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# Closure Equations in the Estimation of Binary Interaction Parameters

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**Abstract**−Binary interaction parameters used in the UNIQUAC activity coefficient model are found to be dependent on each other and related by a linear relation termed as the closure equation. For a ternary system, six binary interaction parameters are related by one closure equation. Similarly for quaternary systems, three independent closure equations are obtained for the twelve binary interaction parameters and for quinary systems there are six closure equations for twenty parameters. Each closure equation consists of six parameters. The binary interaction parameters that do not satisfy the closure equations may lead to a less accurate prediction of liquid-liquid equilibria. In this work the binary interaction parameters have been estimated with and without closure equations for few ternary and quaternary systems. Parameters that satisfy the closure equations exhibit better root mean square deviation than those that do not satisfy the closure equations in most of the cases. A similar behavior is observed for NRTL model also.

Key words: Closure Equation, Binary Interaction Parameters, Energy Interaction Term, Liquid-Liquid Equilibria

## INTRODUCTION

Liquid-liquid extraction is an important unit operation in many petrochemical processes. Design of an extractor needs liquid-liquid equilibrium data for the system under consideration. Such data are either determined experimentally or predicted. Correlations of liquid-liquid equilibrium data use the activity coefficient models such as Universal Quasi Chemical (UNIQUAC) and Non-Random Two Liquid (NRTL). Each of these models requires proper binary interaction parameters. These parameters are usually estimated from the known experimental liquid-liquid equilibrium data via optimization of a suitable objective function. Many investigators have addressed the parameter estimation problem for which Sorensen and Artl [1979a, b] did extensive work on the subject. They obtained the UNIQUAC and NRTL binary interaction parameters for several ternary and quaternary systems from the reported liquid-liquid equilibrium data for these systems. Later other researchers [Bottini, 1986; Cassel et al., 1989a, b, c; Chen et al., 2000a, b, 2001; Ferreira et al., 1984; Lee and Kim, 1995, 1998; Letcher and Naicker, 2000; Letcher et al., 1996; Salem et al., 1994; Varheygi and Eon, 1977] also did parameter estimation work along with the determination of experimental liquid-liquid equilibrium data for ternary, quaternary and quinary systems. Varhegyi and Eon [1977] were the first to point out that only the difference of the energy interaction terms, $g_{ji}$, occurs in the expressions of Gibbs excess energy and the activity coefficient for the NRTL model. Thus the values of these terms do not change if a constant term is added to all $g_{ji}$'s. This means that for a ternary system one of the $g_{ji}$'s can be chosen arbitrarily and the remaining eight terms (five $g_{ji}$'s and three $\alpha_{ji}$'s) can be estimated. This is in contrast to the other workers who have determined the nine parameters (six interaction parameters and three $\alpha_{ji}$'s). Hala [1972] showed, however, that this is not correct since for the arbitrary values of binary interaction parameters the system of equations relating interaction parameters and energy interaction term has no solution for $g_{ji}$'s. One of the interaction parameters therefore should always be expressed in terms of the other five. Hala [1972] showed that for a ternary triplet i-j-k the binary interaction parameters are related as

$$\tau_{jk}-\tau_{kj}=\tau_{ik}-\tau_{ki}-(\tau_{ij}-\tau_{ji}) \tag{1}$$

Hala [1972] further described that the number of such relationships for a c component system is $0.5\times c(c-3)+1$. Varhegyi and Eon [1977] showed that this problem would not arise if energy interaction terms were computed instead of binary interaction parameters. They estimated the $g_{ji}$'s and $\alpha_{ji}$'s by fixing the value of $g_{11}$. Similarly Lee and Kim [1995, 1998] estimated the UNIQUAC and NRTL energy interaction terms by fixing the value of $u_{11}$ and $g_{11}$ respectively. So far, no one has worked on the relationship between the binary interaction parameters and their estimation. In the present work, we have derived the relationships between the binary interaction parameters, and these have been referred to as the closure equations, for the ternary, quaternary and quinary systems. Binary interaction parameters of UNIQUAC and NRTL models, which satisfy the closure equations, have been estimated for several systems. The results thus obtained are compared with those that are obtained without closure equations. In the next section a mathematical formulation of closure equations for ternary, quaternary and quinary systems is presented. A brief outline of the parameter estimation procedure is given in the later section. The results and discussion and conclusion are presented in the following sections.

## FORMULATION OF CLOSURE EQUATIONS

Gibbs excess free energy of a liquid mixture and the component activity coefficients are related by the fundamental thermodynamic relation as

$$g^E/RT=\sum_{i=1}^{c}x_i\ln\gamma_i \tag{2}$$

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and

$$\ln\gamma_i=\frac{g^E}{RT}-\sum_{\substack{k=1\\k\neq i}}^{c}x_k\left[\frac{\partial(g^E/RT)}{\partial x_k}\right] \tag{3}$$

The expressions for the Gibbs excess free energy and activity coefficients of various components in a multicomponent liquid mixture are given by

**1. UNIQUAC Model**

$$g^E/RT=\sum_{i=1}^{c}x_i\ln\frac{\phi_i}{x_i}+\frac{Z}{2}\sum_{i=1}^{c}q_ix_i\ln\frac{\theta_i}{\phi_i}-\sum_{i=1}^{c}q_jx_j\ln\left(\sum_{j=1}^{c}\theta_j\tau_{ji}\right) \tag{4}$$

and

$$\ln\gamma_i=\ln\frac{\phi_i}{x_i}+\frac{Z}{2}q_i\ln\frac{\theta_i}{\phi_i}+l_i-\frac{\phi_i}{x_i}\sum_{j=1}^{c}x_jl_jq_i\left(1-\ln\sum_{j=1}^{c}\theta_j\tau_{ji}-\sum_{j=1}^{c}\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{c}\theta_k\tau_{kj}}\right) \tag{5}$$

The volume or segment fraction and area or surface fraction are given by

$$\phi_i=\frac{r_ix_i}{\sum_{j=1}^{c}r_jx_j};\quad \theta_i=\frac{q_ix_i}{\sum_{j=1}^{c}q_jx_j} \tag{6}$$

and $l_i$ is given by

$$l_i=\frac{Z}{2}(r_i-q_i)+1-r_i \tag{7}$$

$\tau_{ji}$ is defined as

$$\tau_{ji}=\exp(-a_{ji}/T) \tag{8}$$

where:

$$a_{ji}=(u_{ji}-u_{ii})/R \tag{9}$$

**2. NRTL Model**

$$g^E/RT=\sum_{i=1}^{c}x_i\frac{\sum_{j=1}^{c}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{c}G_{ki}x_k} \tag{10}$$

and

$$\ln\gamma_i=\frac{\sum_{j=1}^{c}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{c}G_{ki}x_k}+\sum_{j=1}^{c}\frac{x_jG_{ij}}{\sum_{k=1}^{c}G_{kj}x_k}\left(\tau_{ij}-\frac{\sum_{k=1}^{c}x_k\tau_{kj}G_{kj}}{\sum_{k=1}^{c}G_{kj}x_k}\right) \tag{11}$$

where:

$\tau_{ji}$ and $G_{ji}$ are defined as

$$\tau_{ji}=a_{ji}/T \tag{12}$$

$$G_{ji}=\exp(-\alpha_{ji}\tau_{ji}) \tag{13}$$

$a_{ji}$ is given by

$$a_{ji}=(g_{ji}-g_{ii})/R \tag{14}$$

The expressions for binary interaction parameter $a_{ji}$ are of similar form for both the UNIQUAC and NRTL models. Therefore, the mathematical formulation of closure equations is valid for both the models.

**3. Ternary Systems**

A ternary system has the following six binary interaction parameters $a_{12}$, $a_{21}$; $a_{13}$, $a_{31}$; and $a_{23}$, $a_{32}$. These parameters are expressed in terms of energy interaction terms as follows:

$$\begin{array}{llll} a_{21}=(u_{21}-u_{11})/R & (a) & a_{12}=(u_{12}-u_{22})/R & (b)\\ a_{31}=(u_{31}-u_{11})/R & (c) & a_{13}=(u_{13}-u_{33})/R & (d)\\ a_{32}=(u_{32}-u_{22})/R & (e) & a_{23}=(u_{23}-u_{33})/R & (f)\end{array} \tag{15}$$

With $u_{ji}=u_{ij}$ Eq. (15) can be rewritten as

$$\begin{array}{llll} u_{12}-u_{11}=a_{21}R & (a) & u_{12}-u_{22}=a_{12}R & (b)\\ u_{13}-u_{11}=a_{31}R & (c) & u_{13}-u_{33}=a_{13}R & (d)\\ u_{23}-u_{22}=a_{32}R & (e) & u_{23}-u_{33}=a_{23}R & (f)\end{array} \tag{16}$$

The system of Eq. (16) with the variables $u_{11}$, $u_{22}$, $u_{33}$, $u_{12}$, $u_{13}$, and $u_{23}$ is inconsistent for an arbitrary value of all the variables since the rank of coefficient matrix is 5. Hence only one variable can be fixed and other may be obtained in terms the fixed variable. Fixing the value of $u_{11}$ the other variables can be written in terms of $u_{11}$ as

from (16a) $$u_{12}=u_{11}+a_{21}R \tag{17}$$

from (16b) $$u_{22}=u_{12}-a_{12}R=u_{11}+(a_{21}-a_{12})R \tag{18}$$

from (16e) $$u_{23}=u_{22}+a_{32}R=u_{11}+(a_{32}+a_{21}-a_{12})R \tag{19}$$

from (16f) $$u_{33}=u_{23}-a_{23}R=u_{11}+(a_{32}-a_{23}+a_{21}-a_{12})R \tag{20}$$

from (16d) $$u_{13}=u_{33}+a_{13}R=u_{11}+(a_{13}+a_{32}-a_{23}+a_{21}-a_{12})R \tag{21}$$

from (16c) $$u_{11}=u_{13}-a_{31}R=u_{11}+(a_{13}-a_{31}+a_{32}-a_{23}+a_{21}-a_{12})R \tag{22}$$

The last equation is satisfied only when

$$a_{12}-a_{21}+a_{23}-a_{32}+a_{31}-a_{13}=0 \tag{23}$$

Eq. (23) describes the relationship between the six binary interaction parameters for a ternary system. This relationship is referred to as closure equation in the present work. A generalization of Eq. (23) for a ternary triplet i-j-k will be

$$a_{ij}-a_{ji}+a_{jk}-a_{kj}+a_{ki}-a_{ik}=0 \tag{24}$$

**4. Quaternary Systems**

For a quaternary system the twelve binary interaction parameters are $a_{12}$, $a_{21}$; $a_{13}$, $a_{31}$; $a_{14}$, $a_{41}$; $a_{23}$, $a_{32}$; $a_{24}$, $a_{42}$; and $a_{34}$, $a_{43}$. The energy interaction terms are comprised of four pure interaction terms $u_{11}$, $u_{22}$, $u_{33}$, $u_{44}$ and six cross interaction terms $u_{12}$, $u_{13}$, $u_{14}$, $u_{23}$, $u_{24}$, $u_{34}$ are related to the twelve binary interaction parameters by the following equation:

$$\begin{array}{llll} u_{12}-u_{11}=a_{21}R & (a) & u_{12}-u_{22}=a_{12}R & (b)\\ u_{13}-u_{11}=a_{31}R & (c) & u_{13}-u_{33}=a_{13}R & (d)\\ u_{14}-u_{11}=a_{41}R & (e) & u_{14}-u_{44}=a_{14}R & (f)\\ u_{32}-u_{22}=a_{32}R & (g) & u_{23}-u_{33}=a_{23}R & (h)\\ u_{24}-u_{22}=a_{42}R & (i) & u_{24}-u_{44}=a_{24}R & (j)\\ u_{34}-u_{33}=a_{43}R & (k) & u_{34}-u_{44}=a_{34}R & (l)\end{array} \tag{25}$$

The rank of the coefficient matrix of the system of Eqs. (25) is 9, hence one of the ten variables can be fixed arbitrarily. By fixing $u_{11}$ other variables can be obtained as follows

from (25a) $$u_{12}=u_{11}+a_{21}R \tag{26}$$

from (25b) $u_{22}=u_{12}-a_{12}R=u_{11}+(a_{21}-a_{12})R$ (27)

from (25g) $u_{23}=u_{22}+a_{32}R=u_{11}+(a_{32}+a_{21}-a_{12})R$ (28)

from (25i) $u_{24}=u_{22}+a_{42}R=u_{11}+(a_{42}+a_{21}-a_{12})R$ (29)

from (25h) $u_{33}=u_{23}-a_{23}R=u_{11}+(a_{32}-a_{23}+a_{21}-a_{12})R$ (30)

from (25j) $u_{44}=u_{24}-a_{24}R=u_{11}+(a_{42}-a_{24}+a_{21}-a_{12})R$ (31)

from (25d) $u_{13}=u_{33}+a_{13}R=u_{11}+(a_{13}+a_{32}-a_{23}+a_{21}-a_{12})R$ (32)

from (25k) $u_{34}=u_{33}+a_{43}R=u_{11}+(a_{43}+a_{32}-a_{23}+a_{21}-a_{12})R$ (33)

from (25f) $u_{14}=u_{44}+a_{14}R=u_{11}+(a_{14}+a_{42}-a_{24}+a_{21}-a_{12})R$ (34)

from (25*l*) $u_{34}=u_{44}+a_{34}R=u_{11}+(a_{34}+a_{42}-a_{24}+a_{21}-a_{12})R$ (35)

from (25c) $u_{11}=u_{13}-a_{31}R=u_{11}+(a_{13}-a_{31}+a_{32}-a_{23}+a_{21}-a_{12})R$ (36)

from (25e) $u_{11}=u_{14}-a_{41}R=u_{11}+(a_{14}-a_{41}+a_{42}-a_{24}+a_{21}-a_{12})R$ (37)

Eqs. (36) and (37) are valid only if the terms in the parentheses are each equal to zero, hence

$$a_{12}-a_{21}+a_{23}-a_{32}+a_{31}-a_{13}=0 \quad (38)$$

and

$$a_{12}-a_{21}+a_{24}-a_{42}+a_{41}-a_{14}=0 \quad (39)$$

also from Eqs. (33) and (35)

$$a_{23}-a_{32}+a_{34}-a_{43}+a_{42}-a_{24}=0 \quad (40)$$

Eqs. (38)-(40) constitute the set of three closure equations for the quaternary systems. The total number of closure equations confirms Hala's [1972] finding. It is interesting to note that each closure equation consists only of six binary interaction parameters.

**5. Quinary Systems**

A quinary system has the following twenty binary interaction parameters: $a_{12}$, $a_{21}$; $a_{13}$, $a_{31}$; $a_{14}$, $a_{41}$; $a_{15}$, $a_{51}$; $a_{23}$, $a_{32}$; $a_{24}$, $a_{42}$; $a_{25}$, $a_{52}$; $a_{34}$, $a_{43}$; $a_{35}$, $a_{53}$; and $a_{45}$, $a_{54}$. The energy interaction terms are comprised of five pure interaction terms $u_{11}$, $u_{22}$, $u_{33}$, $u_{44}$, $u_{55}$ and ten cross interaction terms $u_{12}$, $u_{13}$, $u_{14}$, $u_{15}$, $u_{23}$, $u_{24}$, $u_{25}$, $u_{34}$, $u_{35}$, $u_{45}$ are related to the above twenty binary interaction parameters as follows:

$$\begin{array}{llll} u_{12}-u_{11}=a_{21}R & (a) & u_{12}-u_{22}=a_{12}R & (b) \\ u_{13}-u_{11}=a_{31}R & (c) & u_{13}-u_{33}=a_{13}R & (d) \\ u_{14}-u_{11}=a_{41}R & (e) & u_{14}-u_{44}=a_{14}R & (f) \\ u_{15}-u_{11}=a_{51}R & (g) & u_{15}-u_{55}=a_{15}R & (h) \\ u_{23}-u_{22}=a_{32}R & (i) & u_{23}-u_{33}=a_{23}R & (j) \\ u_{24}-u_{22}=a_{42}R & (k) & u_{24}-u_{44}=a_{24}R & (l) \\ u_{25}-u_{22}=a_{52}R & (m) & u_{25}-u_{55}=a_{25}R & (n) \\ u_{34}-u_{33}=a_{43}R & (o) & u_{34}-u_{44}=a_{34}R & (p) \\ u_{35}-u_{33}=a_{53}R & (q) & u_{35}-u_{55}=a_{35}R & (r) \\ u_{45}-u_{44}=a_{54}R & (s) & u_{45}-u_{55}=a_{45}R & (t) \end{array} \quad (41)$$

The rank of the coefficient matrix of the system of Eqs. (41) is 14 hence one variable can be fixed arbitrarily. Fixing $u_{11}$ other energy interaction terms can be expressed as given below

from (41a) $u_{12}=u_{11}+a_{21}R$ (42)

from (41b) $u_{22}=u_{12}-a_{12}R=u_{11}+(a_{21}-a_{12})R$ (43)

from (41i) $u_{23}=u_{22}+a_{32}R=u_{11}+(a_{32}+a_{21}-a_{12})R$ (44)

from (41k) $u_{24}=u_{22}+a_{42}R=u_{11}+(a_{42}+a_{21}-a_{12})R$ (45)

from (41m) $u_{25}=u_{22}+a_{52}R=u_{11}+(a_{52}+a_{21}-a_{12})R$ (46)

from (41j) $u_{33}=u_{23}-a_{23}R=u_{11}+(a_{32}-a_{23}+a_{21}-a_{12})R$ (47)

from (41l) $u_{44}=u_{24}-a_{24}R=u_{11}+(a_{42}-a_{24}+a_{21}-a_{12})R$ (48)

from (41n) $u_{55}=u_{25}-a_{25}R=u_{11}+(a_{52}-a_{25}+a_{21}-a_{12})R$ (49)

from (41d) $u_{13}=u_{33}+a_{13}R=u_{11}+(a_{13}+a_{32}-a_{23}+a_{21}-a_{12})R$ (50)

from (41o) $u_{34}=u_{33}+a_{43}R=u_{11}+(a_{43}+a_{32}-a_{23}+a_{21}-a_{12})R$ (51)

from (41q) $u_{35}=u_{33}+a_{53}R=u_{11}+(a_{53}+a_{32}-a_{23}+a_{21}-a_{12})R$ (52)

from (41f) $u_{14}=u_{44}+a_{14}R=u_{11}+(a_{14}+a_{42}-a_{24}+a_{21}-a_{12})R$ (53)

from (41p) $u_{34}=u_{44}+a_{34}R=u_{11}+(a_{34}+a_{42}-a_{24}+a_{21}-a_{12})R$ (54)

from (41s) $u_{45}=u_{44}+a_{54}R=u_{11}+(a_{54}+a_{42}-a_{24}+a_{21}-a_{12})R$ (55)

from (41h) $u_{15}=u_{55}+a_{15}R=u_{11}+(a_{15}+a_{52}-a_{25}+a_{21}-a_{12})R$ (56)

from (41r) $u_{35}=u_{55}+a_{35}R=u_{11}+(a_{35}+a_{52}-a_{25}+a_{21}-a_{12})R$ (57)

from (41t) $u_{45}=u_{55}+a_{45}R=u_{11}+(a_{45}+a_{52}-a_{25}+a_{21}-a_{12})R$ (58)

from (41c) $u_{11}=u_{13}+a_{31}R=u_{11}+(a_{13}-a_{31}+a_{32}-a_{23}+a_{21}-a_{12})R$ (59)

from (41e) $u_{11}=u_{14}+a_{41}R=u_{11}+(a_{14}-a_{41}+a_{42}-a_{24}+a_{21}-a_{12})R$ (60)

from (41g) $u_{11}=u_{15}+a_{51}R=u_{11}+(a_{15}-a_{51}+a_{52}-a_{25}+a_{21}-a_{12})R$ (61)

Eqs. (59)-(61) are valid only if the terms in the parentheses are each equal to zero, hence

$$a_{12}-a_{21}+a_{23}-a_{32}+a_{31}-a_{13}=0 \quad (62)$$

$$a_{12}-a_{21}+a_{24}-a_{42}+a_{41}-a_{14}=0 \quad (63)$$

and

$$a_{12}-a_{21}+a_{25}-a_{52}+a_{51}-a_{15}=0 \quad (64)$$

also from Eqs. (51) and (54)

$$a_{23}-a_{32}+a_{34}-a_{43}+a_{42}-a_{24}=0 \quad (65)$$

from Eqs. (52) and (57)

$$a_{23}-a_{32}+a_{35}-a_{53}+a_{52}-a_{25}=0 \quad (66)$$

and from Eqs. (55) and (58)

$$a_{24}-a_{42}+a_{45}-a_{54}+a_{52}-a_{25}=0 \quad (67)$$

Eqs. (62)-(67) constitute the set of six closure equations for a quinary system. The number of closure equations satisfies the expression $0.5\times c(c-3)+1$ given by Hala [1972]. Also the number of binary interaction parameters in each equation is again six. An alternative derivation of the closure equation for quaternary and quinary systems is given in Appendix A.

## PARAMETER ESTIMATION PROCEDURE

Parameters are usually obtained from experimental liquid-liquid equilibrium data by minimizing a suitable objective function. The most common objective function is the sum of the square of the error between the experimental and calculated composition of all the components over the entire set of tie-lines. This objective function has been taken by most of the researchers. However, in the present work the objective function is taken as the negative of the log of the likelihood function as suggested by Prausnitz et al. [1980] using the Inside Variance Estimation Method (IVEM) proposed by Vasquez and Whitting [2000]. The key feature of IVEM is that in this method the variance covariance matrix of the errors is modified at each iteration of the optimization procedure, thus giving the most likely values of the estimated parameters. The measured experimental compositions are assumed to be independent of each other so that the covariances of the errors are all zero, that is, the variance covariance matrix of errors is a diagonal matrix. The final objective function to be minimized in this work is of the form

$$F(\boldsymbol{\theta}) = -\ln L = \frac{mn}{2}\ln 2\pi + \frac{m}{2}\ln|\mathbf{V}| + \frac{1}{2}\sum_{k=1}^{m}\mathbf{e}_k^T\mathbf{V}^{-1}\mathbf{e}_k \tag{68}$$

Esposito and Floudas [1998] have presented the detailed derivation of the above objective function. The quality of the estimated parameters have been examined by their *rmsd* values given by

$$rmsd = 100\left[\sum_{k=1}^{m}\sum_{i=1}^{c}\sum_{j=1}^{2}\frac{(x_{ik}^j - \hat{x}_{ik}^j)^2}{2mc}\right]^{1/2} \tag{69}$$

The closure equations have been implemented by the elimination of the parameters equal to the number of closure equations. These eliminated parameters can be obtained by the simultaneous solution of closure equations. There exist several possibilities of parameter elimination. The number of such possibilities for ternary systems is ${}^{6}C_{1}=6$, for quaternary systems is ${}^{12}C_{3}=220$, and for quinary systems is ${}^{20}C_{6}=38760$. However, all such possibilities are not feasible. A feasible set is such that the rank of the coefficient matrix of the eliminated parameters in the closure equations is equal to the number of independent closure equations. The number of such feasible sets has been computed to be 6 for the ternary systems, 128 for the quaternary systems and 8000 for the quinary systems. From this computation it is observed that the following two conditions must be satisfied for each set.

1. Two parameters for the same pair (i.e., $a_{ij}$ and $a_{ji}$) cannot be eliminated simultaneously.
2. Same component cannot appear as subscript in all the eliminated parameters.

## RESULTS AND DISCUSSION

The binary interaction parameters for ternary, quaternary and quinary system have been estimated by using the reported experimental liquid-liquid equilibrium data. Three ternary systems, octane-benzene-sulfolane at 298.15 K, octane-toluene-sulfolane at 298.15 K and octane-m-xylene-sulfolane at 308.15 K and one quaternary system, octane-toluene-m-xylene-sulfolane at 298.15 K have been considered. The experimental liquid-liquid equilibrium data for all the ternary systems have been taken from Lee and Kim [1995]. The experimental liquid-liquid equilibrium data for quaternary system have been taken from Chen et al. [2000b]. The initial guesses of parameters for ternary systems as well as for the quaternary system have been computed from the energy interaction terms for these systems reported by Lee and Kim [1995] so that they satisfy the closure equation as close as possible.

The results of UNIQUAC parameter estimation for the ternary system octane-benzene-sulfolane at 298.15 K are presented in Table 1 both with and without the closure equations. The corresponding *rmsd* values are also shown in the table. It is seen that the *rmsd* value corresponding to the parameters with the closure equations taken into account is less than that without closure equations. This clearly means that parameters obtained with the closure equations will predict the liquid-liquid equilibria more accurately than those obtained without closure equations.

**Table 1. UNIQUAC binary interaction parameters for the system Octane-Benzene-Sulfolane* at 298.15 K**

| i | j | $a_{ij}$ (K) | | |
|---|---|---|---|---|
| | | Initial guess | Regressed parameters | |
| | | | Without closure equations | With closure equations |
| Octane | Benzene | −282.683 | −306.920 | −294.799 |
| Benzene | Octane | −71.166 | −43.186 | −51.245 |
| Benzene | Sulfolane | 90.716 | 107.257 | 124.735 |
| Sulfolane | Benzene | −430.424 | −440.006 | −441.191 |
| Octane | Sulfolane | 430.301 | 473.016 | 453.447 |
| Sulfolane | Octane | 120.687 | 122.459 | 131.076 |
| ***rmsd*** | | **0.4376** | **0.1797** | **0.1641** |

*Experimental LLE data from Lee and Kim [1995].

**Table 2. NRTL binary interaction parameters for the system Octane-Benzene-Sulfolane* at 298.15 K**

| i | j | $a_{ij}$ (K) | | |
|---|---|---|---|---|
| | | Initial guess | Regressed parameters | |
| | | | Without closure equations | With closure equations |
| Octane | Benzene | −545.34 | −491.187 | −467.597 |
| Benzene | Octane | 857.45 | 878.718 | 878.496 |
| Benzene | Sulfolane | 849.32 | 839.916 | 847.876 |
| Sulfolane | Benzene | −534.04 | −568.212 | −545.395 |
| Octane | Sulfolane | 1168.85 | 1211.450 | 1202.190 |
| Sulfolane | Octane | 1188.28 | 1196.860 | 1155.020 |
| ***rmsd*** | | **2.6019** | **0.8523** | **0.8044** |

*Experimental LLE data from Lee and Kim [1995].

Table 2 presents the results of NRTL parameter estimation for the same system. The parameter $\alpha$ has been taken as 0.3 for the octane-sulfolane pair and 0.2 otherwise as reported by Lee and Kim [1995]. The corresponding *rmsd* values are also shown. It is seen that the *rmsd* value corresponding to the parameters obtained with the closure equations taken into account is less than that obtained without the closure equations. This would mean that the liquid-liquid equilibria would be more accurately predicted by these parameters in comparison to that which is predicted by the parameters without closure equations. This result matches with those for UNIQUAC parameters.

The results of UNIQUAC parameter estimation for the second ternary system octane-toluene-sulfolane at 298.15 K are presented in Table 3 again both with and without the closure equations along

**Table 3. UNIQUAC binary interaction parameters for the system Octane-Toluene-Sulfolane* at 298.15 K**

| i | j | $a_{ij}$ (K) | | |
|---|---|---|---|---|
| | | Initial guess | Regressed parameters | |
| | | | Without closure equations | With closure equations |
| Octane | Toluene | 159.089 | 148.209 | 129.040 |
| Toluene | Octane | −104.590 | −102.870 | −68.533 |
| Toluene | Sulfolane | 108.045 | 100.322 | 114.889 |
| Sulfolane | Toluene | 46.055 | 43.100 | 46.308 |
| Octane | Sulfolane | 428.581 | 458.736 | 407.818 |
| Sulfolane | Octane | 103.075 | 128.152 | 141.664 |
| ***rmsd*** | | **0.6428** | **0.3175** | **0.2636** |

*Experimental LLE data from Lee and Kim [1995].

**Table 4. NRTL binary interaction parameters for the system Octane-Toluene-Sulfolane* at 298.15 K**

| i | j | $a_{ij}$ (K) | | |
|---|---|---|---|---|
| | | Initial guess | Regressed parameters | |
| | | | Without closure equations | With closure equations |
| Octane | Toluene | −262.750 | −251.266 | −207.992 |
| Toluene | Octane | 506.729 | 593.433 | 451.768 |
| Toluene | Sulfolane | 654.376 | 684.406 | 650.348 |
| Sulfolane | Toluene | −9.991 | −10.954 | −14.829 |
| Octane | Sulfolane | 1263.620 | 1295.300 | 999.729 |
| Sulfolane | Octane | 1368.740 | 981.562 | 994.312 |
| ***rmsd*** | | **0.9057** | **0.5400** | **0.2267** |

*Experimental LLE data from Lee and Kim [1995].

**Table 5. UNIQUAC binary interaction parameters for the system Octane-*m*-Xylene-Sulfolane* at 308.15 K**

| i | j | $a_{ij}$ (K) | | |
|---|---|---|---|---|
| | | Initial guess | Regressed parameters | |
| | | | Without closure equations | With closure equations |
| Octane | *m*-Xylene | 129.802 | 195.040 | 124.388 |
| *m*-Xylene | Octane | −104.007 | −155.809 | −107.387 |
| *m*-Xylene | Sulfolane | 108.436 | 198.025 | 141.978 |
| Sulfolane | *m*-Xylene | 24.135 | −34.593 | 4.079 |
| Octane | Sulfolane | 446.491 | 451.570 | 470.597 |
| Sulfolane | Octane | 128.381 | 112.032 | 100.923 |
| ***rmsd*** | | **0.4290** | **0.2319** | **0.2288** |

*Experimental LLE data from Lee and Kim [1995].

**Table 6. NRTL binary interaction parameters for the system Octane-*m*-Xylene-Sulfolane* at 308.15 K.**

| i | j | $a_{ij}$ (K) | | |
|---|---|---|---|---|
| | | Initial guess | Regressed parameters | |
| | | | Without closure equations | With closure equations |
| Octane | *m*-Xylene | −264.989 | −262.124 | −271.052 |
| *m*-Xylene | Octane | 257.572 | 290.415 | 271.757 |
| *m*-Xylene | Sulfolane | 616.724 | 617.056 | 595.133 |
| Sulfolane | *m*-Xylene | −23.463 | −25.680 | −27.732 |
| Octane | Sulfolane | 1383.770 | 1425.870 | 973.022 |
| Sulfolane | Octane | 1266.150 | 842.405 | 892.966 |
| ***rmsd*** | | **1.3088** | **0.9241** | **0.4391** |

*Experimental LLE data from Lee and Kim [1995].

with the corresponding *rmsd* values. It is seen, for this system too, that the *rmsd* value for the UNIQUAC parameters with the closure equations taken into account is again less than that without closure equations. This too means that parameters obtained with the closure equations will predict the liquid-liquid equilibria more accurately than that obtained without closure equations.

The results of NRTL parameter estimation for the same system both with and without the closure equations are given in Table 4. The corresponding *rmsd* values are also shown. It is seen that for this system the *rmsd* value corresponding to the parameters obtained with the closure equations taken into account is much less than that obtained without the closure equations. This would mean that the liquid-liquid equilibria prediction using these parameters would be more accurate than those predicted by the parameters that are obtained without the closure equations. This is similar to our previous result for NRTL parameters.

For the third ternary system octane-*m*-xylene-sulfolane at 308.15 K, the results of UNIQUAC parameter estimation both with and without the closure equations along with the corresponding *rmsd* values are given in Table 5. The nature of the results is similar to that for the other two systems, that is, the parameters that are obtained with closure equations predict the liquid-liquid equilibria more accurately than that obtained without the closure equations.

NRTL parameter estimation results for this system both with and without closure equations and the respective *rmsd* values are given in Table 6. The parameters obtained with the closure equations exhibit much less *rmsd* than those obtained without closure equations. Again the result is similar to those for the NRTL parameters for the previous two systems.

While implementing the closure equation for ternary systems all the six possibilities of parameter elimination have been tried. Table 7 shows the *rmsd* values for the eliminated parameter both for UNIQUAC and NRTL. The lowest and highest *rmsd* values are shown bold faced and underlined, respectively. It has been observed that the *rmsd* values change significantly with the eliminated parameters. The maximum *rmsd* is approximately twice of the minimum *rmsd*. This is due to the different search path adopted by the optimization procedure for different eliminated parameter to reach the final optimum point. Another reason could be the biased experimental error in the reported LLE data. The interaction parameters with closure equations shown in Tables 1 to 6 correspond to the lowest *rmsd* for the six possibilities.

The results of the UNIQUAC and NRTL parameter estimation for the quaternary system octane-toluene-xylene-sulfolane at 298.15 K

**Table 7. *rmsd* values with closure equation for the ternary systems Octane-Benzene-Sulfolane, Octane-Toluene-Sulfolane, and Octane-*m*-Xylene-Sulfolane**

| Eliminated parameter | System #1 | | System #2 | | System #3 | |
|---|---|---|---|---|---|---|
| | UNIQUAC | NRTL | UNIQUAC | NRT | UNIQUAC | NRTL |
| $a_{12}$ | <u>0.4378</u> | **0.8044** | **0.2636** | 0.6437 | **0.2288** | 0.4495 |
| $a_{21}$ | 0.3559 | 0.8618 | <u>0.3225</u> | **0.2267** | 0.2550 | 0.5874 |
| $a_{13}$ | 0.3803 | 0.8218 | 0.2808 | 0.2440 | 0.2523 | 0.4504 |
| $a_{31}$ | **0.1641** | 0.8094 | 0.2949 | 0.2356 | 0.2428 | **0.4391** |
| $a_{23}$ | 0.3092 | 0.8467 | 0.3047 | 0.3147 | 0.2926 | 0.5936 |
| $a_{32}$ | 0.4371 | <u>0.8716</u> | 0.3052 | <u>0.6539</u> | <u>0.3211</u> | <u>1.1381</u> |

System #1: Octane(1)-Benzene(2)-Sulfolane(3)
System #2: Octane(1)-Toluene(2)-Sulfolane(3)
System #3: Octane(1)-*m*-Xylene(2)-Sulfolane(3)

**Table 8. UNIQUAC binary interaction parameters for the system Octane-Toluene-*m*-Xylene-Sulfolane* at 298.15 K**

| i | j | $a_{ij}$ (K) Initial guess | Regressed parameters: Without closure equations | Regressed parameters: With closure equations |
|---|---|---|---|---|
| Octane | Toluene | 159.089 | 164.957 | 128.025 |
| Toluene | Octane | −104.590 | −105.110 | −109.001 |
| Toluene | *m*-Xylene | −11.870 | −11.721 | −10.714 |
| *m*-Xylene | Toluene | 11.870 | 11.091 | 9.894 |
| *m*-Xylene | Sulfolane | 107.355 | 111.202 | 155.296 |
| Sulfolane | *m*-Xylene | 21.624 | 22.118 | 15.407 |
| Octane | *m*-Xylene | 127.371 | 101.174 | 120.546 |
| *m*-Xylene | Octane | −112.569 | −110.233 | −95.872 |
| Octane | Sulfolane | 428.744 | 556.440 | 490.256 |
| Sulfolane | Octane | 103.074 | 112.524 | 133.950 |
| Toluene | Sulfolane | 108.045 | 105.353 | 122.436 |
| Sulfolane | Toluene | 46.055 | 43.803 | 3.155 |
| ***rmsd*** | | **2.2693** | **1.1421** | **0.5650** |

*Experimental LLE data from Chen et al. [2000b].

**Table 9. NRTL binary interaction parameters for the system Octane-Toluene-*m*-Xylene-Sulfolane* at 298.15 K**

| i | j | $a_{ij}$ (K) Initial guess | Regressed parameters: Without closure equations | Regressed parameters: With closure equations |
|---|---|---|---|---|
| Octane | Toluene | −262.749 | −259.907 | −343.293 |
| Toluene | Octane | 506.729 | 522.163 | 397.697 |
| Toluene | *m*-Xylene | −6.729 | −6.774 | −6.840 |
| *m*-Xylene | Toluene | 6.729 | 6.701 | 7.506 |
| *m*-Xylene | Sulfolane | 629.887 | 615.731 | 702.011 |
| Sulfolane | *m*-Xylene | −48.020 | −48.488 | −54.135 |
| Octane | *m*-Xylene | −319.893 | −326.438 | −411.802 |
| *m*-Xylene | Octane | 463.116 | 459.078 | 343.174 |
| Octane | Sulfolane | 1428.550 | 1457.530 | 1375.460 |
| Sulfolane | Octane | 1533.670 | 1524.160 | 1374.290 |
| Toluene | Sulfolane | 654.376 | 655.577 | 647.593 |
| Sulfolane | Toluene | −9.991 | −9.940 | −94.568 |
| ***rmsd*** | | **2.5072** | **1.5714** | **0.5451** |

*Experimental LLE data from Chen et al. [2000b].

are presented in Tables 8 and 9, respectively, both with and without the implementation of the closure equations. The parameter $\alpha$ for NRTL parameters has been taken as 0.3 for the octane-sulfolane pair and 0.2 otherwise as reported by Lee and Kim [1995]. The initial guesses have been computed from the reported energy interaction terms of Lee and Kim [1995] for ternary systems. The only missing cross energy interaction terms for the toluene-*m*-xylene pair have been taken as the arithmetic average of the pure energy interaction terms. The binary interaction parameters thus obtained satisfy the closure equations at the initial stage. The corresponding *rmsd* values are also shown. The *rmsd* value for the parameters with the closure equation is better than that without the closure equation. The choice of the parameters to be eliminated to implement the closure equations plays a very important role in decreasing the *rmsd* values. All 128 feasible combinations of parameter elimination have been tried. The *rmsd* values with the eliminated parameters (both for UNIQUAC and NRTL) are given in Table 10. The lowest and highest *rmsd* values are shown bold faced and underlined, respectively. The *rmsd* values have been found to vary significantly with the eliminated parameters. The maximum *rmsd* is approximately four times of the minimum *rmsd*. Reasons explained for the ternary systems apply here also for this large variation. Additionally, the larger deviation is due to the higher dimension of optimization problem encountered. The interaction parameters with closure equation shown in Tables 8 and 9 correspond to the lowest *rmsd* for all feasible combination of parameter elimination. A better initial guess would also probably improve the corresponding *rmsd* values further. Similar approach may be extended for the quinary systems.

## CONCLUSIONS

The binary interaction parameters for UNIQUAC and NRTL models have been found to be dependent of each other following a relationship called closure equation. The closure equations have been derived for ternary, quaternary and quinary systems. The number

**Table 10. *rmsd* values with closure equations for the quaternary system Octane (1)-Toluene (2)-*m*-Xylene (3)-Sulfolane(4)**

| Eliminated parameters | *rmsd* | | Eliminated parameters | *rmsd* | | Eliminated parameters | *rmsd* | |
|---|---|---|---|---|---|---|---|---|
| | UNIQUAC | NRTL | | UNIQUAC | NRTL | | UNIQUAC | NRTL |
| $a_{12}$, $a_{13}$, $a_{23}$ | 1.5858 | 1.6299 | $a_{13}$, $a_{21}$, $a_{43}$ | 1.3778 | 0.8346 | $a_{21}$, $a_{31}$, $a_{32}$ | 1.3740 | 0.8651 |
| $a_{12}$, $a_{13}$, $a_{24}$ | 1.2599 | 1.5270 | $a_{13}$, $a_{23}$, $a_{24}$ | 1.7577 | 0.8379 | $a_{21}$, $a_{31}$, $a_{34}$ | 1.2750 | 0.8755 |
| $a_{12}$, $a_{13}$, $a_{32}$ | 1.1373 | 1.8511 | $a_{13}$, $a_{23}$, $a_{41}$ | 1.4153 | 1.4967 | $a_{21}$, $a_{31}$, $a_{42}$ | 1.1516 | 0.7846 |
| $a_{12}$, $a_{13}$, $a_{34}$ | 1.2406 | 1.6947 | $a_{13}$, $a_{23}$, $a_{42}$ | 0.9861 | 0.6548 | $a_{21}$, $a_{31}$, $a_{43}$ | 1.2973 | 0.9272 |
| $a_{12}$, $a_{13}$, $a_{42}$ | **0.5650** | 1.5017 | $a_{13}$, $a_{24}$, $a_{32}$ | 1.2827 | 1.5127 | $a_{21}$, $a_{32}$, $a_{34}$ | 0.8307 | 0.6434 |
| $a_{12}$, $a_{13}$, $a_{43}$ | 1.3808 | 1.4883 | $a_{13}$, $a_{24}$, $a_{34}$ | 1.2994 | 1.0598 | $a_{21}$, $a_{32}$, $a_{41}$ | 1.5364 | 1.1379 |
| $a_{12}$, $a_{14}$, $a_{23}$ | 1.4712 | 0.7534 | $a_{13}$, $a_{24}$, $a_{41}$ | 1.4495 | 1.3944 | $a_{21}$, $a_{32}$, $a_{43}$ | 1.4944 | 0.7088 |
| $a_{12}$, $a_{14}$, $a_{24}$ | 1.3773 | 1.4198 | $a_{13}$, $a_{24}$, $a_{43}$ | 1.6181 | 0.7689 | $a_{21}$, $a_{34}$, $a_{41}$ | 1.4843 | 1.5697 |
| $a_{12}$, $a_{14}$, $a_{32}$ | 1.6085 | 0.9172 | $a_{13}$, $a_{32}$, $a_{41}$ | 1.4251 | 1.4908 | $a_{21}$, $a_{34}$, $a_{42}$ | 1.1104 | 1.4842 |
| $a_{12}$, $a_{14}$, $a_{34}$ | 1.1930 | 1.5065 | $a_{13}$, $a_{32}$, $a_{42}$ | 1.2393 | 1.5639 | $a_{21}$, $a_{41}$, $a_{42}$ | 1.4238 | 1.4000 |
| $a_{12}$, $a_{14}$, $a_{42}$ | 0.5787 | **0.5451** | $a_{13}$, $a_{34}$, $a_{41}$ | 1.3934 | 1.5919 | $a_{21}$, $a_{41}$, $a_{43}$ | 1.3495 | 1.5293 |
| $a_{12}$, $a_{14}$, $a_{43}$ | 1.2455 | 1.4538 | $a_{13}$, $a_{34}$, $a_{42}$ | 0.7786 | 1.3776 | $a_{21}$, $a_{42}$, $a_{43}$ | 2.3861 | 1.5961 |
| $a_{12}$, $a_{23}$, $a_{31}$ | 1.2572 | 0.7734 | $a_{13}$, $a_{41}$, $a_{42}$ | 1.4638 | 1.4891 | $a_{23}$, $a_{24}$, $a_{31}$ | 1.0674 | 0.7194 |
| $a_{12}$, $a_{23}$, $a_{34}$ | 1.3409 | 0.6732 | $a_{13}$, $a_{41}$, $a_{43}$ | 1.2644 | 1.5915 | $a_{23}$, $a_{24}$, $a_{34}$ | 0.8599 | 0.8456 |
| $a_{12}$, $a_{23}$, $a_{41}$ | 1.4201 | 1.4028 | $a_{13}$, $a_{42}$, $a_{43}$ | 1.2566 | 1.5514 | $a_{23}$, $a_{24}$, $a_{41}$ | 1.6153 | 1.4661 |
| $a_{12}$, $a_{23}$, $a_{43}$ | 1.3347 | 1.6617 | $a_{14}$, $a_{21}$, $a_{23}$ | 1.2890 | 1.4460 | $a_{23}$, $a_{24}$, $a_{43}$ | 1.3558 | 0.7498 |
| $a_{12}$, $a_{24}$, $a_{31}$ | 1.4446 | 0.7961 | $a_{14}$, $a_{21}$, $a_{24}$ | 1.3653 | 1.4968 | $a_{23}$, $a_{31}$, $a_{41}$ | 1.4914 | 0.8925 |
| $a_{12}$, $a_{24}$, $a_{34}$ | 1.2914 | 0.9940 | $a_{14}$, $a_{21}$, $a_{34}$ | 1.4037 | 1.4187 | $a_{23}$, $a_{31}$, $a_{43}$ | 1.1112 | 1.4834 |
| $a_{12}$, $a_{24}$, $a_{41}$ | 1.4470 | 1.4979 | $a_{14}$, $a_{21}$, $a_{42}$ | 1.1328 | 1.7578 | $a_{23}$, $a_{34}$, $a_{41}$ | 1.2923 | 1.3686 |
| $a_{12}$, $a_{24}$, $a_{43}$ | 1.3510 | 0.6922 | $a_{14}$, $a_{21}$, $a_{43}$ | 0.7814 | 1.3714 | $a_{23}$, $a_{34}$, $a_{42}$ | 0.6299 | 1.4208 |
| $a_{12}$, $a_{31}$, $a_{32}$ | 1.3349 | 0.8083 | $a_{14}$, $a_{21}$, $a_{43}$ | 0.9712 | 1.4903 | $a_{23}$, $a_{41}$, $a_{42}$ | 1.4832 | 1.2597 |
| $a_{12}$, $a_{31}$, $a_{34}$ | 1.4541 | 0.6830 | $a_{14}$, $a_{23}$, $a_{24}$ | 1.1962 | 1.6479 | $a_{23}$, $a_{41}$, $a_{43}$ | 1.3702 | 1.5727 |
| $a_{12}$, $a_{31}$, $a_{42}$ | 1.0267 | 0.5545 | $a_{14}$, $a_{23}$, $a_{31}$ | 1.1257 | 0.8802 | $a_{23}$, $a_{42}$, $a_{43}$ | 0.7975 | 1.5907 |
| $a_{12}$, $a_{31}$, $a_{43}$ | 1.0192 | 0.6663 | $a_{14}$, $a_{23}$, $a_{34}$ | 1.2449 | 1.9016 | $a_{24}$, $a_{31}$, $a_{32}$ | 1.4483 | 0.8493 |
| $a_{12}$, $a_{32}$, $a_{34}$ | 0.9140 | 0.7016 | $a_{14}$, $a_{23}$, $a_{42}$ | 1.0769 | 1.5112 | $a_{24}$, $a_{31}$, $a_{34}$ | 1.4313 | 1.5909 |
| $a_{12}$, $a_{32}$, $a_{41}$ | 1.2216 | 0.7300 | $a_{14}$, $a_{23}$, $a_{43}$ | 1.4337 | 1.6298 | $a_{24}$, $a_{31}$, $a_{41}$ | 1.5657 | 1.4390 |
| $a_{12}$, $a_{32}$, $a_{43}$ | 1.5837 | 1.5403 | $a_{14}$, $a_{24}$, $a_{31}$ | 1.3931 | 1.6295 | $a_{24}$, $a_{31}$, $a_{43}$ | 1.6309 | 0.8901 |
| $a_{12}$, $a_{34}$, $a_{41}$ | 1.2813 | 1.5961 | $a_{14}$, $a_{24}$, $a_{32}$ | 1.3429 | 1.4482 | $a_{24}$, $a_{32}$, $a_{34}$ | 1.2701 | 1.7004 |
| $a_{12}$, $a_{34}$, $a_{42}$ | 0.9228 | 1.5342 | $a_{14}$, $a_{31}$, $a_{32}$ | 1.5299 | 1.0203 | $a_{24}$, $a_{32}$, $a_{41}$ | 1.4705 | 1.6551 |
| $a_{12}$, $a_{41}$, $a_{42}$ | 1.1186 | 1.3631 | $a_{14}$, $a_{31}$, $a_{34}$ | 1.0965 | 1.6776 | $a_{24}$, $a_{32}$, $a_{43}$ | 1.5599 | 0.6882 |
| $a_{12}$, $a_{41}$, $a_{43}$ | 1.4192 | 0.7343 | $a_{14}$, $a_{31}$, $a_{42}$ | 1.1758 | 1.5240 | $a_{31}$, $a_{32}$, $a_{41}$ | 1.2872 | 0.6448 |
| $a_{12}$, $a_{42}$, $a_{43}$ | 1.2794 | 1.5520 | $a_{14}$, $a_{31}$, $a_{43}$ | 1.3401 | 0.8159 | $a_{31}$, $a_{32}$, $a_{42}$ | 0.8920 | 1.3529 |
| $a_{13}$, $a_{14}$, $a_{23}$ | 1.4353 | 0.7765 | $a_{14}$, $a_{32}$, $a_{34}$ | 0.6169 | 2.0213 | $a_{31}$, $a_{34}$, $a_{41}$ | 1.3537 | 1.5159 |
| $a_{13}$, $a_{14}$, $a_{24}$ | 1.4625 | 1.4150 | $a_{14}$, $a_{32}$, $a_{42}$ | 0.9961 | 1.4331 | $a_{31}$, $a_{34}$, $a_{42}$ | 0.8248 | 0.6240 |
| $a_{13}$, $a_{14}$, $a_{32}$ | 0.8451 | 1.5061 | $a_{14}$, $a_{32}$, $a_{43}$ | 0.6386 | 0.7289 | $a_{32}$, $a_{41}$, $a_{42}$ | 1.2980 | 1.2755 |
| $a_{13}$, $a_{14}$, $a_{34}$ | 1.2636 | 1.5666 | $a_{21}$, $a_{23}$, $a_{31}$ | 1.4295 | 0.9216 | $a_{31}$, $a_{41}$, $a_{43}$ | 1.3331 | 0.8004 |
| $a_{13}$, $a_{14}$, $a_{42}$ | 1.2128 | 1.4268 | $a_{21}$, $a_{23}$, $a_{34}$ | 1.5391 | 1.4882 | $a_{31}$, $a_{42}$, $a_{43}$ | 1.6976 | 1.5420 |
| $a_{13}$, $a_{14}$, $a_{43}$ | 1.1798 | 0.7535 | $a_{21}$, $a_{23}$, $a_{41}$ | 1.3146 | 1.4044 | $a_{32}$, $a_{34}$, $a_{41}$ | 0.9185 | 0.7889 |
| $a_{13}$, $a_{21}$, $a_{23}$ | 1.3137 | 0.6931 | $a_{21}$, $a_{23}$, $a_{43}$ | 2.3899 | 0.6936 | $a_{32}$, $a_{34}$, $a_{42}$ | 0.8181 | 1.5044 |
| $a_{13}$, $a_{21}$, $a_{24}$ | 1.3427 | 0.8461 | $a_{21}$, $a_{24}$, $a_{31}$ | 1.4348 | 0.8562 | $a_{32}$, $a_{41}$, $a_{42}$ | 1.4053 | 1.4357 |
| $a_{13}$, $a_{21}$, $a_{32}$ | 1.0797 | 0.7603 | $a_{21}$, $a_{24}$, $a_{34}$ | 1.2175 | 1.5600 | $a_{32}$, $a_{41}$, $a_{43}$ | 1.3837 | 0.6888 |
| $a_{13}$, $a_{21}$, $a_{34}$ | 1.3215 | 0.7726 | $a_{21}$, $a_{24}$, $a_{41}$ | 1.4190 | 1.4552 | $a_{32}$, $a_{42}$, $a_{43}$ | 2.1280 | 1.5574 |
| $a_{13}$, $a_{21}$, $a_{42}$ | 1.0144 | 0.6785 | $a_{21}$, $a_{24}$, $a_{43}$ | 1.5074 | 0.7620 | | | |

of closure equations is one for ternary, three for quaternary and six for quinary system, which is the same as calculated from the expression given by Hala [1972]. The UNIQUAC and NRTL binary interaction parameters for three ternary and one quaternary system have been estimated with and without incorporating the closure equations. It has been observed that the both UNIQUAC and NRTL parameters obtained with the closure equations taken into account exhibit better *rmsd* values than those obtained without the closure equations for the ternary as well as the quaternary system. The *rmsd* values for the parameters with the closure equations have been found to be dependent of the selected set of parameters for elimination. It is, therefore, concluded that a good prediction of liquid-liquid equilibria requires the UNIQUAC and NRTL binary interaction parameters that satisfy the closure equations.

## APPENDIX A

A quaternary system may be considered of consisting of four ternary triplet ,namely 1-2-3, 1-2-4, 2-3-4 and 1-3-4. Using equation Closure equations, the corresponding to these triplets are

$$\text{for 1-2-3} \quad a_{12}-a_{21}+a_{23}-a_{32}+a_{31}-a_{13}=0 \tag{A.1}$$

$$\text{for 1-2-4} \quad a_{12}-a_{21}+a_{24}-a_{42}+a_{41}-a_{14}=0 \tag{A.2}$$

$$\text{for 2-3-4} \quad a_{23}-a_{32}+a_{34}-a_{43}+a_{42}-a_{24}=0 \tag{A.3}$$

$$\text{for 1-3-4} \quad a_{13}-a_{31}+a_{34}-a_{43}+a_{41}-a_{14}=0 \tag{A.4}$$

Eqs. (A.1)-(A.4) are linearly dependent and each equation can be written as a linear combination of the remaining three equations. It can be easily seen that

$$(A.4)=-(A.1)+(A.2)+(A.3) \tag{A.5}$$

Hence Eqs. (A.1)-(A.3) are linearly independent equations. These are same as Eqs. (38)-(40) hence be the closure equations for a quaternary system.

Similarly, a quinary system may be considered as consisting of ten ternary triplets, namely 1-2-3, 1-2-4, 1-2-5, 2-3-4, 2-3-5, 2-4-5, 1-3-4, 1-3-5, 1-4-5 and 3-4-5. Closure equations corresponding to these triplets are

$$\text{for 1-2-3} \quad a_{12}-a_{21}+a_{23}-a_{32}+a_{31}-a_{13}=0 \tag{A.6}$$

$$\text{for 1-2-4} \quad a_{12}-a_{21}+a_{24}-a_{42}+a_{41}-a_{14}=0 \tag{A.7}$$

$$\text{for 1-2-5} \quad a_{12}-a_{21}+a_{25}-a_{52}+a_{51}-a_{15}=0 \tag{A.8}$$

$$\text{for 2-3-4} \quad a_{23}-a_{32}+a_{34}-a_{43}+a_{42}-a_{24}=0 \tag{A.9}$$

$$\text{for 2-3-5} \quad a_{23}-a_{32}+a_{35}-a_{53}+a_{52}-a_{25}=0 \tag{A.10}$$

$$\text{for 2-4-5} \quad a_{24}-a_{42}+a_{45}-a_{54}+a_{52}-a_{25}=0 \tag{A.11}$$

$$\text{for 1-3-4} \quad a_{13}-a_{31}+a_{34}-a_{43}+a_{41}-a_{14}=0 \tag{A.12}$$

$$\text{for 1-3-5} \quad a_{13}-a_{31}+a_{35}-a_{53}+a_{51}-a_{15}=0 \tag{A.13}$$

$$\text{for 1-4-5} \quad a_{14}-a_{41}+a_{45}-a_{54}+a_{51}-a_{15}=0 \tag{A.14}$$

$$\text{for 3-4-5} \quad a_{34}-a_{43}+a_{45}-a_{54}+a_{53}-a_{35}=0 \tag{A.15}$$

Only six of the above ten Eqs. (A.6)-(A.15) are linearly independent. Hence any four equations can be expressed as the linear combination of the remaining six equations. Again it can be shown that the last four equations can be expressed as

$$(A.13)=-(A.7)+(A.10)+(A.8) \tag{A.16}$$

$$(A.14)=-(A.7)+(A.11)+(A.9) \tag{A.17}$$

$$(A.15)=-(A.13)+(A.12)+(A.9) \tag{A.18}$$

$$(A.16)=(A.10)+(A.12)+(A.11) \tag{A.19}$$

The linearly independent Eqs. (A.6)-(A.11) are same as Eqs. (62)-(67) and are therefore the required closure equations for a quinary system.

## NOMENCLATURE

$a_{ij}$ : binary interaction parameters [K]
c : total number of components
**e** : error vector of measured variables
$g^E$ : excess Gibbs free energy
g : NRTL energy interaction term [J/mol]
L : likelihood function
m : total number of tie lines
n : total number of measured variables
q : surface or area parameter
r : volume or segment parameter
*rmsd* : root mean square deviation
R : universal gas constant [J/mol-K]
T : absolute temperature [K]
u : UNIQUAC energy interaction term [J/mol]
**V** : variance-covariance matrix of errors
x : experimental composition, mole fraction
$\hat{x}$ : predicted composition, mole fraction
Z : lattice coordination number

### Greek Letters

$\alpha$ : non randomness Parameter in NRTL model
$\gamma$ : activity coefficient
$\theta$ : surface or area fraction
$\boldsymbol{\theta}$ : vector of parameters
$\phi$ : volume or segment fraction
$\tau_{ij}$ : adjustable binary parameter in NRTL and UNIQUAC models

### Subscripts

i : component
j : component
k : tie line

### Superscript

j : phase

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