

## TERNARY LIQUID-LIQUID PHASE BEHAVIOR BY DECORATED-UNIQUAC

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**Abstract** - To investigate the applicability of the decorated-UNIQUAC model for multicomponent multiphase liquid mixtures, equilibrium calculations were carried out for a variety of model ternary systems, and some typical predictions were introduced. The predicted phase behavior was less limited and more complicated than that of UNIQUAC without disagreement with experimental observations on the progressional behavior of tie lines. The binodal predictions were found very sensitive with respect to the model parameters, as expected in condensed phases. The general features of non-island type of ternary LLE were excellently reproduced by the decorated-UNIQUAC.

*Key words:* Decorated-UNIQUAC, LLE, Multicomponent, Multiphase, Equilibrium

### INTRODUCTION

Multicomponent multiphase liquid-liquid equilibrium data are of fundamental importance in the design and/or in the optimal operation of chemical processes. However, in reality, the reliable experimental data themselves are not sufficient to be used for the complete requirements of process engineering. A variety of equilibrium models are frequently used to predict the phase equilibria in wide range of process variables from these limited reliable experimental data [Sandler, 1993; Prausnitz et al., 1986; Modell and Reid, 1983; Francis, 1963; Rowlinson and Swinton, 1959]. It is well-known, however, that they cannot afford all kinds of phase diagrams and their applications are also limited to some categories of phase behaviors [Mollerup, 1981; Van Konynenberg and Scott, 1980; Furman and Griffiths, 1978]. These models are highly non-linear with respect to the model parameters, and the sensitivities in the binodal predictions are very different according to the selected models. For the model which is not sensitive to the model parameters, the predicted phase behavior can be inconsistent with the experimental observations, in the overall sense, due to the used model parameters are often located in the extended parameter subspace, physically meaningless or forbidden [Wheeler and Anderson, 1980; Anderson and Wheeler, 1978a; Mulholland and Rehr, 1974]. If the model is too sensitive, its applications may be limited because of the practical difficulty in the experimental data reduction to get the optimal model parameters in numerical way [Kemeny et al., 1982; Prausnitz et al., 1980; Varhegyi and Eon, 1977]. Various studies have been made to develop the equilibrium models reproducing a variety of phase behaviors including, in particular, the characteristic features of the systems of concern, with proper sensitivity [Skjold-Jørgensen et al., 1980; Anderson and Wheeler, 1978b; Abrams and Prausnitz, 1975]. Therefore, in the equilibrium simulation of a

specific system, it is prerequisite to examine whether the chosen proposed models can predict the phase equilibria of interest with appropriate model parameters or not.

In the calculation of phase equilibria for non-ideal liquid mixtures at low pressure, highly non-linear activity models are often used to take account of the deviation from the ideality [Sandler, 1993; Prausnitz et al., 1986; Modell and Reid, 1983; Rowlinson and Swinton, 1959]. Most of the well-established activity models are lattice-based assuming the analyticity of the partition function and the additivity of the free energy, and they are usually modified in minor, on the basis of their original mathematical structure, to enhance their predictability and to control the sensitivity in predictions [Prausnitz et al., 1986; Mollerup, 1981; Abrams and Prausnitz, 1975; Rowlinson and Swinton, 1959]. Van Konynenberg and Scott [1980], examining the van der Waals model, successfully manipulated the various types of phase diagrams, indicating that the mean field approximation of lattice model well represents the nature of the statistics and the intermolecular forces in overall schemes except those of the type VI, the closed-loop phase diagrams of binary mixtures, e.g., aqueous surfactant solutions [Lang and Morgan, 1980] and pyridine derivative solutions [Kim and Kim, 1986].

UNIQUAC, one of the solution models, has been applied to the predictions of phase equilibria, and the types of its predictable phase behavior are well-known [Prausnitz et al., 1980]. In some cases, however, its applicability is inherently limited. In the liquid-liquid equilibrium calculations, in spite of the accurate reproduction of the experimental equilibrium data in some simple systems governed by the classical interactions, UNIQUAC cannot predict complex phase behavior of the non-classical systems in which the formation of molecular structure cannot be ignored, e.g., hydrogen bonding or chemical complexes [Kim and Kim, 1986; Kim, 1985]. For these systems, many models and methods for the phase equilibrium calculations have been devised [Cheluget et al., 1993; Hino et al., 1993; Hu

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et al., 1991; Jung and Jhon, 1984; Goldstein, 1986, 1985; Goldstein and Walker, 1983; Vause and Walker, 1982; Anderson and Wheeler, 1978a, 1978b]. All these works make use of rigorous statistical mechanical calculation procedures which are limited only to binary systems, and they are considered very difficult to be transformed into corresponding solution models like UNIQUAC. Although these statistical mechanical procedures can provide precise binodal structure numerically in the critical region governed by the singular point, their equilibrium predictions are restricted to the binary one or two phase systems due to the complexity in the above transformations. On the other hand, the UNIQUAC model, one of the promising solution models, can be applied to the multicomponent multiphase systems in principle [Prausnitz et al., 1980; Abrams and Prausnitz, 1975]. The decorated-UNIQUAC model [Kim et al., 1989; Kim and Kim, 1988], developed by the authors, is expected to be able to predict the multicomponent multiphase liquid-liquid equilibria, because it is inherently one of the activity models possessing the mathematical structure of UNIQUAC, even though it represents the orientational statistics in the microscopic molecular world, e.g., the hydrogen bonding. To the best of the authors' knowledge, there is no works for the multicomponent multiphase equilibrium predictions of the systems in which some kinds of molecular structure formation are involved. The immiscibility gap predicted by UNIQUAC changes simply with temperature [Kim 1985; Skjold-Jørgensen et al., 1980; Prausnitz et al., 1980]. However, it is naturally considered that the decorated-UNIQUAC model, which successfully reproduces the type VI phase behavior, guarantees much more complicated and general temperature dependence of the coexisting region than UNIQUAC [Kim, 1988]. As shown in the Meijering's works [1950, 1951] of arbitrary expansions of the isothermal regular ternary solution model, the phase behavior in the multicomponent multiphase systems may exhibit topologically various internal structures in phase space. In particular, unexpected internal phase structure, which is not found in the constituting binary phase diagrams, may appear [Becker and Richter, 1989; Wisniak, 1984; Robard and Patterson, 1977; Zeman and Patterson, 1972; Meijering, 1950, 1951]. In the course of developing the decorated-UNIQUAC model, authors have performed not a few trial calculations for the model ternary systems, for the model characterization, such as testing the predictable types of liquid-liquid equilibria and the sensitivity with respect to the model parameters, together with comparing the equilibrium calculations by UNIQUAC. In this paper, typical ternary predictions for some model systems constructed by the decorated-UNIQUAC model will be introduced, and their distinguishing features will be compared with those of the UNIQUAC model.

### UNIQUAC MODEL FOR CONDENSED PHASES

The model of UNIQUAC is based on the concepts of volume fraction and the local compositions: it recognizes the molecular geometric difference with their volume and surface area [Prausnitz et al., 1986; Abrams and Prausnitz, 1975]. Molecules are assumed as a polysegment, the linear chain of constituting moieties, ignoring the connectivity. The molecular size

and shape are characterized as each sum of the segment volume and surface area which are proportional to the molecular van der Waals volume and surface area, respectively. The numerical values of these molecular parameters are the multiples of those of standard segments. The molecules are assumed to exist in the state of non-uniform microscopic mixing. The model equations can be derived, through the statistical mechanical procedure, from the lattice model incorporating the physicochemistry of UNIQUAC.

The first derivation of the highly non-linear expressions of UNIQUAC for activity coefficients was performed with quasi-chemical approximation for the partition function and the neglect of the pressure-volume contribution [Abrams and Prausnitz, 1975]. However, convenient derivation is available using two-fluid theory [Maurer and Prausnitz, 1978]. Applying the Wilson's assumption [Wilson, 1964] to the molar excess internal energy, Eqs. (1)-(6) are obtained for the expressions of excess Gibbs free energy change of mixing and activity coefficients, respectively.

$$\left(\frac{\Delta g^E}{RT}\right) = x_1 \ln \left(\frac{\Phi_1}{x_1}\right) + x_2 \ln \left(\frac{\Phi_2}{x_2}\right) + \frac{1}{2} z \left\{ q_1 x_1 \ln \left(\frac{\theta_1}{\Phi_1}\right) + q_2 x_2 \ln \left(\frac{\theta_2}{\Phi_2}\right) \right\} - x_1 q_1 \ln(\theta_1 + \theta_2 \tau_{21}) - x_2 q_2 \ln(\theta_2 + \theta_1 \tau_{12}) \quad (1)$$

where,

$$\tau_{21} = \exp \left( \frac{-\Delta u_{21}}{RT} \right) \quad (2)$$

$$\tau_{12} = \exp \left( \frac{-\Delta u_{12}}{RT} \right) \quad (3)$$

$$\Phi_k = \frac{x_k r_k}{\sum_s x_s r_s} \quad (4)$$

$$\theta_k = \frac{x_k q_k}{\sum_s x_s q_s} \quad (5)$$

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \left(\frac{z}{2}\right) q_i \ln \frac{\theta_i}{\Phi_i} + \Phi_j \left( l_i - \frac{r_i}{r_j} l_j \right) - q_i \ln(\theta_i + \theta_j \tau_{ji}) + \theta_j q_j \left( \frac{\tau_{ji}}{\theta_i + \theta_j \tau_{ji}} - \frac{\tau_{ij}}{\theta_j + \theta_i \tau_{ij}} \right) \quad (6)$$

where,

$$(i, j) = (1, 2) \text{ or } (2, 1)$$

and

$$l_k = \frac{z}{2} (r_k - q_k) - (r_k - 1) \quad (k=1, 2) \quad (7)$$

The exactly derived, as above, original UNIQUAC equations were not successful in the expected precise reproduction of the

phase equilibria [Abrams and Prausnitz, 1975]. The introduction of the additional term including the third semi-adjustable molecular parameter was recommended, and the UNIQUAC model, in this extended form as shown in the Eq. (8), has been widely applied to the calculations for a variety of mixtures with improved accuracy [Prausnitz et al., 1980]. Equating the third molecular parameter with the molecular surface area parameter makes the extended UNIQUAC equations reduce to the original ones. However, even with these modifications, it is considered impossible to overcome the problem of limited applicability: the phase behavior observed in the polymer solutions and of the type VI cannot be reproduced by the extended UNIQUAC [Kim, 1985, 1988; Skjold-Jørgensen et al., 1980, Prausnitz et al., 1980].

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \left(\frac{z}{2}\right) q_i \ln \frac{\theta_i}{\Phi_i} + \Phi_j \left( l_i - \frac{r_i}{r_j} l_j \right) - q_i' \ln(\theta_i' + \theta_j' \tau_{ji}) + \theta_j' q_i' \left( \frac{\tau_{ji}}{\theta_i' + \theta_j' \tau_{ji}} - \frac{\tau_{ij}}{\theta_j' + \theta_i' \tau_{ij}} \right) \quad (8)$$

where,

$$(i, j) = (1, 2) \text{ or } (2, 1)$$

and

$$\theta_i' = \frac{x_i q_i'}{x_1 q_1' + x_2 q_2'} \quad (9)$$

### DECORATED-UNIQUAC MODEL

The transformations introducing new site between neighboring sites in lattice models result in new lattice-based models, which are called by the decorated lattice models [Fisher, 1959]. These transformations are not restricted to the lattice models: cell models can be modified to the corresponding decorated ones with similar topological consideration [Wheeler and Anderson, 1980; Anderson and Wheeler, 1979, 1978a, 1978b; Mulholland et al., 1975; Wheeler, 1975; Mulholland and Rehr, 1974; Zollweg and Mulholland, 1972; Mermin 1971; Widom, 1967]. In the decorated lattice models, two sets of sublattice (sites) coexist, i.e., primary lattice (sites) of the original lattice, and the secondary lattice (sites) of the decorated one [Fisher, 1957]. The statistical mechanical relations are well known interrelating one lattice model and its decorated ones. Therefore, the decorated lattice models can be inverse-transformed, with the reduction of the lattice degrees of freedom by, e.g., renormalization transformations and/or the effective interactions [McMahon et al., 1988; Goldstein, 1985, 1986; Burkhardt and Van Leeuwen, 1982].

Because of the increased lattice degrees of freedom, the decorated lattice model can accommodate complicated physicochemical phenomena which cannot be simulated by the lattice models. Furthermore, the inherent interactional symmetries of the lattice models can be broken, by the difference in the coordination numbers of the primary and secondary lattices of the decorated lattice models, and therefore, they are able to reproduce the physical chemistry of asymmetric interactions found

in nature [Fisher, 1959].

By inserting the secondary lattice elements between the neighboring (primary) UNIQUAC lattice sites, the lattice for decorated-UNIQUAC was constructed [Kim and Kim, 1988]. Orientational interactions were permitted to the entities occupying the decoration cells, in addition to the classical non-directional interactions. To make the combinatorics consistent, the entities in the secondary decorated cells were assumed to be ghost molecules, with the same characteristics of real molecules except the mass. That is to say, they exert their influence over the neighboring primary lattice cells just like ghost field which cannot be counted [Burkhardt and Van Leeuwen, 1982; Reynolds et al., 1977, 1978, 1980]. Physically, the effects of higher order interactions may be lumped into the decorated lattice cell contributions [Elrod and Saykally, 1994; Reichl, 1980]. The renormalized primary interactions between the nearest neighboring sites of the reduced UNIQUAC lattice are determined by the parameters of secondary decorated lattice elements and the original interactions [Kim and Kim, 1988; Burkhardt and Van Leeuwen, 1982]. Lattice coordination was relaxed to that of hyper-dimensionality for the proper balance of prediction sensitivity of the decorated-UNIQUAC which is constructed from the models of a different nature. The number of directionally active sites (or arrows) is different molecule by molecule [Barker and Fock, 1953; Barker, 1952]. However, it was simplified that a molecular segment has one or two directionally active site(s), according to the molecular structure. The directionality,  $\omega$ , representing the number of possible orientations for a directionally active site of segments, was assumed to be proportional to  $q$ , and the reference value of  $\omega$  was parametrized to a constant of 9000. In case that there are two directionally active sites for a segment, the number of possible orientations of the second site is restricted by the segment geometry, the angle,  $\psi$ , between the sites, as shown in Fig. 1. Interactions were classified to directional ones ( $E_d$ ) and non-directional ones ( $e_n$ ) according to their dependence on molecular orientation. Eq. (10) shows the renormalization transformations between the specific UNIQUAC variables and the partition functions for the primary bond of the decorated-UNIQUAC model [Kim and Kim, 1988].

$$\tau_{ij} = \frac{Q_{jj}}{Q_{ij}} \quad (10)$$

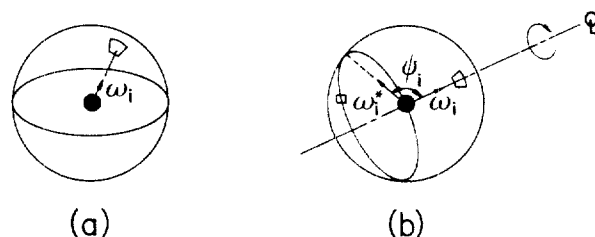


Fig. 1. (a) Directionality of a molecular segment having only one directionally active site; (b) directionalities of a molecular segment having two directionally active sites. The directionality of the second site,  $\omega_i'$  is determined by segment geometry,  $\psi$ .

where, the partition functions for the primary bonds are given by

$$Q_{ij} = Q_{i2j} + \zeta Q_{i1j} \tag{11}$$

and  $\zeta$ , the fugacity ratio satisfies the following nonlinear equality:

$$\zeta \left( \frac{W_1}{W_2} \right) \left( \frac{Q_{11}}{Q_{22}} \right)^3 - 1 = 0 \tag{12}$$

where the total segment directionalities,  $W_i$ 's are determined by Eq. (13), depending on the number of directionally active site(s) per segment of component  $i$ .

$$W_i = \delta_{\eta_i,1} \omega_i + \delta_{\eta_i,2} \frac{\omega_i \omega_i^*}{2} \tag{13}$$

The partition functions for decorated cells are represented by the original interactions, as shown in Eq. (14) and Table 1:

$$Q_{ikj} = \sum_{\sigma} g(\mathbf{k}, \sigma) \exp \left\{ - \frac{E(\mathbf{k}, \sigma)}{RT} \right\} \tag{14}$$

The activity coefficient expressions of the decorated-UNIQUAC model are not different from those of the UNIQUAC model except the fact that the UNIQUAC variables,  $\tau_{ij}$ , are determined by Eq. (10). This type of transformation is different, in essence, from the arbitrary polynomial expansions of temperature dependence. Physically, the transformations, Eq. (10), are the mathematical mappings of the effects of multi-bodies and the orientation of molecular segments in the decorated lattice model onto the UNIQUAC model. The expressions in the forms of the excess Gibbs free energy change of mixing and the activity coefficients were already introduced in the Eqs. (1), (6), or (8), which are useful in equilibrium calculations.

### LLE PREDICTIONS FOR MULTICOMPONENT MULTIPHASE SYSTEMS

The calculations of multicomponent multiphase liquid-liquid equilibria are the procedures getting the physical solutions from the simultaneous equations of the same fugacity values for each component distributed in the coexisting phases [Sandler, 1993; Modell and Reid, 1983]. In a numerical sense, these calculations are very similar to the flash VLE calculations. The convenient iteration variables are the equilibrium ratio for each component and the phase split ratio of the mass in the feed stream. The well-known Newton-Raphson iteration, is applied,

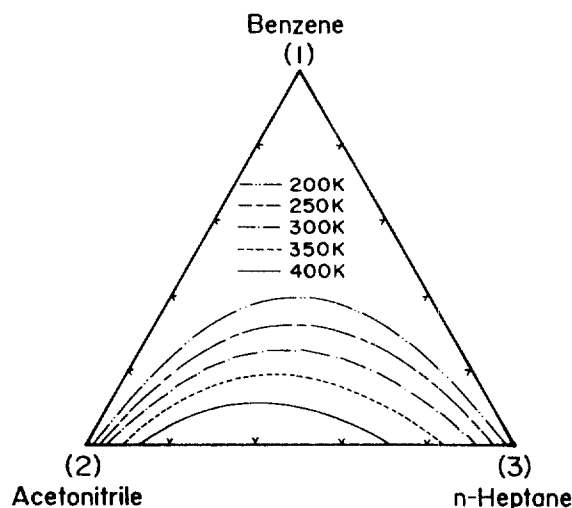
**Table 1. Degeneracies,  $g(\mathbf{k}, \sigma)$ , and interactional energies for the decorated cell partition function,  $Q_{ikj}$ , depending on the configuration of a  $\mathbf{k}$ -ghost molecular segment,  $\sigma$ , in the decorated cell**

$\sigma$	$g(\mathbf{k}, \sigma)$	$E(\mathbf{k}, \sigma)$
i)	$\delta_{\eta_k,2}$	$E_k + E_{ij} + e_{ij} + e_{ij}$
ii)	$\delta_{\eta_k,2} (\omega_k^* - 1) + \delta_{\eta_k,1}$	$E_k + e_{ij} + e_{ij}$
iii)	$\delta_{\eta_k,2} (\omega_k^* - 1) + \delta_{\eta_k,1}$	$E_{ij} + e_{ij} + e_{ij}$
iv)	$\delta_{\eta_k,2} \{ (\omega_k \omega_k^* / 2) - 2(\omega_k^* - 1) \} + \delta_{\eta_k,1} (\omega_k - 1)$	$e_{ij} + e_{ij}$

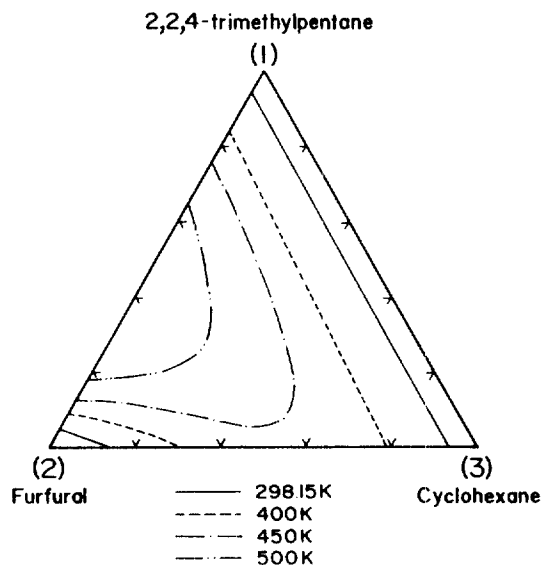
$$\omega_k^* = \sqrt{\omega_k} \pi \cdot \sin \psi_k$$

usually in a modified form to accelerate the convergence, e.g., the Wegstein's acceleration [Wegstein, 1955]. This type of iteration guarantees the fast convergence to the binodal compositions except those under the influence of a critical (or plait) point [Kim, 1985]. The subject of robust initial guess for the equilibrium compositions is a matter worthwhile to be studied extensively [Kwon and Park, 1995].

As mentioned above, UNIQUAC can predict only the LLE behaviors of the simple systems exhibiting simple topological coexistence plane in phase space. The calculated examples are shown in Figs. 2 and 3 exhibiting the temperature dependence of the ternary liquid-liquid equilibria predicted by the original UNIQUAC [Eqs. (1), (2)]. In Fig. 2, the phase diagrams of benzene (component 1)-acetonitrile (component 2)-n-heptane (component 3) at different temperatures are projected at the same



**Fig. 2. Change of the liquid-liquid coexistence curves wrt. temperature for the ternary system of benzene-acetonitrile-n-heptane predicted with UNIQUAC.**



**Fig. 3. Change of the liquid-liquid coexistence curves wrt. temperature for the ternary system of 2,2,4-trimethylpentane-furfural-cyclohexane predicted with UNIQUAC.**

planar triangle. Fig. 3 shows the similar equilibrium calculations for the system of 2,2,4-trimethylpentane (component 1)-furfural (component 2)-cyclohexane (component 3). The molecular and interactional parameters used in these calculations are listed in Table 2. Just like the case of the van der Waals model [Van Konynenberg and Scott, 1980], the UNIQUAC model predicts only the phase behavior governed by the simple interactions. As shown in Figs. 2 and 3, the UNIQUAC model and the modified one reproduce only the phase behavior having monotonic temperature dependence, i.e., the regional area of partial miscibility increases or decreases monotonically with the change of temperature. Furthermore, the predictability of the UNIQUAC model is topologically restricted to the simple case of no cross-over of the coexistence curves projected onto the isothermal plane in the phase space of temperature-com-

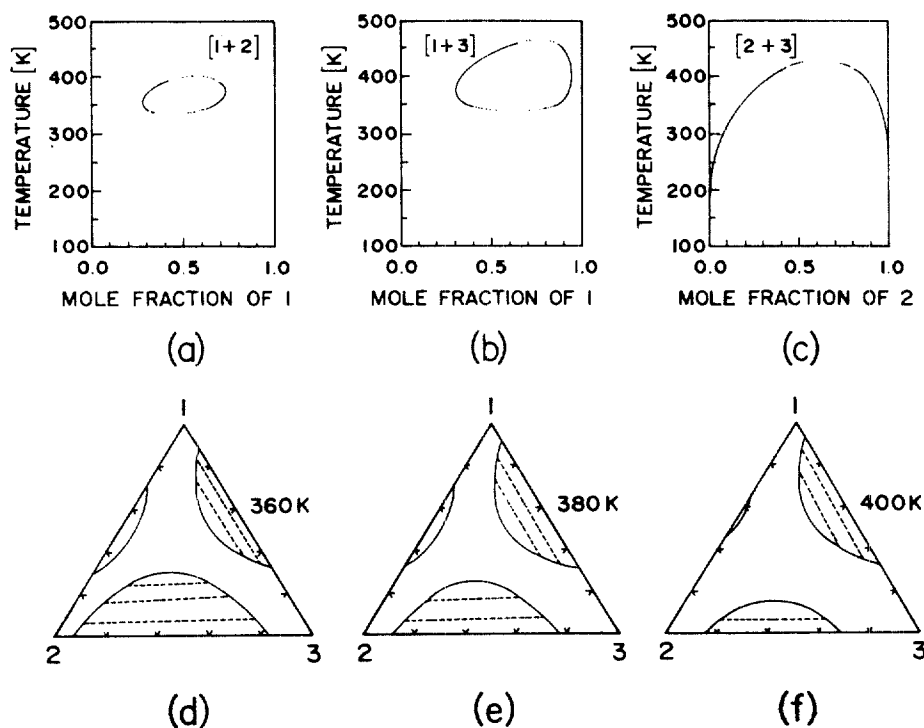
position prism [Kim, 1988].

To the best of the authors' knowledge, there is no adequate literature reporting the complicated change of the multicomponent multiphase behavior with temperature for the systems in which the effects of the molecular orientation become important. However, it is not difficult to analogize the whole ternary phase behavior out of those of the constituting binary pairs. To set up the prediction boundary of the decorated-UNIQUAC model, not a few multicomponent multiphase calculations were performed for the several assumed model systems. The typical calculations are shown in Figs. 4, 5, and 6, for the model ternary systems. In these figures, 2-3 binary pairs were assumed to experience no directional interaction, and therefore they exhibit classical type of binary T-x diagrams with no lower critical solution temperature. Component 1 was given two directionally active sites per segment, in contrast to only one active site per segment permitted to molecules 2 and 3. Figs. 4 to 6 show calculated phase envelopes which can be usually observed in real ternary mixtures. For each model mixture, three T-x diagrams of three binary pairs were drawn from a given set of interaction energies,  $\{E_{ij}, e_{ij}\}$ , and the isothermal binodal compositions were calculated at some system temperatures. The molecular and interactional parameters are listed in Table 3, together with the number of the directionally active sites per segment. The angle  $\psi_i$  was assumed to be that of the  $sp^3$  hybrid orbital, as in case of water. In the figures, the smooth and flexible penetrations are observed from the binary phase boundaries toward the inner-prism phase space. Because of the poor convergence in the vicinity of the plait points [Sadus, 1994; Prausnitz et al., 1980], the phase boundaries in the critical re-

**Table 2. Molecular and interactional parameters used in the LLE calculations of Fig. 2 and 3.**

	Molecular parameters				Binary interaction parameters, $A_{ij}$ [K]			
	$i$	$r_i$	$q_i$	$q'_i$	$i \setminus j$	1	2	3
Fig. 2								
	1	3.19	2.40	2.40	1	-	89.57	-135.93
	2	1.87	1.72	1.72	2	60.28	-	23.71
	3	5.17	4.40	4.40	3	245.42	545.79	-
Fig. 3								
	1	5.85	4.94	4.94	1	-	410.08	141.01
	2	3.17	2.48	2.48	2	-4.98	-	41.17
	3	3.97	3.01	3.01	3	112.66	354.83	-

$$A_{ij} = \Delta u_{ij} / R$$



**Fig. 4. Liquid-liquid phase diagrams constructed by decorated-UNIQUAC for a model ternary mixture {(d), (e) and (f)} and its constituting three binary pairs {(a), (b) and (c)} at different temperatures. Each immiscibility gap in ternary phase diagrams behave independently wrt. temperature.**

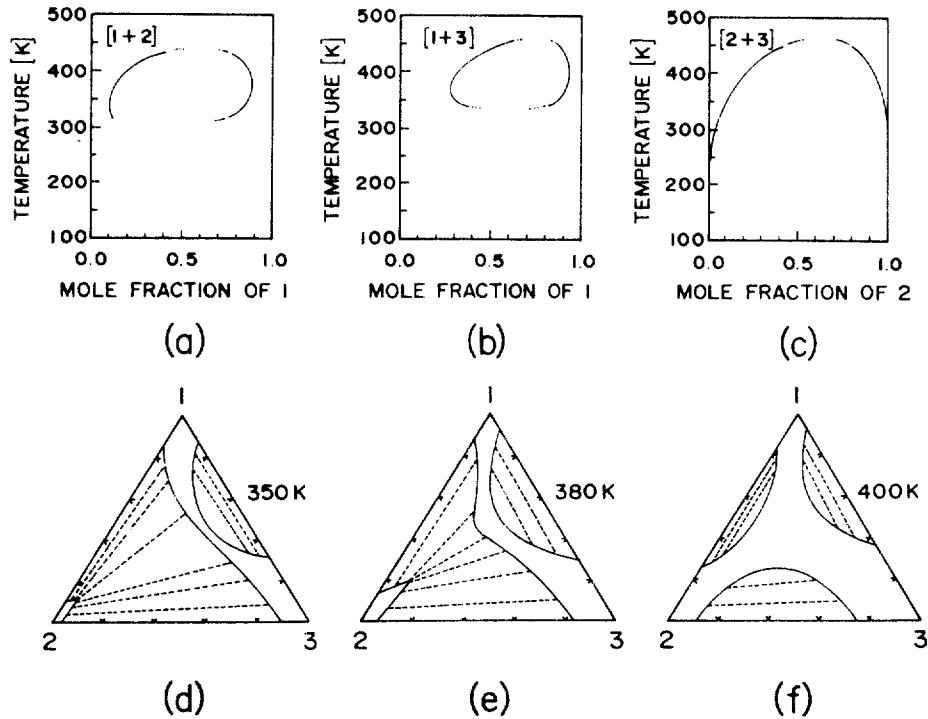


Fig. 5. Liquid-liquid phase diagrams constructed by decorated-UNIQUAC for a model ternary mixture {(d), (e) and (f)} and its constituting three binary pairs {(a), (b) and (c)} at different temperatures. Temperature change exhibits typical merging behavior of the coexistence curves and progressional change of their tie lines.

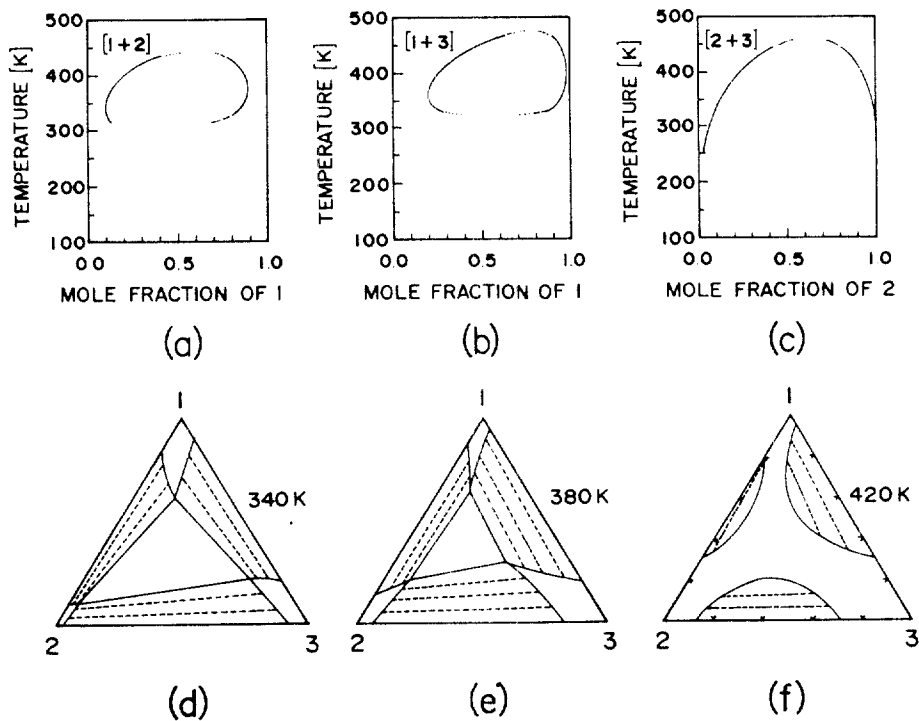


Fig. 6. Liquid-liquid phase diagrams constructed by decorated-UNIQUAC for a model ternary mixture {(d), (e) and (f)} and its constituting three binary pairs {(a), (b) and (c)} at different temperatures. Temperature change results in complex ternary phase behavior involving three phase regions.

gions are the results of the spline interpolation. The location of the critical points is possible with the well-known combination

of the interpolated binodal compositions and the extrapolated diameter of the coexistence curves [Treybal et al., 1946; Hand,

Table 3. Molecular and interactional parameters used in the LLE calculations of Fig. 4, 5 and 6

	Molecular parameters							Directional interactions $E_{ij}$ [k joule/mole]			Nondirectional interactions $e_{ij}$ [k joule/mole]				
	i	$r_i$	$q_i$	$q_i'$	$\omega_i$	$\eta_i$	$\psi_i$	i \ j	1	2	3	i \ j	1	2	3
Fig. 4	1	1.00	2.00	2.00	9000	2	1.911	1	28.16	23.97	25.10	1	2.09	3.35	3.56
	2	2.00	3.00	3.00	13500	1	-	2	-	0.00	0.00	2	-	1.26	4.18
	3	3.00	4.00	4.00	18000	1	-	3	-	-	0.00	3	-	-	1.26
Fig. 5	1	1.00	2.00	2.00	9000	2	1.911	1	28.16	23.97	24.69	1	2.09	3.78	3.35
	2	2.00	3.00	3.00	13500	1	-	2	-	0.00	0.00	2	-	1.26	4.39
	3	3.00	4.00	4.00	18000	1	-	3	-	-	0.00	3	-	-	1.26
Fig. 6	1	1.00	2.00	2.00	9000	2	1.911	1	28.16	23.97	24.69	1	2.09	3.78	3.56
	2	2.00	3.00	3.00	13500	1	-	2	-	0.00	0.00	2	-	1.26	4.39
	3	3.00	4.00	4.00	18000	1	-	3	-	-	0.00	3	-	-	1.26

1930]. For all that, the predicted progressional trends of the tie lines towards the plait points are in accordance with the experimental observations without inconsistency. Temperature evolution of ternary phase envelopes is also consistent with the closed-loops in binary T-x diagrams. As shown in Fig. 5, the immiscibility regions can merge together at suitable conditions, making the plait points vanish, as frequently observed in experimental works [Francis, 1963; Rowlinson and Swinton, 1959]. Particularly, in Fig. 6, three plait points disappear to generate a triangular region where three phases coexist with the apex compositions of the triangle. In these trial calculations for the characteristic test of the decorated-UNIQUAC model, the island type of inner-prism phase structure [Becker and Richter, 1989; Wisniak, 1984; Robard and Patterson, 1977; Zeman and Patterson, 1972; Meijering, 1950, 1951] and the phase diagrams with solutropes [Francis, 1963] have not been observed in the subspace of interactional parameters chosen. However, the possibility of predicting the island curves cannot be excluded, in the sense of the physical chemistry of the island type of phase behavior included in the decorated-UNIQUAC model.

As given in Table 3, the number of orientational active sites of the segment is fixed consistently for each component and binary pairs constituting the system, and therefore, equations for the calculations of the lattice partition functions can be chosen with no ambiguity. It appears, as in Figs. 4 to 6, and Table 3, that the decorated-UNIQUAC is a very sensitive model in the LLE prediction with respect to the energy parameters used, in comparison with other frequently used solution models, e.g., the models of UNIQUAC, NRTL, and Wilson [Abrams and Prausnitz, 1975; Renon and Prausnitz, 1968; Wilson, 1964]. Even the small change of the interaction energies, either directional or non-directional, corresponding to the one to ten percents of thermal mixing energy, makes drastic changes in the phase behavior such as the phase boundaries and the number of coexisting phases. Although similar behavior is often found in the condensed phases [Hirschfelder et al., 1937], practical difficulties on the convergence arise in the reduction procedure of experimental data obtaining optimal interactional adjustables for the decorated-UNIQUAC model. The strength of the hydrogen bonding in liquid phase is known to be in the range of

- 10~ - 30 kjoule/mole [Joesten and Schaad, 1974; Pimentel and McClellan, 1960]. It is expected that the decorated-UNIQUAC can successfully reproduce various more complicated types of ternary phase behavior within the physicochemically meaningful energy parameter subspace, just like the cases for the binary systems [Kim and Kim, 1988].

## CONCLUSIONS

To examine the predictability for the multicomponent multiphase equilibria by the decorated-UNIQUAC, the comparative LLE calculations of non-island types were performed for some real and model ternary systems, after the brief illustration for the physical chemistries on which the UNIQUAC and decorated-UNIQUAC models are based. The characteristics of the decorated-UNIQUAC model were also investigated. It was proved that the decorated-UNIQUAC model can construct the overall phase structure in temperature-composition phase space which cannot be reproduced by other solution models including the (modified) UNIQUAC. The qualitative consistency was also investigated in precise, comparing the predicted inner-prism binodal structures and the merging behaviors accompanying the rearrangement of tie lines with the experimental LLE observations at low pressures. The appearance of three phase domain in phase diagram resulted from the expansions of the partially miscible areas, making the plait points vanish. From these model calculations, we conclude the decorated-UNIQUAC model well-represents the general features found in the phase diagrams of ternary liquid mixtures.

Although the decorated-UNIQUAC model possesses the predictability for the multicomponent multiphase LLE within the physicochemically meaningful range of the parameter subspace with high sensitivity, it seems to be worthwhile, for engineering practice, developing the modified decorated-UNIQUAC model in the direction of relieving the model sensitivity, as in the case of UNIQUAC. The predictability for the island type of isothermal ternary phase diagrams with this model is considered to be worthwhile to study hereafter for low molecular and/or polymeric solutions. Authors prospect that some kind of testable experimental equilibrium data will be available in near

future, and then the experimental phase diagrams will be, at least, fairly reconstructed with this decorated-UNIQUAC model on the basis of this work.

### NOMENCLATURE

- $A_{ij}$  : adjustable energy parameters in UNIQUAC, defined as  $\Delta u_{ij}/R$  [K]  
 $e_{ij}$  : non-directional interaction energy between segments  $i$  and  $j$  [joule/mole]  
 $E$  : interaction energy between segments [joule/mole]  
 $E_{ij}$  : directional interaction energy between segments  $i$  and  $j$  [joule/mole]  
 $g$  : degeneracy [dimensionless]  
 $\Delta g^E$  : excess molar Gibbs free energy change of mixing [joule/mole]  
 $l_i$  : quantity defined by Eq. (7) [dimensionless]  
 $q_i$  : molecular surface area parameter of UNIQUAC [dimensionless]  
 $q'_i$  : additional molecular parameter of UNIQUAC [dimensionless]  
 $Q_{ij}$  : partition function for primary bond connecting molecular segments  $i$  and  $j$  [dimensionless]  
 $Q_{kij}$  : partition function for decorated ghost molecular segment  $k$  between real segments  $i$  and  $j$  [dimensionless]  
 $R$  : gas constant [joule/(mole · K)]  
 $r_i$  : molecular volume parameter of UNIQUAC [dimensionless]  
 $T$  : absolute temperature [K]  
 $\Delta u_{ij}$  : UNIQUAC interaction energy parameters [joule/mole]  
 $W_i$  : total segment directionality of component  $i$  [dimensionless]  
 $x_i$  : mole fraction of component  $i$  [dimensionless]  
 $z$  : coordination number of UNIQUAC lattice [dimensionless]

### Greek Letters

- $\gamma_i$  : activity coefficient of component  $i$  [dimensionless]  
 $\delta_{ij}$  : the Kronecker delta (0 if  $i \neq j$ ; 1 if  $i = j$ ) [dimensionless]  
 $\zeta$  : fugacity ratio [dimensionless]  
 $\eta_i$  : number of active sites in a segment of the component  $i$  [dimensionless]  
 $\theta_i$  : surface area fraction of component  $i$  [dimensionless]  
 $\theta'_i$  : fractional parameter of component  $i$  corresponding to additional molecular parameter  $q'_i$  [dimensionless]  
 $\sigma$  : configuration identity variable of  $k$ -ghost molecular segment in the decorated cell [dimensionless]  
 $\tau_{ij}$  : variables of UNIQUAC defined by Eqs. (2) and (3) [dimensionless]  
 $\Phi_i$  : volume fraction of component  $i$  [dimensionless]  
 $\psi_i$  : angle between the directionally active sites of the component  $i$  [radian]  
 $\omega_i$  : segment directionality for the first active site of the component  $i$  [dimensionless]  
 $\omega'_i$  : segment directionality for the second active site of the component  $i$  [dimensionless]

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