# Calculation of ternary liquid—liquid equilibria

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Some new pieces of knowledge concerning the calculation of equilibrium liquid—liquid concentrations in the ternary systems hydrocarbon—hydrocarbon—polar solvent are presented in this paper.

В работе приводятся некоторые данные, полученные расчетом равновесных концентраций в системе жидкость—жидкость для тройных систем углеводород—углеводород—полярный растворитель.

At present, the modern experimental and molecular thermodynamics in conjunction with machine-computing technique enables us to calculate the liquid—liquid equilibrium data with relatively good and sometimes very good accuracy. That makes possible to use computers for the calculation of extraction devices. Of course, the problem of calculation of the liquid—liquid equilibrium data cannot be at all regarded as solved because of intricacy of structure of the liquid systems. This fact is also confirmed by a great number of papers dealing with this problem which appear in professional literature. In this contribution, we mention some observations obtained in the calculation of liquid—liquid equilibrium concentrations in some ternary systems hydrocarbon—hydrocarbon—polar solvent.

As known, the composition of equilibrium liquid phases is usually calculated by minimization of the function

$$Q = \sum_i (a'_i - a''_i)^2 \qquad (1)$$

where the indices ' and " denote the raffinate and extract phases, respectively. The search for the minimum of the function $Q$ is made by current procedures of optimization, for instance by the Newton—Raphson method described *e.g.* in the monograph by *Renon et al.* [1]. This method is also applied in our investigations [2—4].

## Selection of equations for the calculation of activity coefficients

One of the major problems is the selection of equations for the calculation of activity coefficients. We chose the NRTL [1], van Laar—Mansanto [5], and UNIQUAC [6] equation from many equations published in literature and more-

*Table 1*

Percentage deviations of distribution coefficients of extracted
component $K_2$ and selectivity of solvent

| System | Type of binodal curve | Percentage deviations from experimental data | | | |
| --- | --- | --- | --- | --- | --- |
| | | NRTL | | UNIQUAC | |
| | | $K_2$ | $\beta$ | $K_2$ | $\beta$ |
| $n$-Hexane—cyclohexane—NMP $t = 25°C$ | $I$ | 10.4 | 5.4 | Calculation did not converge | |
| $n$-Hexane—cyclohexane—DEG $t = 50°C$ | $II$ | 5.3 | 11.1 | 25.1 | 12.8 |
| $n$-Hexane—cyclohexane—sulfolane $t = 50°C$ | $II$ | 5.4 | 8.2 | 18.3 | 34.2 |
| $n$-Hexane—cyclohexane—DMSO $t = 50°C$ | $II$ | 2.9 | 5.9 | 14.9 | 8.8 |

Type $I$ — closed binodal curve.
Type $II$ — open binodal curve.

*Table 2*

Values of the coefficients of the NRTL and UNIQUAC equations
for binary systems [2]

| System $i—j$ | $t$, °C | Coefficients of equation | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | NRTL | | | UNIQUAC | |
| | | $\tau_{ij}$ | $\tau_{ji}$ | $\alpha_{ij}$ | $\tau_{ij}$ | $\tau_{ji}$ |
| $n$-Hexane—cyclohexane | 25 | −0.7426 | 1.0416 | 0.1865 | 1.4183 | 0.6481 |
| $n$-Hexane—NMP | 25 | 2.2967 | 1.6596 | 0.37 | 0.5356 | 0.8357 |
| Cyclohexane—NMP | 25 | 2.3350 | 1.2363 | 0.4001 | 0.5548 | 0.8025 |
| $n$-Hexane—cyclohexane | 50 | −0.9843 | 1.2950 | 0.1691 | 1.5343 | 0.5854 |
| $n$-Hexane—DEG | 50 | 7.1003 | 4.8379 | 0.4208 | 0.1551 | 0.7348 |
| $n$-Hexane—sulfolane | 50 | 5.7011 | 5.1862 | 0.4639 | 0.0277 | 0.8748 |
| $n$-Hexane—DMSO | 50 | 3.6459 | 2.7895 | 0.30 | 0.1668 | 0.8133 |
| Cyclohexane—DEG | 50 | 6.3059 | 3.5650 | 0.3669 | 0.1861 | 0.7290 |
| Cyclohexane—sulfolane | 50 | 4.6680 | 3.3896 | 0.4016 | 0.0330 | 0.8599 |
| Cyclohexane—DMSO | 50 | 3.4339 | 2.0491 | 0.30 | 0.2010 | 0.8098 |

NMP — $N$-methylpyrrolidone.
DEG — diethylene glycol.
DMSO — dimethyl sulfoxide.

over, we also verified the modifications of the Wilson equation put forward by *Katayama et al.* [7] and *Hiranuma* [8] for some systems. Though we cannot generalize on the basis of the calculations made for about ten ternary systems, our observations are consistent with the observations of other authors [9, 10]. The three-parameter equations are more suited for the description of liquid—liquid systems because of imperfection of the physical models and ideas used for derivation of the equations. According to our results, the NRTL equation put forward by Renon and Prausnitz seems to be the most universal.

For illustration, we give a comparison of the average deviations of the experimental values of distribution coefficients of the extracted component ($K_2$) and selectivity of the solvent ($\beta$) from the values calculated by means of the NRTL and UNIQUAC equations for four systems [2] investigated by us (Table 1). The calculation was performed with the coefficients adjusted according to binary data (Table 2).

### Adjustment of the parameters of the NRTL equation

In our papers we used the parameters of the NRTL equation adjusted according to binary equilibrium data. Of course, in order to utilize the benefits of three-parameter equation to the full, all three parameters ought to be adjusted, which could be connected with certain difficulties.

For fully soluble pairs of liquids, we used the relationship between the pressure of saturated vapour and composition as experimental basis. The pressure was measured with a simple static instrument [11]. The parameters of the NRTL equation were calculated by minimization of the function

$$Q_P = \sum_j \left[ \frac{1}{P_{exp}} (P_{exp} - P_{calc}) \right]_j^2 \tag{2}$$

For simultaneous calculation of three parameters and zero approximation chosen by chance, satisfactory results, *i.e.* sufficiently low values of the function $Q_P$ were not always obtained. As a matter of fact, this function is considerably articulate in the space of three iterative parameters. The procedure put forward by *Waradzin* proved to be good for the selection of zero approximation of the parameters [12]. The value of $Q_P$ was calculated for different combinations of the parameters $C_{ij}$, $C_{ji}$, and $\alpha_{ij}$ in periodic intervals and the parameters corresponding to the least value of $Q_P$ were used as zero approximation for minimization.

For partially miscible binary systems the parameters of the NRTL equation were determined from the data expressing mutual solubilities and vapour pressure in the heterogeneous region. The vapour pressure was measured with a static apparatus analogously to the case of fully soluble liquids. The calculation of the parameters involved solution of the following system of transcendent equations

$$F_1(C_{ij}, C_{ji}, \alpha_{ij}) = \frac{\gamma_i'' x_i''}{\gamma_i' x_i'} - 1 = 0 \tag{3/1}$$

$$F_2(C_{ij}, C_{ji}, \alpha_{ij}) = \frac{\gamma_j'' x_i''}{\gamma_j' x_j'} - 1 = 0 \tag{3/2}$$

$$F_3(C_{ij}, C_{ji}, \alpha_{ij}) = \left( \frac{\gamma_i x_i f_i^{OL}}{\varphi_i^G} + \frac{\gamma_j x_j f_j^{OL}}{\varphi_j^G} \right) \frac{1}{P_{exp}} - 1 = 0 \tag{3/3}$$

This system was solved by the Newton method. The convergence of the calculation was good in all systems investigated.

### Influence of optional data on calculation of the composition of ternary equilibrium data

Before starting to calculate the composition of liquid equilibrium phases, we must fix the limiting value of the function $Q$ (1) at the attainment of which the calculation stops and the initial estimate, the so-called zero approximation, of the composition of equilibrium phases. We verified the influence of the choice of these quantities in four ternary liquid systems the binary liquid—liquid and liquid—vapour equilibrium data as well as the ternary liquid—liquid equilibrium data of which were known. The following systems were investigated: *a*) *n*-heptane (1)—toluene (2)—acetonitrile (3); *b*) *n*-heptane (1)—benzene (2)—dimethyl sulfoxide (3); *c*) *n*-hexane (1)—cyclohexane (2)—N-methylpyrrolidone (3); *d*) *n*-heptane (1)—cyclohexane (2)—dimethylformamide (3). Three of these systems (*a*, *b*, and *c*) are of type *I* (closed binodal curve) and one (*d*) is of type *II* (open binodal curve).

Provided the activity values are of equal decimal order as the values of mole fractions, it follows from a simple reasoning that the value $Q = 10^{-2}$ corresponds to the accuracy $x_i \pm 0.1$ and the value $Q = 10^{-4}$ to the accuracy $x_i \pm 0.01$, etc. This reasoning was also confirmed in the practice. It means that the limiting values $10^{-8} \leqslant Q \leqslant 10^{-6}$ must be used for usual requirements of accuracy in the range $x_i \pm 10^{-3}$—$10^{-4}$

For testing the applicability of equations to the description of liquid—liquid equilibrium, the experimental equilibrium concentrations are usually used as zero approximations which, of course, does not come into consideration in the calculations of extractors. Therefore we investigated the above systems as regards the convergence of computation for different values of zero approximation. For better understanding, we present a scheme of liquid—liquid diagram with the survey of symbols for the mole fractions used in Fig. 1. The content of the extracted component in extract $(x_2'')$ was always used as a fixed value of the coordinates of individual tie lines in check computations. The results may be summarized as follows:
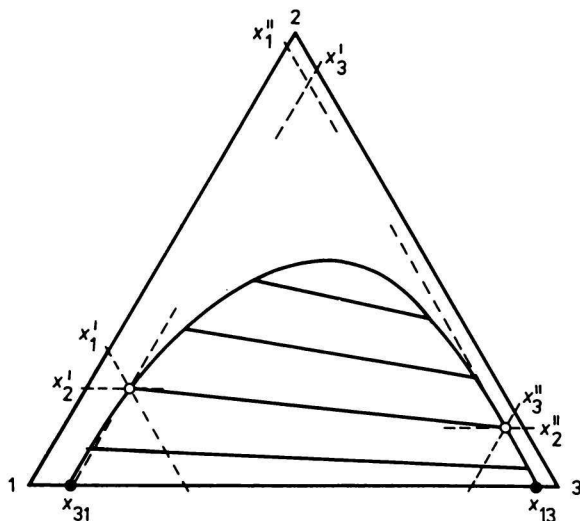
Fig. 1. Equilibrium liquid—liquid diagram.

1. The calculations of $x_i'$ and $x_i''$ are not too sensitive to the zero approximation provided the points chosen are situated near to the binodal curve. For instance, the calculation always converged for an extract chosen in systems $a$, $b$, and $d$ if an arbitrary point in proximity to the raffinate branch of the binodal curve was chosen as zero approximation.

2. For all systems investigated, it appeared to be sufficient to choose the composition of raffinate and the value $x_1''$ for the vicinal lower tie line (which was nearer to the base of triangle $\overline{13}$) for a given $x_2''$.

3. The selection of zero approximation may be made more precise as follows: By using the distribution coefficient $K_2$ of the nearest lower tie line, the value of $x_2'$ is calculated for a given $x_2''$

$$x_2' = \frac{x_2''}{K_2} \tag{4}$$

The values of $x_1''$ and $x_3'$ are chosen according to the nearest lower tie line. The remaining values of $x_i$ are to be found from the balance equations

$$\sum_i x_i' = 1; \qquad \sum_i x_i'' = 1 \tag{5}$$

For the first calculated tie line (near to the base of $\overline{13}$) the zero approximation of $K_2$ is calculated from binary limiting activity coefficients

$$K_2 \equiv K_2^\infty = \frac{\gamma_{21}^\infty}{\gamma_{23}^\infty} \qquad (6)$$

The binary solubilities $x_{13}$ and $x_{31}$ are substituted for the values of $x_1''$ and $x_3'$.

## Symbols

| | |
|---|---|
| $a_i$ | activity of the $i$-th component in solution |
| $C_{ij}$, $C_{ji}$, $\alpha_{ij}$ | parameters of the NRTL equation |
| $f_i^{OL}$, $f_i^{OL}$ | fugacity of the pure liquid component at the temperature and pressure of system |
| $K_2$ | distribution coefficient of the 2nd component |
| $P_{exp}$, $P_{calc}$ | experimental and calculated pressure of saturated vapour of binary solution |
| $x_i'$, $x_i''$ | mole fraction of the $i$-th component in raffinate and extract |
| $\beta$ | coefficient of selectivity of solvent |
| $\gamma_i'$, $\gamma_i''$ | activity coefficient of the $i$-th component in raffinate and extract |
| $\gamma_{21}^\infty$, $\gamma_{23}^\infty$ | limiting activity coefficient of the 2nd component in liquid component 1 and 3 |
| $\tau_{ij} = \dfrac{C_{ij}}{RT}$, $\tau_{ji} = \dfrac{C_{ji}}{RT}$ | parameters of the NRTL equation |
| $\varphi_i^G$, $\varphi_j^G$ | fugacity coefficients of the $i$-th and $j$-th component in vapour |

## Indices

| | |
|---|---|
| $i$, $j$ | components of binary solution |
| $i = 1, 2, 3$ | components of ternary solution |

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