrator and 6' × 1/8" (outer diameter) copper columns packed with Porapak N (80/100 mesh). The flow rate of the hydrogen carrier gas was kept constant at 20 ml min<sup>-1</sup>. Oven, injector and detector temperatures: 180°C. The compositions of the liquid phases were determined by using an area analysis of the peak size of the three components. The gas chromatograph was calibrated with mixtures, whose compositions were known, near the solubility curve at 298.15 and 318.15 K, respectively. Calibrations curves were obtained by using several chromatograms for each mixture. Three or four analysis were performed to obtain a mean value, whose accuracy was within 0.1 wt%.

## 3 RESULTS AND DISCUSSION

Densities and refractive indices of the chemicals at 298.15 K agree with literature values<sup>9</sup>.

The experimental solubility data for the ternary system: water-ethanol-MEK at 298.15 and 318.15 K are listed in Tables 1 and 2, respectively.

Table 3 lists the tie-lines data at the same temperatures.

Figures 1 and 2 show the complete liquid-liquid diagrams at 298.15 and 318.15 K, respectively. These figures show that the immiscibility regions grow slightly with temperature. Predicted LLE data by the UNIFAC method are also shown in broken lines.

The tie-lines data at the two temperatures are satisfactorily correlated by the Othmer and Tobias' method<sup>6</sup>. The correlation is shown in Figure 3 where the

**Table 1** Binodal compositions (wt %) for water(1)-ethanol(2)-MEK(3) system at 298.15 K.

| <i>water-rich layer</i> |            |            | <i>MEK-rich layer</i> |            |            |
|-------------------------|------------|------------|-----------------------|------------|------------|
| $W_{11}$ %              | $W_{21}$ % | $W_{31}$ % | $W_{13}$ %            | $W_{23}$ % | $W_{33}$ % |
| 75.06                   | 0.00       | 24.94      | 42.75*                | 4.95*      | 52.30*     |
| 74.07                   | 1.02       | 24.91      | 42.50                 | 4.90       | 52.60      |
| 70.98                   | 2.13       | 26.89      | 39.85                 | 4.84       | 55.31      |
| 66.01                   | 3.40       | 30.59      | 36.97                 | 4.68       | 58.35      |
| 62.67                   | 3.97       | 33.36      | 34.27                 | 4.58       | 61.15      |
| 57.69                   | 4.50       | 37.81      | 31.60                 | 4.50       | 63.90      |
| 53.69                   | 4.75       | 41.56      | 28.41                 | 4.35       | 67.24      |
| 49.74                   | 4.90       | 45.36      | 22.34                 | 3.71       | 73.95      |
| 45.90                   | 5.00       | 49.10      | 17.00                 | 2.90       | 80.10      |
|                         |            |            | 15.33                 | 2.40       | 82.27      |
|                         |            |            | 13.25                 | 1.06       | 85.69      |
|                         |            |            | 11.57                 | 0.00       | 88.43      |

\* Estimated PP by Othmer and Tobias' method. Linear correlation coefficient = 0.9993.

**Table 2** Binodal compositions (wt %) for water(1)-ethanol(2)-MEK(3) system at 318.15 K.

| <i>water-rich layer</i> |            |            | <i>MEK-rich layer</i> |            |            |
|-------------------------|------------|------------|-----------------------|------------|------------|
| $W_{11}$ %              | $W_{21}$ % | $W_{31}$ % | $W_{13}$ %            | $W_{23}$ % | $W_{33}$ % |
| 79.42                   | 0.00       | 20.58      | 45.67                 | 5.53       | 48.80      |
| 75.99                   | 1.26       | 22.75      | 42.78                 | 5.52       | 51.70      |
| 72.96                   | 2.51       | 24.53      | 39.57                 | 5.51       | 54.92      |
| 70.18                   | 3.15       | 26.67      | 36.73                 | 5.29       | 57.98      |
| 65.60                   | 4.28       | 30.12      | 32.55                 | 5.05       | 62.40      |
| 62.14                   | 4.85       | 33.01      | 28.30                 | 4.72       | 66.98      |
| 57.32                   | 5.25       | 37.43      | 22.24                 | 4.17       | 73.59      |
| 53.15                   | 5.45       | 41.40      | 16.89                 | 3.14       | 79.89      |
| 49.41                   | 5.52       | 45.07      | 15.32                 | 2.44       | 82.24      |
| 48.16*                  | 5.52*      | 46.32*     | 13.05                 | 1.66       | 85.29      |
|                         |            |            | 10.65                 | 0.00       | 89.35      |

\* Estimated PP by Othmer and Tobias' method. Linear correlation coefficient = 0.9996.

**Table 3** Tie-lines data (wt. %) for water(1)-ethanol(2)-MEK(3) system.

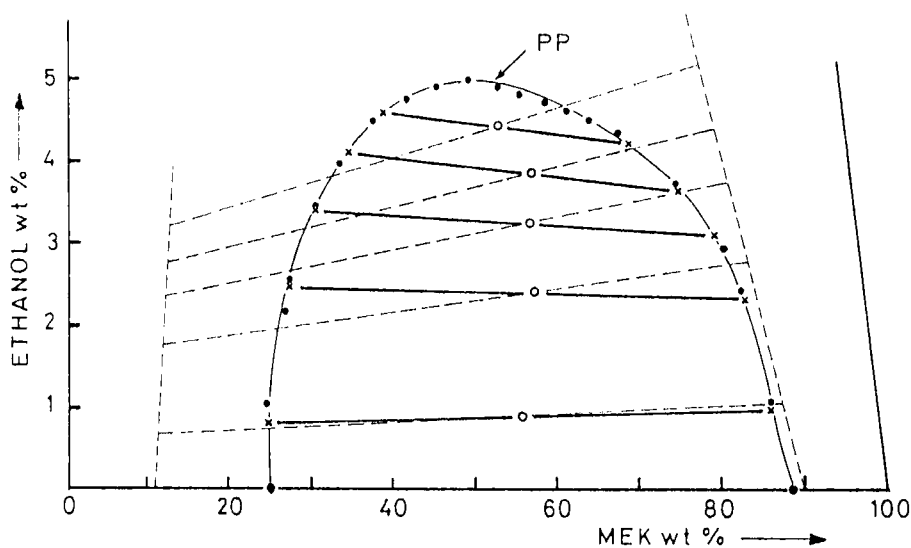
| water-rich layer |            |            | MEK-rich layer |            |            |
|------------------|------------|------------|----------------|------------|------------|
| $W_{11}$ %       | $W_{21}$ % | $W_{31}$ % | $W_{13}$ %     | $W_{23}$ % | $W_{33}$ % |
| 298.15 K         |            |            |                |            |            |
| 74.2             | 0.8        | 25.0       | 13.0           | 1.0        | 86.0       |
| 70.0             | 2.5        | 27.5       | 14.7           | 2.3        | 83.0       |
| 65.8             | 3.4        | 30.8       | 18.1           | 3.1        | 78.8       |
| 61.2             | 4.1        | 34.7       | 22.1           | 3.7        | 74.2       |
| 56.1             | 4.6        | 39.3       | 27.2           | 4.2        | 68.6       |
| 318.15 K         |            |            |                |            |            |
| 76.4             | 1.1        | 22.5       | 12.3           | 1.1        | 86.6       |
| 72.1             | 2.6        | 25.3       | 15.5           | 2.5        | 82.0       |
| 68.6             | 3.6        | 27.8       | 18.7           | 3.5        | 77.8       |
| 65.3             | 4.3        | 30.4       | 22.9           | 4.2        | 72.9       |
| 61.1             | 4.9        | 34.0       | 29.2           | 4.8        | 66.6       |

$W_{1i}$ : weight fraction of the component  $i$  in aqueous phase.

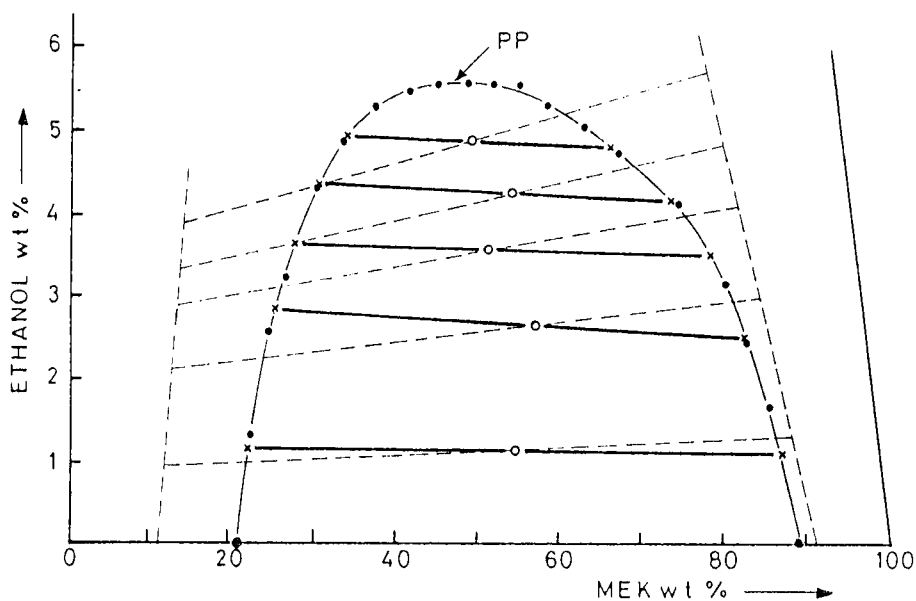
$W_{3i}$ : weight fraction of the component  $i$  in organic phase.

dependence of solubility with temperature is clearly seen. Experimental plait point coordinates calculated by this method are listed in Tables 1 and 2 along with the linear correlation coefficients.

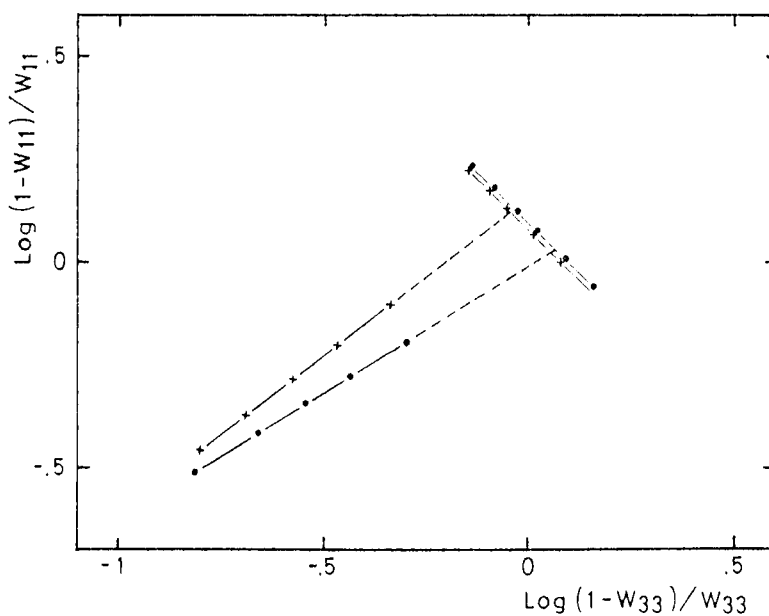
The organic phase data for the equilibrium compositions of the binary water + MEK system are discrepant from different sources<sup>1,11-16</sup>. Our experimental values



**Figure 1** Binodal curves and tie-lines for the system water-ethanol-MEK at 298.15 K. (x—x), Experimental tie-lines. (●), Experimental binodal curve. (----), UNIFAC predictions. (○), Overall composition for tie-lines. PP = Plait point.



**Figure 2** Binodal curves and tie-lines for the system water-ethanol-MEK at 318.15 K. ( $\times$ - $\times$ ), Experimental tie lines. ( $\bullet$ ), Experimental binodal curve. (----), UNIFAC predictions. ( $\circ$ ), Overall compositions for tie-lines. PP = Plait point.



**Figure 3** Correlation of the LLE data at: ( $\times$ ), 298.15 K and ( $\bullet$ ), 318.15 K by the method of Othmer and Tobias. Straight lines are fitted by least-square method.

are in agreement with the Ginnings' values<sup>11</sup> at 298.15 K and with the Siegelman and Sorum's ones at 318.15 K<sup>12</sup>.

#### 4 CORRELATION OF THE EXPERIMENTAL DATA

##### a) NRTL and UNIQUAC equations

Thermodynamic models, such as the NRTL<sup>17</sup> and UNIQUAC<sup>18</sup>, utilize the excess Gibbs energy and related activity coefficients to correlate LLE data of ternary mixtures. A useful assumption of models for the excess Gibbs energy is that only experimental data of binary systems are needed to estimate multicomponent activity coefficients. Both models were derived by introducing the local composition concept into the quasichemical theory of Guggenheim<sup>19</sup>. The NRTL and UNIQUAC equations were fitted to the experimental data by using an iterative computer program developed by Sørensen *et al.*<sup>20</sup> to minimize the value of the following objective functions:

$$F_a = \sum^k \sum^i [(a_{ik}^I - a_{ik}^{II}) / (a_{ik}^I + a_{ik}^{II})]^2 + Q \sum^n P_n^2 \quad (1)$$

$$F_x = \sum^k \min \sum^i \sum^j (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum^n P_n^2 \quad (2)$$

where:  $a$  = activity obtained directly from the model by insertion of the experimental concentrations.

$x$  = experimental liquid phase mole fraction.

$\hat{x}$  = mole fraction of the predicted tie line lying close to the considered experimental tie line.

$i$  = 1, 2, 3 (components).

$j$  = I, II (phases)

$k$  = 1, 2, ...,  $M$  (tie lines).

$Q$  = constant in the penalty term of both equations.

$P_n$  = parameter value in the penalty term of both equations.

$n$  = 1, 2, ..., NP (parameters).

Both functions include a penalty term designed to reduce the risk of multiple solutions associated with high parameters values. We start the parameters estimation using the relative objective function in terms of activities,  $F_a$ , since this requires no qualified guess at the parameters. After convergence, the objective function in terms of mole fractions,  $F_x$ , was used in order to obtain the definitive parameters fitted to the experimental mole fractions.

The necessary structural parameters for UNIQUAC equation have been obtained from Anderson and Prausnitz<sup>21</sup>.

The values of the residual function,  $F$  (mole %), and the mean error of the ethanol distribution coefficient,  $\Delta D_e$ , gave an idea of the goodness of fit.

$$F = 100 \left[ \sum^k \min \sum^i \sum^j (x_{ijk} - \hat{x}_{ijk})^2 / 6M \right]^{1/2} \quad (3)$$

$$\Delta D_e = 100 \left[ \sum^k [(\hat{D}_e^k - D_e^k) / D_e^k]^2 / M \right]^{1/2} \quad (4)$$

where:  $D_e$  = experimental ethanol distribution coefficient.

$\hat{D}_e$  = calculated ethanol distribution coefficient.

$M$  = number of tie-lines.

The nonrandomness of the liquid mixture, which is represented by the third parameter for the NRTL equation ( $\alpha_{ij}$ ) was set at a value of 0.2 in the present study.

Table 4 shows, for each temperature, the values of  $F$ ,  $\Delta D_e$  and the estimated parameters for the two equations. Curves calculated using these parameters are compared with the experimental data in Figures 4 and 5.

#### b) Prediction by the UNIFAC method

The LLE data of the ternary system were also predicted using the UNIFAC method<sup>4</sup>, which allows the activity coefficients of the three components of both phases to be calculated. The group interaction parameters used were those obtained by

**Table 4** Residuals  $F$  and  $\Delta D_e$  and optimized parameters of the NRTL ( $\alpha_{ij} = 0.2$ ) and UNIQUAC equations fitted to LLE data for the system water-ethanol-MEK at 298.15 and 318.15 K.

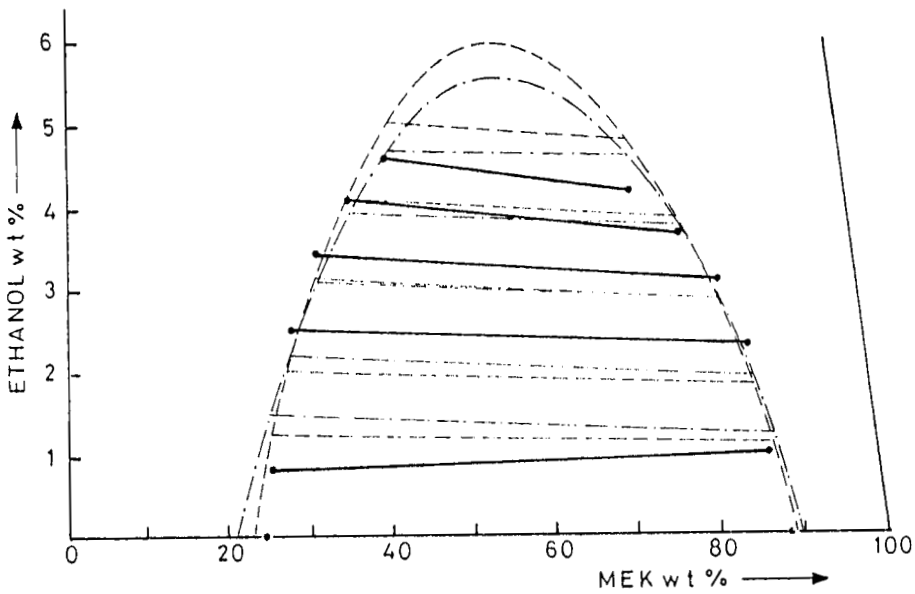
| Temp. K          | F%    | $\Delta D_e$ % | $i-j$ | $a_{ij}$ | $a_{ji}$ |
|------------------|-------|----------------|-------|----------|----------|
| NRTL equation    |       |                |       |          |          |
| 298.15           | 25.34 | 16.7           | 1-2   | -580.53  | -688.09  |
|                  |       |                | 1-3   | 891.59   | 39.158   |
|                  |       |                | 2-3   | -1002.2  | 571.53   |
| 318.15           | 25.85 | 16.5           | 1-2   | -614.26  | -711.44  |
|                  |       |                | 1-3   | 951.33   | 40.103   |
|                  |       |                | 2-3   | -1054.3  | 602.18   |
| UNIQUAC equation |       |                |       |          |          |
| 298.15           | 21.35 | 21.1           | 1-2   | 195.76   | -402.85  |
|                  |       |                | 1-3   | 8.4868   | 346.94   |
|                  |       |                | 2-3   | -129.90  | -274.77  |
| 318.15           | 21.37 | 21.0           | 1-2   | 204.41   | -427.78  |
|                  |       |                | 1-3   | 8.9399   | 370.07   |
|                  |       |                | 2-3   | -135.37  | -296.95  |

$a_{ij} = (g_{ij} - g_{ji})/R$  (K) for NRTL equation, where  $g_{ij}$  is the energy of interaction between an  $i-j$  pair of molecules ( $\text{cal mol}^{-1}$ ).

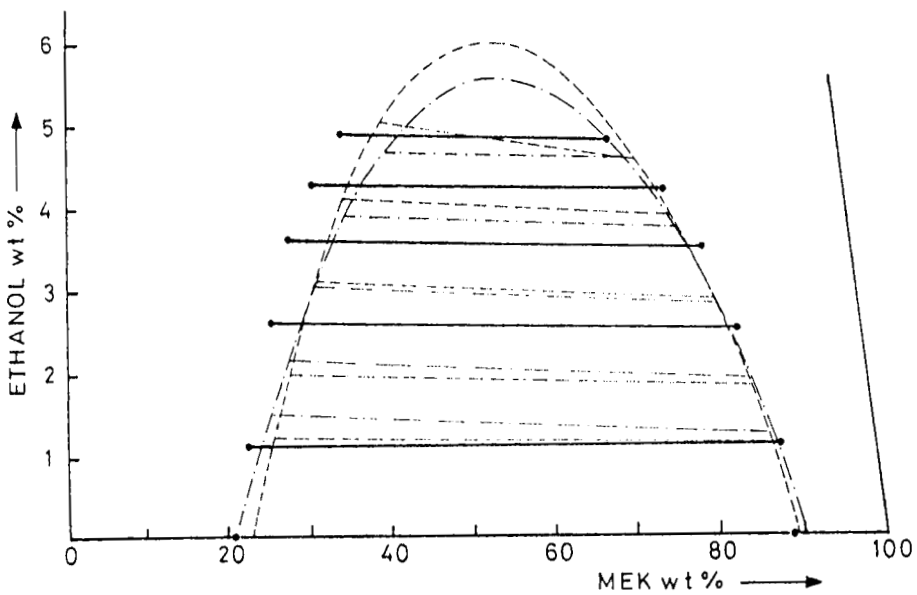
$a_{ij} = (u_{ij} - u_{ji})/R$  (K) for UNIQUAC equation, where  $u_{ij}$  is the UNIQUAC binary interaction parameter ( $\text{cal mol}^{-1}$ ).

$R$  = universal gas constant ( $\text{cal mol}^{-1}\text{K}^{-1}$ ).





**Figure 4** Binodal curves and tie-lines calculated for the system water-ethanol-MEK at 298.15 K using the equations (----) NRTL and (-·-·-) UNIQUAC, together with the corresponding experimental tie-lines (●—●).



**Figure 5** Binodal curves and tie-lines calculated for the system water-ethanol-MEK at 318.15 K using the equations (----) NRTL and (-·-·-) UNIQUAC, together with the corresponding experimental tie-lines (●—●).

**Table 5** UNIFAC interaction parameters\*.

| Main group            | CH <sub>2</sub> | OH .   | H <sub>2</sub> O | CH <sub>2</sub> CO |
|-----------------------|-----------------|--------|------------------|--------------------|
| 1 CH <sub>2</sub>     | 0               | 644.6  | 1300.0           | 472.6              |
| 5 OH                  | 328.2           | 0      | 28.73            | 67.07              |
| 8 H <sub>2</sub> O    | 342.4           | -122.4 | 0                | -171.8             |
| 10 CH <sub>2</sub> CO | 66.56           | 216.0  | 634.8            | 0                  |

\* From Reference 5.

Magnussen *et al.*<sup>5</sup> from experimental LLE data and they are listed in Table 5. The equilibrium compositions of the ends of tie-lines are found starting from hypothetical mixtures giving rise to conjugate experimental phases. Figures 1 and 2, in which the predicted binodal curves and tie-lines are displayed in broken lines, show that the UNIFAC method predicts an immiscibility region larger than that experimentally observed.

## 5 CONCLUSIONS

LLE data for the ternary mixture water-ethanol-MEK were determined at 298.15 and 318.15 K. Comparison of the experimental data for the two temperatures studied here, shows that the immiscibility region becomes rather larger as the temperature rises.

The NRTL and UNIQUAC equations fitted to the experimental data by using an iterative computing programming developed by Sørensen are considerably more accurate than the UNIFAC method for this system. The residuals  $F$  and  $\Delta D_e$  are nevertheless still quite large.

For the two temperatures the NRTL equation with  $\alpha_{ij} = 0.2$  is the most accurate if one takes into account both overall error,  $F$  and  $\Delta D_e$ .

From Figures 1 and 2 we can conclude that the UNIFAC method affords no more than qualitative results for this system. More reliable experimental data on LLE are necessary to improve the group interaction parameters for these type of systems with a flat binodal curve before that this group contribution method could be accurately applied.

### Acknowledgements

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