

## DECORATED LATTICE MODEL FOR CLOSED-LOOP LIQUID-LIQUID EQUILIBRIA AND ITS APPLICATIONS TO PYRIDINE DERIVATIVES-WATER MIXTURES

Yeong-Cheol KIM and Jong-Duk KIM\*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,

P.O. Box 131, Chungryang, Seoul, Korea

(Received 27 January 1986 • accepted 12 April 1986)

---

**Abstract**—A decorated lattice model, that consists of decorated bonds and orientational configurations of basis in the decorated cell is presented with the use of arbitrary directionality and temperature-independent interaction energies of sites to calculate the closed-loop coexistence curves of two equilibrated binary liquid phases. For mixtures containing hydrogen bonding compounds, the closed-loop diagrams obtained by the decorated lattice model are in fair agreement with experiments in the size, the shape and the flatness near the lower consolute solution temperatures, and fairly reproduced for pyridine derivatives-water mixtures. The directional interaction energies between unlike molecules, representing the strong interactions such as hydrogen bonding, are found responsible for the enhanced miscibility below the lower consolute solution temperatures. Finally, an application of the modified solution model, based on the effective interaction energies is demonstrated in the prediction of the closed-loop behaviors.

---

### INTRODUCTION

The solubility or partitioning of a solute in the liquid phases is one of the main concerns in solvent extraction, solubilization or purification processes when fine and pharmaceutical chemicals are produced by fermentation and chemical synthesis [1]. For a simple liquid-liquid system, the solubility could be estimated by equating the fugacities of species in two equilibrated liquid phases obtained from the equations of state, the polynomial expansions of activity coefficients or any solution models developed [2,3]. In predicting the liquid behaviors of the strongly polar and solvating groups [4], however, any systematic procedure is not available, because of their high specificities in molecular structure and interaction.

According to Rowlinson and Swinton [5], the binary diagrams of pressure, temperature, and concentration are classified to six classes and the phase behaviors of closed-loop coexistence curves in a temperature and concentration diagram, having two consolute points of the upper consolute solution temperature (UCST) and the lower consolute solution temperature (LCST) [6], are categorized as type VI. Since the closed-loops, in most cases, are strongly asymmetric and the curvatures near

the LCST's are extremely flat [6], such behaviors can not be described by any of the solution models with the use of the temperature-independent interaction parameters. Often the interaction energy parameters, however, were expanded as a function of temperature [3,7] to calculate the closed-loops bounded at the upper and lower consolute points.

In this study, after a brief introduction of the decorated lattice model proposed by Anderson and Wheeler [8], the shape and the upper and lower consolute points of a closed-loop diagram are calculated using temperature-independent interaction parameters and applied to the pyridine derivatives-water mixtures. Further, a modification of the model is presented for the predictions of the asymmetric closed-loop coexistence curves.

### DECORATED LATTICE MODELS

A pseudo-crystal lattice of a mathematical structure occupied with bases of chemicals is often assumed to calculate the thermodynamic properties of solutions with the use of the partition function of the structure. In this decorated lattice model, there are two different aspects in calculating the partition function depending on whether the lattice or basis is decorated or not. The one calculated the partition function of the lattice con-

---

\*To whom all correspondence should be addressed

sisting of decorated sites and obtained its mathematical transformation renormalizing the decorated bond into a form of the regular lattice [9-12]. The other used a simple lattice to calculate the partition function from the interaction energies of a basis quantized from site to site or from the renormalized energies of the site interactions [8,13,14].

In transforming the partition function, Fisher [9] used the bond decimation technique and examined the various types of lattice with decorated bonds, but did not attempt to calculate the closed loop behaviors. Applying the excluded volume concept, Widom [10] demonstrated the asymmetry of the shapes of coexistence curves and the critical exponents. Later, Widom's cell model was modified to the bar cell model [11], dividing the volume into the primary cells and the decorated cells according to the types of interactions, and the various types of spectra in the phase behaviors [12] were calculated in the variation of the ratio of the interaction energies between the different types of cells, and the coordination number. The decoration method, however, did not explicitly show whether the model could predict the closed loop coexistence curves or not.

Barker and Fock [13], on the other hand, modelled the basis of the species in the primary lattice, which has the multiple interaction sites with different energies, and obtained the essentially symmetric shapes of the closed-loop behaviors including the upper and lower critical points. In recent, Walker [14] could calculate the closed loop behavior with the effective hamiltonian of a lattice obtained from the q-state interaction energies and found that the closed-loop behavior was symmetric about the axis of  $x = 0.5$ . Anderson and Wheeler [8] proposed two decorated lattice models depending on whether one of the components in the decorated has one directional interaction among the total spatial orientations or has two, and obtained asymmetric closed-loop behaviors.

From the partition function obtained one can calculate the equilibrium concentrations. Here, the procedure is briefly presented.

### Theoretical backgrounds

A decorated lattice structure, constructed with primary cells and with decorated cells between the primaries, is shown in figure 1. To calculate the partition function, several assumptions are set as;

1. Volume is divided into two classes of the bar cells and molecules are distributed in both the primary and the decorated cells.
2. The basis located in a decorated cell interacts only with those of two neighboring primary cells.
3. The intermolecular potential is calculated from the sum of the pair potentials of sites specified by the molecular orientations.
4. One of the species (A) has two specific interacting

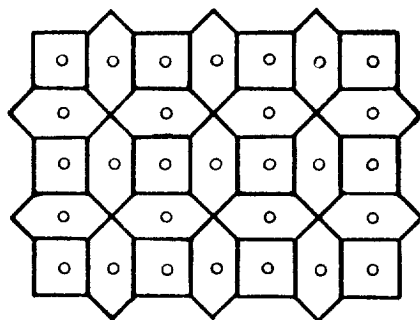


Fig. 1. Two-dimensional representation of a decorated lattice model divided by bar cells.

sites restricted within the orientational space by an angle  $\theta$ , but the other (B) has only one among the  $\omega$  molecular orientations independent of the number of the lattice coordinates.

For a binary mixture of the species, A and B, the grand partition function appropriate for two species filled in the cells can be calculated in a closed form summing up the pair potentials of the nearest neighbors of the primary cells. The pair potential consists of directional interactions,  $E_{ij}^d$  ( $i, j = A, B$ ) and of non-directional interactions,  $E_{ij}^e$  ( $i, j = A, B$ ). The directional or non-directional interactional energies are summed up along the proper configurations in the decorated bond, regardless of the orientations of the primary cells.

Dividing the summation along the occupancy of molecules in the primary or decorated cells, the partition function is given.

$$\Xi(\zeta, T, C) = \sum^{(1)} \sum^{(2)} \zeta^{N_A^{(1)}} \zeta^{N_A^{(2)}} \exp(-E/kT) \quad (1)$$

where  $\zeta (= Z_A/Z_B)$  is the fugacity ratio of species A and B. The sum  $\sum$  runs over all the possible configurations of A and B in the lattice and of spatial orientations of molecule itself and (1) and (2) denote the primary and decorated cells respectively and  $E$  is the interaction energy corresponding to each configuration.  $N_A^{(1)}$  and  $N_A^{(2)}$  indicate the numbers of A species in the primary and decorated cells.

The Boltzmann factors of the interaction energies of configurations at a given temperature, can be constructed by,

$$\eta_{ij}^l = \exp(-E_{ij}^l/kT) \quad (2)$$

where  $T$  is the absolute temperature and  $k$  is the Boltzmann constant. The superscript  $l$  represents the directional ( $\phi$ ) or nondirectional ( $\epsilon$ ) interaction. Since two directional interacting sites are restricted within the space of a specific angle  $\theta$  by the internal arrangement of molecular structure, the number of the available configurations of the second arrow of the directional interac-

tion differs from that of the first ones by  $w^* = \sqrt{\omega\pi} \sin\theta$ . Therefore, once the first arrow of the directional interaction is selected, the total number of orientations available can be determined by,  $\omega\omega^*/2$ . Then, the partition function of the decorated bond at a fixed primary cell,  $Q_{ij}$  ( $i, j, k = A, B$ ) can be calculated [8] and shown in appendix. Using the partition functions of the decorated bonds, the partition function of the primary cells of A-A, A-B, and B-B nesting the species of A or B in the decorated cell, can be evaluated as follows,

$$Q_{AA} = Q_{AAA} (R_{AA} + \xi) \quad (3-a)$$

$$Q_{AB} = Q_{AAB} (R_{AB} + \xi) \quad (3-b)$$

and

$$Q_{BB} = Q_{BBB} (R_{BB} + \xi) \quad (3-c)$$

where  $R_j$  ( $i, j = A, B$ ) is the ratio of the partition functions of  $ij$  bond decorated with the species B to A. Following the lattice identities and the cell partition functions, the partition function of the equation (1) can be reduced as,

$$\Xi(\xi, T, C) = \sum^{(1)} \xi^{N_A} \cdot Q_{AA}^{N_{AA}} \cdot Q_{AB}^{N_{AB}} \cdot Q_{BB}^{N_{BB}} \quad (4-a)$$

or

$$\Xi(\xi, T, C) = Q_{BB}^{q/2} W_B^q \sum \lambda^{N_A} \xi^{N_{AB}} \quad (4-b)$$

where  $N_{AA}$ ,  $N_{AB}$  and  $N_{BB}$  are the numbers of the pairs A-A, A-B and B-B, in the primary cells and  $q$  the number of the lattice coordinate. The  $\lambda$  and  $\xi$  in the equation (4-b) are given by

$$\lambda = \xi \left( \frac{W_A}{W_B} \right) \cdot \left( \frac{Q_{AA}}{Q_{BB}} \right)^{q/2} \quad (5)$$

and

$$\xi = \frac{Q_{AB}}{(Q_{AA} \cdot Q_{BB})^{1/2}} \quad (6)$$

where  $W_A$  and  $W_B$  are the total number of orientations of molecules. From the analogy of the spin 1/2 Ising model, the  $\lambda$  and  $\xi$  are found to be equivalent to those of the spontaneous magnetization [8].

### Calculations and Modifications

Along the standard statistical mechanics of ensemble average method [8], the compositions of the coexistence curve can be calculated by,

$$\begin{aligned} X_A = & \frac{q \xi}{(2+q)(\xi + R_{BB})} + \frac{\{1 \pm m_o(\xi)\}}{(2+q)} \cdot \left\{ 1 + \frac{q \xi}{2} \right. \\ & \times \left( \frac{1}{\xi + R_{AA}} - \frac{1}{\xi + R_{BB}} \right) \} + \frac{W(\xi) \xi}{(2+q)} \\ & \times \left\{ \frac{2}{\xi + R_{AB}} - \left( \frac{1}{\xi + R_{AA}} + \frac{1}{\xi + R_{BB}} \right) \right\} \end{aligned} \quad (7)$$

where  $m_o(\xi)$ , equivalent to the spontaneous magnetization and  $w(\xi)$ , the reduced energy per unit cell could be calculated from the Padé approximations by Scesney [14]. The calculations of the closed-loop behaviors can

be carried out solving the equation (7) with the intrinsic restriction of  $\lambda = 1$ .

Applications of the equation (7) to multicomponent systems is not easy without any modifications, since the cell partition functions become much complicated. The activity coefficient methods from excess Gibbs free energy are convenient to estimate the activities of liquid phases, if the decorated lattice model is transformed without losing the native structures of the decorated lattice model. A transformation of the decorated lattice to a pseudo-lattice can be done [16] calculating the effective interaction energy of the normalized lattice by,

$$2kT \ln \xi(\xi) \leftrightarrow (U_{AA} - U_{AB}) + (U_{BB} - U_{AB}) \quad (8)$$

The transformation can be incorporated to any lattice-born activity models. One of the solution model, UNIQUAC, which was derived from the lattice model and the local composition concept, can be remodeled by this decorated lattice, incorporating the energy parameters by the equation (8).

## RESULTS AND DISCUSSIONS

In predicting the liquid-liquid equilibria, several solution models are applicable except for the closed loop behavior. Among the available models, UNIQUAC is known to be one of the most successful model when two binary interaction parameters are used. Therefore, the results of the computer calculations of the decorated lattice model were compared with the results of the UNIQUAC equation by the same method of Prausnitz, et. al. [18]. The computer calculations of the equation (7) were performed with the help of the interactive computer graphics.

### Decorated Lattice Model and UNIQUAC

The parameters of the decorated lattice model include the directional and non-directional interactional energies, the number of spatial orientation, and the lattice coordination number. In calculations, the lattice coordination number and the number of spatial orientations are fixed. Among the interaction energies,  $E_{ij}^l$  ( $i, j = A$  or  $B$ , and  $l =$  directional or non-directional), the only energy parameters between unlike molecules are the binary parameters. Depending on the values of energy parameters, the shapes of the closed-loops calculated vary in following fashions,

1. As the directional interaction energies of like-molecules become smaller, the size of the closed-loop turns smaller and the shape becomes more distorted.
2. As the directional interaction of unlike-molecules becomes larger, the range of the phase separation in temperature narrower.
3. The dependence of the shape and size of the closed-loop is more sensitive to the nondirectional interac-

tion energies than to the directional interaction energies.

4. In certain values, the loops are cut by a pure component boundary as often observed in mixtures containing the surface active components.

In addition, the model in the meaningful range of the parameters generates the various shapes of the diagrams which are often found in the polymer solutions, liquid crystals or some systems accompanying the chemical reaction or structural transition [21].

For the closed-loop coexistence curves, the solution models developed thus far are not useful if the interaction parameters are not expanded at least to a quadratic function of temperature or an arbitrary function of temperature [3,6,17]. In figure 2, the calculated phase boundaries of the UNIQUAC equation and the decorated lattice model for the ethylene glycol isobutyl ether-water system are shown in the dotted and solid lines. The tendency of the two-parametric solution model, comparing that of the decorated lattice model of the equation (7), is poor in predicting the shape and size of the closed-loop. If the temperature-independent energy parameters are used, the UNIQUAC equation lacks any pieces of information near the critical points, in particular, near the LCST's. Further, since all the solution models of lattice-borns or the generalized van der Waals models can be related to the UNIQUAC model [19], the conclusion may

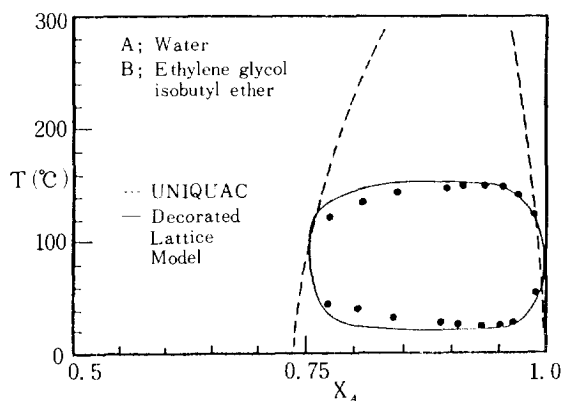


Fig. 2. Temperature-concentration diagram of ethylene glycol isobutyl ether-water mixtures.

The solid and dotted lines indicate the calculated diagrams by the decorated lattice model and the UNIQUAC equation respectively and the filled circles are the experimental data from reference 6.

Decorated lattice model;  $\omega=9000$ ,  $E_{AA}^{\phi} = -3.70$  Kcal/mole,  $E_{AB}^{\phi} = -6.30$ ,  $u_a=5.00$ ,  $u_s=0.03$

UNIQUAC;  $r_A=0.92$ ,  $r_B=4.917$ ,  $q_A=1.40$ ,  $q_B=4.36$ ,  $\Delta u_{AB}=884.5$  Kcal/mole,  $\Delta u_{AA} = -324.2$

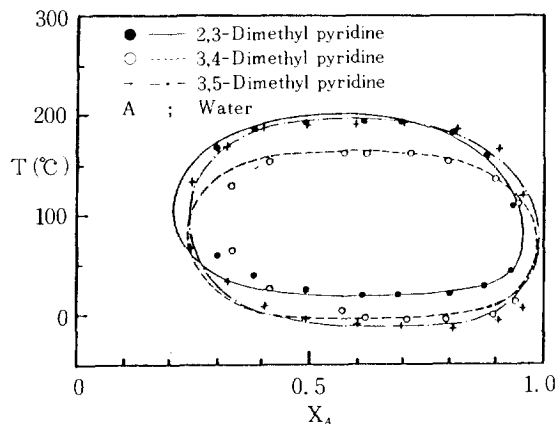


Fig. 3. Closed loop phase diagrams of three isomers of dimethyl pyridines and water systems.

The lines are calculated by the decorated lattice and the experimental data[6] also shown.  $\omega=5000$

2, 3-Dimethyl pyridine;  $E_{AA}^{\phi} = -3.96$  Kcal/mole,  $E_{AB}^{\phi} = -4.40$ ,  $u_a=0.96$ ,  $u_s=1.0$

3, 4-Dimethyl pyridine;  $E_{AA}^{\phi} = -5.90$ ,  $E_{AB}^{\phi} = -5.30$ ,  $u_a=2.0$ ,  $u_s=0.83$

3, 5-Dimethyl pyridine;  $E_{AA}^{\phi} = -5.43$ ,  $E_{AB}^{\phi} = -5.29$ ,  $u_a=1.87$ ,  $u_s=1.1$

extend to other solution models.

### Pyridine derivatives-water mixtures

Remembering the general dependence of the shape and size of the decorated lattice model in mind, the closed-loop diagrams of three isomers of dimethyl pyridine and two of ethyl pyridine systems [6] were calculated and shown in figures 3 and 4. Since the hydrogen bonding energy is about  $-3$  to  $-6$  Kcal/mole [20], the values of the directional interaction energy are assigned to be the same order of magnitude. One of the nondirectional interactions is fixed 1.0 Kcal/mole to represent the repulsive force, and the others are parameterized. The number of directional orientations is also fixed at  $\omega=5000$  and the angle between two arrows is selected to be  $109.5^\circ$ , the angle of the  $sp^3$  hybrid orbital of tetragonal structure. In diagrams, the data points are used in mass fraction, since the mole fraction diagrams are too sided toward the water phase (see figure 2) and since mass or volume fraction is convertible to mole fraction without any difficulties [8].

According to the model calculations shown in figure 3, one may find that, when the UCST's of both the 2, 3-dimethyl pyridine- and 3, 5-dimethyl pyridine-water mixtures are similar but the LCST's are not, the sets of parameters are significantly different, and also find that the interaction energies of both 3, 4-dimethyl pyridine- and 3, 5-dimethyl pyridine-water mixtures are similar,

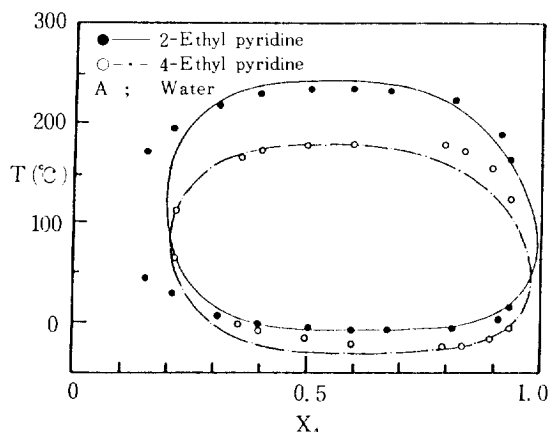


Fig. 4. Closed loop phase diagrams of two isomers of ethyl pyridine and water systems.

The lines are calculated by the decorated lattice model and the experimental data [6] also shown.  $\omega = 5000$

2-Ethyl pyridine;  $E_{AA}^\phi = -5.39$  Kcal/mole,

$E_{AB}^\phi = -5.41$ ,  $u_a = 1.1$ ,  $u_s = 1.11$

4-Ethyl pyridine;  $E_{AA}^\phi = -4.20$ ,  $E_{AB}^\phi = -4.37$ ,  
 $u_a = 0.99$ ,  $u_s = 0.96$

when the LCST's are same though the UCST's are much different. In comparing the isomers of 2-ethyl pyridine and 3, 5-dimethyl pyridine, the values of LCST's follow same tendency. As the variations of the LCST's are mainly attributed to the strong molecular interactions or hydrogen bonding [4,5], it is of no doubt to conclude that the directional interaction energies of the decorated

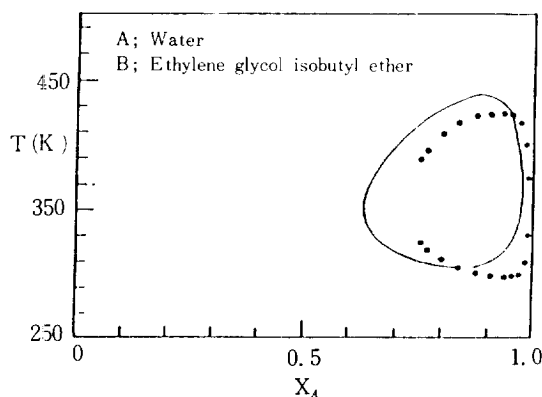


Fig. 5. Closed loop phase diagram of ethylene glycol isobutyl ether and water system.

The solid loop was calculated by the modified UNIQUAC following the suggestion of the equation (8).  $\omega_A = 5000$ ,  $\omega_B (= \omega_A \cdot \frac{q_B}{q_A})$

$= 15600$ ,  $E_{AA}^\phi = -5.45$  Kcal/mole,  $E_{AB}^\phi = -5.15$ ,  
 $u_a = 0.48$ ,  $u_s = 0.55$

lattice model have a very important role in determining the shape of the phase diagrams near the LCST's. Further, from the figures 3 and 4 it is also found that, as the methyl groups are located far from the ring nitrogen atom, the directional interaction energies increase with lowering the LCST's, and that if the directional interaction energies are similar, the UCST's increase as the interaction parameters become more repulsive.

#### Decorated solution model

The closed-loop phase diagram in figure 2 was recalculated by the modified UNIQUAC equation, incorporating the original decorated lattice model, suggested by the equation (8). In figure 5, the transformation was demonstrated to be done without losing the characteristics of the decorated lattice model and the intrinsic concentration dependence of the UNIQUAC equation.

#### CONCLUSIONS

The closed-loop diagrams were calculated with a decorated lattice model which consists of decorated bonds and the proper orientations of molecules. Compared with results of the UNIQUAC equation, the calculated compositions of a closed-loop diagram by the model fitted better with experiments in predicting the shape and size, and the trends near the critical solution temperatures.

With the use of temperature-independent interaction parameters, the decorated lattice model fairly reproduced the shapes of the phase diagrams of the dimethyl pyridines and ethyl pyridines-water mixtures, and exhibited that the strong interactions such as hydrogen bonding between the unlike molecules are responsible for the lower consolute solution temperatures.

A simplified modification to activity models was given renormalizing the decorated bond by means of the effective interactional energies and demonstrated to predict the closed loop behavior and the near-critical behavior.

#### ACKNOWLEDGEMENT

The financial support provided by Korea Science Foundation is gratefully acknowledged.

#### NOMENCLATURES

- C : total number of primary cells
- E : molecular interaction energy at a given configuration, Kcal/mole
- $E_{ij}^i$  : interaction energy of sites between  $i$  and  $j$ , Kcal/mole
- $m_o$  : spontaneous magnetization
- $N_A^{(1)}, N_A^{(2)}$  : number of species  $A$  in the primary and

	secondary cells, respectively
$N_{ij}$	: number of pair $i, j$
$Q_{ij}$	: partition function of the primary cell $i, j$ which nested a decorated lattice point
$Q_{ikj}$	: partition function of the decorated cell of $k$ nested by a primary cell $i, j$
$q$	: coordination number of the lattice
$R_{ij}$	: ratio of the partition functions of the decorated cell $Q_{ikj}/Q_{iAj}$
$T$	: absolute temperature, K
$u_{ij}$	: interaction energy of sites in the solution model, Kcal/mole
$u_a$	: asymmetric nondirectional energy, $E_{AA}^\epsilon - E_{BB}^\epsilon$ , Kcal/mole
$u_s$	: symmetric nondirectional energy, $E_{AB}^\epsilon - 1/2 (E_{AA}^\epsilon + E_{BB}^\epsilon)$ , Kcal/mole
$W_i$	: total number orientations of molecules
$w$	: reduced energy per unit cell
$X_A$	: mole fraction of A
$\zeta$	: ratio of the absolute fugacities
$\eta_{ij}^l$	: Boltzmann factor of $i$ - $j$ pair with $l$ directionality
$\theta$	: angle between two directional interaction sites, degree
$\lambda$	: parameter defined in the equation (5)
$\xi$	: parameter defined in the equation (6)
$\Xi$	: Grand partition function
$\omega$	: number of molecular orientations

### Superscripts

$l$	: directionality of arrows, directional or non-directional
$\epsilon$	: nondirectional interaction
$\phi$	: directional interaction

## APPENDIX

### Partition functions of primary bonds nesting a decorated cell

A partition function  $Q_{AAB}$ , for an example, of a decorated cell with the primary cell occupied by A and B, can be calculated from the Boltzmann factors and the orientational degeneracies. Among the  $\omega\omega^*/2$  orientations of A molecule in the decorated cell, one configuration is that both directional arrows simultaneously indicate the primary cells. The energy of this configuration is  $E_{AA}^\phi + E_{AB}^\phi + E_{AA}^\epsilon + E_{AB}^\epsilon$ . There will be  $2(\omega^* - 1)$  configurations for the cases that only one directional arrow indicates the primary cells and the energy is  $E_{AA}^\phi + E_{AA}^\epsilon + E_{AB}^\epsilon$  or  $E_{AB}^\phi + E_{AA}^\epsilon + E_{AB}^\epsilon$  depending on whether the arrow of A is directed toward A or B in the primary cells. Then, the cases, none of the directional arrows in the decorated cell indicating the primary cells, are counted as  $\{(w\omega^*/2) - 2(\omega^* - 1) - 1\}$ , and the energy of the confi-

guration is  $E_{AA}^\epsilon + E_{AB}^\epsilon$ . Then, the configurational partition function  $Q_{AAB}$  can be given,

$$Q_{AAB} = \{ \eta_{AA}^\phi \eta_{AB}^\phi + (\omega^* - 1) (\eta_{AA}^\phi + \eta_{AB}^\phi) + (\omega\omega^*/2) - 2(\omega^* - 1) - 1 \} \eta_{AA}^\epsilon \eta_{AB}^\epsilon \quad (A-1)$$

and the same procedure applies for the remaining  $Q_{ikj}$  giving

$$Q_{AAA} = \{ (\eta_{AA}^\phi)^2 + 2(\omega^* - 1) \eta_{AA}^\phi + (\omega\omega^*/2) - 2(\omega^* - 1) - 1 \} (\eta_{AA}^\epsilon)^2 \quad (A-2)$$

$$Q_{BAB} = \{ (\eta_{AB}^\phi)^2 + 2(\omega^* - 1) \eta_{AB}^\phi + (\omega\omega^*/2) - 2(\omega^* - 1) - 1 \} (\eta_{AB}^\epsilon)^2 \quad (A-3)$$

$$Q_{ABB} \simeq (\eta_{AB}^\phi + \omega - 1) \eta_{AB}^\epsilon \eta_{BB}^\epsilon \quad (A-4)$$

$$Q_{ABA} = (2\eta_{AB}^\phi + \omega - 2) (\eta_{AB}^\epsilon)^2 \quad (A-5)$$

$$Q_{BBB} \simeq \omega (\eta_{BB}^\epsilon)^2 \quad (A-6)$$

with the simplification of  $E_{BB}^\phi = 0$ [8].

## REFERENCES

- Lo, T.C., Baird, M.H. and Hanson, C.: "Handbook of Solvent Extraction," eds., John Wiley & Sons, N.Y. 1983.
- Prausnitz, J.M.: "Molecular Thermodynamics of Fluid-Phase Equilibria," Prentice-Hall, Inc., Englewood Cliffs, N.J. 1969.
- Van Ness, H.C. and Abbott, M.M.: "Classical Thermodynamics of Nonelectrolyte Solution," McGraw-Hill, New York, 1982.
- Lang J.C. and Morgan, R.D.: *J. Chem. Phys.* **73**, 5849 (1980).
- Rowlinson, J.S. and Swinton, F.L.: "Liquid and Liquid Mixtures," 3rd ed., Butterworth Sci., London, 1982.
- Francis, A.W.: "Critical Solution Temperatures," Advances in Chemistry Series No. 31, American Chemical Society, Washington, 1961.
- Jung, H.Y. and Jhon, M.S.: *The Korean J. of Chem. Eng.* **1**, 59 (1984).
- Anderson, G.R. and Wheeler, J.C.: *J. Chem. Phys.* **69**, 3413 (1978).
- Fisher, M.E.: *Phys. Rev.* **113**, 969 (1959).
- Widom, B.: *J. Chem. Phys.* **46**, 3324 (1967).
- Mermin, N.D.: *Phys. Rev. Lett.* **26**, 169 (1971).
- Mulholland, G.W. and Rehr, J.J.: *J. Chem. Phys.* **60**, 1297 (1974).
- Barker, J.A. and Fock, W.: *Discuss. Farad. Soc.* **15**, 188 (1953).
- Goldstein, R.E. and Walker, J.S.: *J. Chem. Phys.* **78**, 1492 (1983).
- Scesney, P.E.: *Phys. Rev.* **B1**, 2274 (1970).
- Kim, Y.C. and Kim, J-D: prepared for World Congress III of Chem. Eng., Tokyo, Japan, 1986.

17. Patterson, D., Bhattacharyya, S.N. and Picker, P.: *Trans. Farad. Soc.* **64**, 648 (1968).
18. Prausnitz, J.M., Anderson, T.F., Grens, E.A., Eckert, C.A., Hsieh, R. and O'Connell, J.P.: "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria," Prentice-Hall, Englewood Cliffs, N.J., 1980.
19. Mollerup, J.: *Fluid Phase Equilibria* **7**, 121 (1981).
20. Pimentel, G. and Mc Clellan, A.L.: "The Hydrogen Bond," Freeman, San Francisco, C.A., 1960.
21. Francis, A.W.: "Liquid-Liquid Equilibriums," Wiley Interscience, N.Y., 1963.