The use of different types of objective function for calculating parameters of the ternary correction of G^E and liquid—liquid equilibrium composition

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On the basis of four ternary systems hydrocarbon—hydrocarbon—polar solvent, different types of objective function are appreciated from the view-point of calculation of parameters of universal ternary correction of the molar excess Gibbs energy by which the NRTL equation is extended. The quality of prediction of equilibrium data is judged in the form of residues of mole fractions and distribution coefficients.

На примере четырех трехкомпонентных систем углеводород—углеводород—полярный растворитель сравниваются различные виды специальной функции для расчета параметров универсальной тройной коррекции мольной дополнительной энергии Гиббса, на которую расширено уравнение NRTL. В форме остатков мольных долей и коэффициентов распределения оценивается качество предсказания равновесных величин.

It is known from the hitherto published papers dealing with the calculation of ternary equilibrium data for the liquid—liquid system that the calculated equilibrium data are very little likely in quantitative agreement with experimental data if only binary parameters determined from binary equilibrium data are used in the equations expressing the dependence of the excess Gibbs energy on composition. Thus a valuable calculation of the ternary L—L equilibrium data requires that the experimental L—L equilibrium data must be respected for identification of the parameters in the G^E equations. There are two ways used for this purpose. In the first case, all binary parameters or their part are replaced by the parameters calculated from the ternary equilibrium data. This procedure is usual especially for the G^E equations derived from the concept of local composition (NRTL, UNIQUAC, *etc.*). In the second case, the G^E equations based on empirical expansions (*e.g.* Wohl, Redlich, or Kister expansion) are extended by ternary terms and the coefficients of these terms are determined by means of ternary L—L equilibrium data and the binary coefficients remain preserved in their original value. While the

determination of the parameters of the G^E equations according to the first procedure is very tedious because of a great number of these parameters (up to 9), the equations mentioned in the second case are without theoretical basis and frequently show a smaller flexibility when compared with the equations derived from structural ideas.

In order to preserve the merit of the G^E equations as well as the advantage consisting in simplicity of determination of the parameters, *Surový* and coworkers [1] introduced a ternary correction of universal form into the G^E equations of all types. Their first results have shown that the precision of the calculated equilibrium data was considerably improved by inserting the ternary correction. The NRTL and Redlich—Kister equation especially excelled in this line.

The quality of the calculated equilibrium data is usually dependent on the type of the used G^E equation and the method of determination of its parameters and equilibrium composition. By using the example involving four ternary liquid systems hydrocarbon—hydrocarbon—polar solvent, we are going to examine different forms of the objective function with respect to identification of the parameters of the ternary correction of universal type used for the NRTL equation. The relationship between the form of the objective function and precision of the calculated L—L equilibrium data will be presented at conclusion of this communication.

Theoretical

Equation used for G^E

The NRTL equation [2] has the following form

$$\frac{G^E}{RT} = \sum_i x_i \sum_j \tau_{ji} G_{ji} x_j \Big/ \sum_l G_{li} x_l; \quad i, j, l = 1, 2, \ldots, K \qquad (1)$$

where

$$G_{ji} = \exp\left(-\alpha_{ji} \tau_{ji}\right); \quad \alpha_{ij} = \alpha_{ji}$$

The parameters of eqn *(1)* are parameters of the binary kind. In application of the G^E equation to ternary systems, we extended eqn *(1)* by the ternary correction of universal type [1]

$$\frac{\Delta_t G^E}{RT} = x_1 x_2 x_3 \left(E_1 x_1 + E_2 x_2 + E_3 x_3\right) \qquad (2)$$

where E_1, E_2, and E_3 are parameters dependent on temperature and pressure. Correction *(2)* expresses the difference between the experimental value of the

excess Gibbs energy in ternary solution and the value calculated on the basis of binary data according to eqn *(1)*.

Determination of ternary correction parameters

In order to determine the ternary parameters E_1, E_2, and E_3 in the G^E equation, we used five different variants of objective function on the basis of the mole fractions of components in L—L equilibrium phases and distribution coefficients.

1. Objective function (*Várhegyi* and *Eon* [3])

$$F(E)_1 = \sum_l \min \sum_i \sum_j w_{il}^j (a_{il}^j - \hat{x}_{il}^j)^2 \tag{3}$$

2. Relative form of function *(3)*

$$F(E)_2 = \sum_l \min \sum_i \sum_j w_{il}^j \left(\frac{x_{il}^j - \hat{x}_{il}^j}{x_{il}^j}\right)^2 \tag{4}$$

3. Objective function on the basis of distribution coefficients

$$F(E)_3 = \sum_l \min \sum_i w_{il} \left(\frac{K_{il} - \hat{K}_{il}}{K_{il}}\right)^2 \tag{5}$$

4. Objective function obtained by combination of *(3)* and *(5)*

$$F(E)_4 = \sum_l \min \left[\sum_i \sum_j w_{il}^j (x_{il}^j - \hat{x}_{il}^j)^2 + \sum_i w_{il} \left(\frac{K_{il} - \hat{K}_{il}}{K_{il}}\right)^2\right] \tag{6}$$

5. Objective function obtained by combination of *(4)* and *(5)*

$$F(E)_5 = \sum_l \min \left[\sum_i \sum_j w_{il}^j \left(\frac{x_{il}^j - \hat{x}_{il}^j}{x_{il}^j}\right)^2 + \sum_i w_{il} \left(\frac{K_{il} - \hat{K}_{il}}{K_{il}}\right)^2\right] \tag{7}$$

It is valid for all objective functions $i = 1, 2, 3$; $j = \text{I, II}$; $l = 1, 2, ..., m$, with the constraints

$$\Delta\hat{a}_{il} = \hat{a}_{il}^I - \hat{a}_{il}^{II} = 0; \quad \sum_i \hat{x}_{il}^j = 1 \tag{8}$$

Functions *(3—7)* were minimized for $w_{il} = 1$ by the method of maximum likelihood, *i.e.* it was minimized not only according to the parameters of ternary correction (or in general case according to the parameters of the G^E equation), but also with respect to incidental parameters — independent variables $\hat{x}_{il}^j$ (in our case $\hat{x}_{2l}^{II}$). The procedure of minimization was described in one of our preceding papers [1].

Results and discussion

Calculation of ternary L—L equilibrium concentrations

Objective functions (3—7) were applied to the following four systems: a) heptane(1)—toluene(2)—DMFA(3) at 40 °C; b) heptane(1)—cyclohexane(2)——DMFA(3) at 25 °C; c) cyclohexane(1)—benzene(2)—fural(3) at 25 °C; d) heptane(1)—benzene(2)—DMSO(3) at 40 °C. The experimental equilibrium data for these systems are to be found in paper [4] where the values of binary parameters of eqn (1) as well as the methods of their calculation are also presented.

The ternary parameters were identified according to functions (3—7) for G^E equation (1) extended by correction (2). The inverse calculation of equilibrium mole fractions was carried out by the isoactivity method, i.e. minimization of the function

$$F(\hat{x}_i) = \sum_i (a_i^{II} - a_i^I)^2 \qquad (9)$$

for such $\hat{x}_2^{II}$ at which

$$F(\hat{x}_{2l}^{II}) = \sum_i \sum_j w_{il}^j (x_{il}^j - \hat{x}_{il}^j)^2 \qquad (10)$$

is minimum. The values of $\hat{x}_{2l}^{II}$ were calculated by iterative procedure described in detail in paper [1].

The fitting of the calculated equilibrium data was appreciated on the basis of residues of mole fractions

$$F_x = 100 \sqrt{\left[\sum_l \sum_i \sum_j (x_{ijl} - \hat{x}_{ijl})^2 / 6m\right]} \qquad (11)$$

$$l = 1, 2, ..., m; \qquad i = 1, 2, 3; \qquad j = I, II$$

as well as residues of solute distribution coefficient

$$F(K_2) = 100 \sqrt{\left[\sum_l \left(\frac{K_{2l} - \hat{K}_{2l}}{K_{2l}}\right)^2 / m\right]} \qquad (12)$$

where $K_{2l} = x_{2l}^{II} / x_{2l}^I$ and $\hat{K}_{2l} = \hat{x}_{2l}^{II} / \hat{x}_{2l}^I$. The appreciation of the fitting of equilibrium data by means of residues K_2 is especially important for the calculation of the number of equilibrium stages of extractor because the precision of the results of this calculation is, to a great degree, dependent on the value of $F(K_2)$, as discussed in one of our papers [5].

The values of F_x and $F(K_2)$ for the investigated systems and different objective functions are given in Table 1. It results from the data in this table that the type of

Table 1

Values of residues of mole fractions and of solute distribution coefficients for different types of objective functions of ternary correction in the NRTL equation

System	F_x according to eqn (11) with objective function (3—7)					$F(K_2)$ according to eqn (12) with objective function (3—7)				
	(3)	(4)	(5)	(6)	(7)	(3)	(4)	(5)	(6)	(7)
Heptane(1)—toluene(2)—DMFA(3); $t = 40\ °C$	0.250	0.344	0.651	0.610	0.459	8.84	7.27	5.76	5.87	6.60
Heptane(1)—cyclohexane(2)—DMFA(3); $t = 25\ °C$	0.155	0.156	0.157	0.157	0.155	2.62	2.66	2.55	2.55	2.61
Cyclohexane(1)—benzene(2)—fural(3); $t = 25\ °C$	0.146	0.210	0.384	0.355	0.292	6.45	6.30	5.52	5.55	5.83
Heptane(1)—benzene(2)—DMSO(3); $t = 40\ °C$	0.139	0.157	0.158	0.158	0.157	2.56	2.53	2.53	2.53	2.53

DMFA — dimethylformamide; DMSO — dimethyl sulfoxide.

the objective function applied to two of the systems, *i.e.* n-heptane—cyclohex-ane—DMFA and n-heptane—benzene—DMSO, did not practically affect the precision in determination of the individual mole fractions of components as well as solute distribution coefficients. The variation of the values of residues F_x and $F(K_2)$ is only very slight. As for further two systems, *i.e.* n-heptane—toluene—DMFA and cyclohexane—benzene—fural, it is obvious that the type of objective function has influence on the values of residues $F(K_2)$ and especially F_x. While the values of residues of solute distribution coefficients for the system with DMFA differ from the lowest value $F(K_2) = 5.76$ at most by 50 % and for the system with fural from the value $F(K_2) = 5.52$ by less than 20 %, the values of residues of mole fractions reach even 2.5-fold values with respect to $F_x = 0.250$ or $F_x = 0.146$.

Though we cannot draw broad conclusions on the basis of such small number of investigated systems, it seems that objective function *(3)* is most convenient for the calculation of equilibrium data. As a matter of fact, this type of objective function makes possible to obtain the most correct course of the binodal curve though the position of tie lines is not the best. However, the unfavourable influence of objective function *(3)* on the precision of distribution data is of relative character because the fluctuation of the K_2 values is fairly small. The objective function of type *(7)* may be useful for those applications of the L—L equilibrium relationships which require accurate data about distribution as well as solubility.

Symbols

a_i	activity
E_1, E_2, E_3	parameters of ternary correction of G^E
$F(E), F(x_i)$	objective functions
$F_x, F(K_2)$	residues
G^E	molar excess Gibbs free energy
Δ, G^E	ternary correction of the molar excess Gibbs free energy
K	total number of components
K_i, K_2	distribution coefficient of the *i*-th component or solute distribution coefficient
m	number of measurements
R	gas constant
T	absolute temperature
w_i	statistical weight
x_i, x_j	mole fraction
$\alpha_{ij}, \tau_{ij}, \tau_{ji}$	binary parameters in the NRTL equation

Indices and denotations

Upper:

j	j-th phase
I, II	denotation of phase (II — solvent phase)
^	calculated value

Lower:

i	i-th component
j	j-th component
l	l-th measurement
1, 2, 3	ordinal number of component (2 — solute, 3 — solvent)
1, 2, ..., 5	ordinal number of objective function

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