

Approximate Nonrandom Two-Fluid Lattice-Hole Theory. Thermodynamic Properties of Real Mixtures

Ki-Pung Yoo, Hun Yong Shin, and Chul Soo Lee[†]

[‡]Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea

[†]Department of Chemical Engineering, Korea University, Seoul 136-701, Korea

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A simple molecular theory of mixtures is formulated based on the nonrandom two-fluid lattice-hole theory of fluids. The model is applicable to mixtures over a density range from zero to liquid density. Pure fluids can be completely characterized with only two molecular parameters and an additional binary interaction energy is required for a binary mixture. The thermodynamic properties of ternary and higher order mixtures are completely defined in terms of the pure fluid parameters and the binary interaction energies. The Quantitative prediction of vapor-liquid, and solid-vapor equilibria of various mixtures are demonstrated. The model is useful, in particular, for mixtures whose molecules differ greatly in size. For real mixtures, satisfactory agreements are resulted from experiment. Also, the equation of state (EOS) is characterized well, even the liquid-liquid equilibria behaviors of organic mixtures and polymer solutions with a temperature-dependent binary interaction energy parameter.

Introduction

In a next publication (here after referred to as I),¹ the general derivation of an approximate molecular theory will be presented, and its applicability to pure fluids will be demonstrated. The fundamental concept of the theory was based on the quasichemical approximation of the Guggenheim's lattice combinatory.² It was shown that the model contains the feature of lattice fluid and quantitatively describes the phase-equilibrium properties of complex fluids.

Different formulations of solutions can be considered in the framework of the Guggenheim combinatory.^{2,3} A regular lattice without holes has been the basis for excess function theories of liquid mixtures.^{4,5-8} However, the excess function models for liquid mixtures cannot be applied to the vapor phase of mixtures and to pure fluid properties. If one assigns vacant sites to the Guggenheim's partition function, a volumetric EOS can be formulated. In principle, an EOS can be applied to condensed phases as well as to the gas phase, including the two-phase region. However, due to the intrinsic complex nature of the Guggenheim's combinatory of mixtures, it is inevitable to introduce a gross assumption in order to obtain EOS-type models.⁹ Furthermore, one has to a resort to numerical procedure for mixtures.¹⁰⁻¹³ The authors¹⁴ recently devoted much efforts to obtain explicit-form EOS from the lattice theory. In this article we present our effort to make the most generalized but simple theory of mixtures by the two-fluid approximation.^{5,7}

Theory

Model Description of Helmholtz Free Energy.

Since a complete description of the EOS is given in I, we discuss here only the fundamental expressions for mixtures. The Helmholtz free energy was obtained from the lattice partition function. It is given by

$$\beta A^c = -\ln \Omega^c = -\ln g_R - \ln g_{NR} + \beta U^c \quad (1)$$

where g_R is the random contribution of molecules and vacant sites in the lattice cells, g_{NR} is the nonrandom case, and U^c is the potential energy which are given by

$$g_R = (N_r! / I N_r!) (N_q! / I N_r!)^{z-2} \quad (2)$$

$$g_{NR} = [I N_r^0! I (N_{ij}^0/2)!]^2 / [I N_r! I (N_{ij}/2)!]^2 \quad (3)$$

$$U^c = \sum_i N_i (-\epsilon_i) + \sum_{i>j} N_{ij} (-\epsilon_{ij}) \quad (4)$$

where, $N_r = N_0 + \sum_{i=1}^c N_i r_i$, $N_q = N_0 + \sum_{i=1}^c N_i q_i$, and $z q_i = z r_i - 2 r_i + 2$. N_0 and N_i are the number of holes and the number of molecules of species i . r_i and q_i are the segment number and the surface area parameter. The summation is over all molecular species, and c denotes the number of components. N_{ij} is the number of i - j segment contacts, and the quantities with superscript zero denote the same for random mixing. N_{ij} is related to N_{ij}^0 by quasichemical approximation with the nonrandomness factor (Γ_{ij}) by, $N_{ij} = \Gamma_{ij} N_{ij}^0$ where $\Gamma_{ij}^2 = \Gamma_{ii} \Gamma_{jj} \exp(-\beta \Delta \epsilon_{ij})$ and $\Delta \epsilon_{ij} = \epsilon_{ii} + \epsilon_{jj} - 2 \epsilon_{ij}$. $\beta = 1/kT$ and ϵ_{ij} is the interaction energy between segments i and j . When $g_{NR} = 1$ and $U = 0$, this solution corresponds to the 'athermal solution'. The dependence of N_{ij} on the interaction energy was obtained by the quasichemical approximation for mixture. Various formulations of excess functions for liquid mixtures and EOSs can be obtained with judicious assumptions of Eq. (1).

As given in I, the Helmholtz free energy from Eq. (1) can be expressed as

$$\beta A^c = \beta A^{c(A)} + \beta A^{c(R)} \quad (5)$$

where the athermal part, $A^{c(A)}$, is equivalent to a combinatorial contribution in the random array in conjunction to Eq. (1) and $A^{c(R)}$ is due to the residual nonrandom interaction energy. The athermal part for a mixture is given by,

$$\beta A^{c(A)} = \sum_{i=1}^c N_i \lambda_i + \sum_{i=0}^c N_i \ln N_i - \sum_{i=0}^c N_i - N_r \ln N_r + N_r$$

$$= \sum_{i=1}^c N_i \ln \rho_i + N_0 \ln(1-\rho) - \frac{z}{2} N_q \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] \quad (6)$$

where, $q_M = \sum x_i q_i$, $r_M = \sum x_i r_i$, $\rho_i = N_i r_i / N_r$, $\rho = \sum \rho_i$. x_i is the mole fraction of species i . For polymeric substances, x_i can be replaced by weight fraction, w_i .

While preserving the athermal part, we replace the residual part by the two-fluid approximation.⁵⁻⁷ Using the thermodynamic relation at constant volume and composition,

$$\beta A^c(\beta) = \int_{\beta_0}^{\beta} U^c d\beta \quad (7)$$

where the configurational internal energy, U^c , is the residual part in the nonrandom two-fluid theory. If we take β_0 to a very high temperature, the solution becomes an ideal mixture (β_0 goes to 0).

Now N_{ij} are evaluated in the two-fluid theory,⁵

$$N_{ij} = \frac{z}{2} \left(N_i q_i \frac{\theta_j \tau_{ji}}{\sum_{k=0}^c \theta_k \tau_{ki}} + N_j q_j \frac{\theta_i \tau_{ij}}{\sum_{k=0}^c \theta_k \tau_{kj}} \right) \quad (8)$$

$$\tau_{ij} = \exp[\beta(\epsilon_{ij} - \epsilon_{ii})] \quad (9)$$

$$\epsilon_{ij} = (\epsilon_{ij} \epsilon_{ii})^{0.5} (1 - \lambda_{ij}) \quad (10)$$

where, $\theta_i = N_i q_i / N_q$, and $\theta = \sum_i \theta_i$.

Eq. (10) is the combining rules for general mixtures, where λ_{ij} is the binary interaction parameter. ϵ_{ii} between holes and molecular species set as zero. When the algebra is done, we have the configurational Helmholtz free energy,

$$\beta A^c = \sum_{i=1}^c N_i \ln \rho_i + N_0 \ln(1-\rho) - \frac{z}{2} N_q \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] - \left(\frac{z N_q}{2} \right) \sum_{i=1}^c \theta_i \left[\ln \left(\sum_{j=0}^c \theta_j \tau_{ji} \right) + \beta \epsilon_{ii} \right] \quad (11)$$

Thermodynamic Functions for General Mixtures.

Since the volume, V , is represented by, $V = V_H(N_0 + \sum_i N_i r_i)$, the EOS is obtained from the configurational Helmholtz free energy. It is given by,

$$P = \frac{1}{\beta V_H} \left\{ \frac{z}{2} \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] - \ln(1-\rho) + \frac{z}{2} \sum_{i=1}^c \theta_i \left(\frac{\tau_{0i}}{\sum_{k=0}^c \theta_k \tau_{ki}} - 1 \right) \right\} \quad (12)$$

Also, from Eq. (12), the chemical potential of component i in multicomponent fluids is obtained by

$$\frac{\mu_i}{RT} = \lambda_i(T) - r_i \ln(1-\rho) + \ln \frac{\theta_i}{q_i} + r_i \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] + \frac{z q_i \theta}{2} \left\{ 1 - \frac{r_i}{q_i} - \frac{q}{\theta} \left[\ln \sum_{k=0}^c \theta_k \tau_{ki} + \beta \epsilon_{ii} + \sum_{i=1}^c \frac{\theta_i (\tau_{ii} - \tau_{ii}(r_i/q_i))}{\sum_{k=0}^c \theta_k \tau_{ki}} \right] \right\} \quad (13)$$

where $\lambda_i(T)$ is the reference chemical potential which depends only on temperature.

If we define segment number, ϕ_i for component i by

$$\phi_i = \frac{r_i N_i}{N_r} = \theta_i \frac{1 + (q_M/r_M - 1)\rho}{\rho(q_i/r_i)} \quad (14)$$

the activity expression of the Flory-Huggins⁴ is written by,

$$\ln a_i = \ln(w_i \gamma_i) = \ln \phi_i + \left(1 - \frac{r_i}{r_j} \right) \phi_j + \chi_{ij} \phi_j^2 \quad (15)$$

where a_i and γ_i are activity and activity coefficient of the component i in a liquid mixture and w_i is the mass fraction.

Mixing Functions. The volume change of mixing $\Delta_M V$ is given by

$$\frac{\Delta_M V}{n_T} = r_M V_H (V - \sum_i \phi_i V_i) \quad (16)$$

The enthalpy of mixing $\Delta_M H$ is

$$\Delta_M H = \Delta_M U + P \Delta_M V \quad (17)$$

Critical Loci and Multiphase Behaviors. The conditions of criticality of the homogeneous phase of a pure system requires

$$\left(\frac{\partial P}{\partial \rho} \right)_T = \left(\frac{\partial^2 P}{\partial \rho^2} \right)_T = 0 \quad (18)$$

These equations are given in Appendix as eq A1 and A2. The critical and stability condition for a mixture in terms of Helmholtz free energy¹⁴ are given by

$$\left(\frac{\partial^2 A}{\partial x^3} \right)_{T,V} + \left(\frac{\partial P}{\partial x} \right)_{T,V} Q = 0 \quad (19)$$

$$\left(\frac{\partial^3 A}{\partial x^3} \right)_{T,V} - 3 \left(\frac{\partial^3 A}{\partial V \partial x^2} \right)_T Q - 3 \left(\frac{\partial^2 P}{\partial x \partial V} \right)_T Q^2 + \left(\frac{\partial^2 P}{\partial V} \right)_{T,x} Q^3 = 0 \quad (20)$$

where

$$Q = \frac{(\partial P / \partial x)_{T,V}}{(\partial P / \partial V)_{T,x}} \quad (21)$$

and the quantities underlined denote molar quantities. The final explicit expressions are given in Appendix A.

Three phase equilibria is determined by the relation,

$$\mu_i^\alpha(T, P, x_i^\alpha) = \mu_i^\beta(T, P, x_i^\beta) = \mu_i^\gamma(T, P, x_i^\gamma) \quad (22)$$

where α , β and γ denote different phases. The expression for the chemical potential of fluids is given as Eq. (14). For a pure solid, the chemical potential is written as,

$$\mu_i^{\text{solid}}(T, P) = \Delta \mu_i(T, P) + \mu_i^{\text{liquid}}(T, P) \quad (23)$$

where the second term on r.h.s. of Eq. (23) is again given by Eq. (14). $\Delta \mu_i$ represents the departure from solid to hypothetical liquid at the same temperature and pressure.

Various types of multiphase equilibrium behaviors, including the binodal and spinodal stabilities, can be calculated by using the equations given in Appendix A. They include liquid-liquid-vapor (LLV), solid-liquid-vapor equilibria (SLV) as well as two-phase equilibria such as VLE,

LLE, and VSE, including UCST and LCST. A three-phase equilibrium locus ends at a critical end point where it is intersected by a mixture critical locus.

Since the degree of freedom for a three-phase binary mixture is one, the existing phase equilibria are expressed by a locus. With one variable fixed, one can readily calculate three phase equilibria. To calculate LLVE for a fixed pressure, for example, the total number of variables to be calculated become seven (*i.e.*, $T, x_1^g, x_2^g, x_1^l, x_2^l, y_1, y_2$), and there are seven corresponding relations (*i.e.*, four phase equilibrium criteria and three mass balance constraints). In the calculation of SLV equilibria the solid phase can be assumed to be a pure solid. Again, we have one degree of freedom. If pressure is fixed, for example, we have five unknowns (*i.e.*, T, x_1, x_2, y_1, y_2) and five relations (*i.e.*, three equilibrium relations and two mass balance relations). Thus, by utilizing appropriate functions based on the present EOS, any type of phase equilibrium behavior can be calculated.

Molecular Parameters and Interaction Energy of Mixtures

As presented in I, the present EOS requires two molecular parameters, V_i^* ($=N_A V_{HFR1}$) and ϵ_{11} , for a pure fluid. We are obtained the pure parameters from experimental data. Thus, to characterize a binary mixture a single interaction parameter (λ_{12}) is required where it may be temperature dependent for LLE systems. In principle, a single mixture datum is sufficient to determine λ_{12} . For example, vapor-liquid equilibria data, heat or volume change of mixing, etc. can be used. The numerical parameters for pure fluids can direct-

ly be used which summarized in I. The best-fitted values of λ_{12} for various types of binary mixtures are shown in the next section.

Comparison of the Theory with the Experiment

In the previous article (I), we compared the present theory with other theories in the same genre and discussed the salient features of the theory. Here we demonstrated the quantitative applicability of the model to experimental phenomena of real mixtures. Indeed, we compared the theory with various types of phase equilibria such as low and high pressure VLE, high pressure VSE and LLE including closed loop critical solution phenomena.

Low Pressure Vapor-Liquid Phase Equilibria (VLE). By the chemical potential, the VLE can be calculated by the equilibrium relations,

$$\mu_i^v(T, P, \{y\}) = \mu_i^l(T, P, \{x\}) \quad i = 1, 2, \dots, C \quad (24)$$

where $\{y\}$ and $\{x\}$ denote sets of mole fractions of all components in vapor and liquid phases.

Since we discussed elsewhere,¹⁴ we omit here the computational aspects with the present model. In Table 1, the λ_{12} for low pressure VLE of hydrocarbon systems are summarized. Figure 1 illustrates the low pressure distillation behavior of ethanol(1)/water(2) system ($\lambda_{12}=0.02053$) where, the calculated results using the random lattice-hole theory³ are compared together. For two isotherms, the theory predicts the VLE well enough to the accurate process design purposes. Similarly in Figure 2, the isobaric VLE for the

Table 1. Binary interaction parameters and error percent for low pressure VLE

System	λ_{12}	T[K]	P[KPa]	Isothermal [%]		Isobaric [%]	
				AADP ^a	AADY ^b	AADT ^c	AADY
Benzene-c Hexane	.01735	343	101.3	.483	.046	1.658	.621
Benzene-Heptane	.01776	328-353	98.63-101.3	1.849	3.022	.110	1.179
Benzene-Toluene	.00156	-	101.3	-	-	.096	1.196
c Hexane-Toluene	.01138	-	101.3	-	-	.072	1.460
Pentane-Hexane	-.00187	298	99.97	.456	1.110	.175	2.977
Hexane-Benzene	.01677	343	101.3	.500	1.660	.030	1.291
Hexane-c hexane	.00090	343	101.3	.271	1.187	.017	.952
Hexane-c Methylpentane	.00222	-	101.3	-	-	.025	1.178
c Methylpentane-Benzene	.01603	333	101.3	.913	3.210	.098	1.025
c Methylpentane-c Hexane	.00152	-	101.3	-	-	.019	.411
c Methylpentane-Toluene	.00899	-	101.3	-	-	.206	2.529
Acetone-Benzene	.01967	298-318	99.97-101.3	.819	1.681	.337	3.127
Acetone-c Hexane	.07527	318-328	101.3	3.434	5.692	.299	5.920
Acetone-Hexane	.07152	318-328	101.3	2.776	6.459	.249	6.315
Diethylamine-Benzene	.00073	308-328	101.3	1.097	.931	.136	3.311
Diethylamine-Heptane	.01697	308-328	-	.570	-	-	2.543
Ethanol-Benzene	.07805	323-333	101.3	4.303	9.507	.458	10.272
Acetone-Methanol	.02004	318-328	101.3	.916	2.227	.197	1.843
Acetone-Ethanol	.02828	305-321	-	2.455	4.593	-	-
Methanol-Water	.00118	333	101.3	.893	1.355	.170	4.166
Ethanol-Water	.02053	328-342	66.64-101.3	3.090	2.833	.275	2.800

^a AADP: average error deviation of pressure defined by $(1/N) |P_{\text{experimental}} - P_{\text{model}}| / P_{\text{experimental}} \times 100$. ^b AADY: average error deviation of the vapor phase mole fraction as defined in 1). ^c AADT: absolute error deviation of temperature as defined in 1).

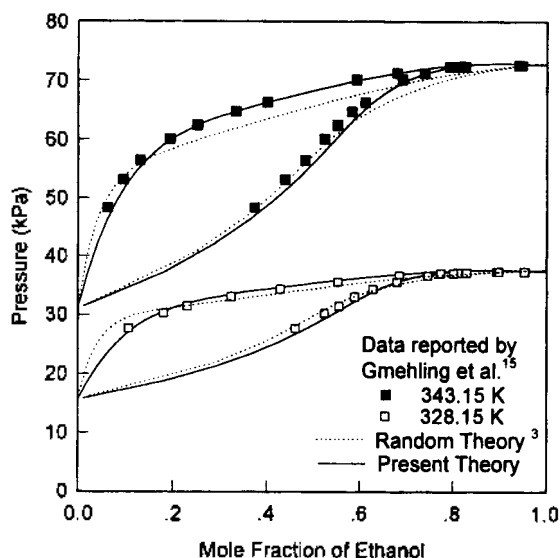


Figure 1. A comparison of lattice models for isothermal low pressure VLE of ethanol(1)/water(2) system at 328.15 and 343.15 K.

ethanol/water system is illustrated. With a single value of $\lambda_{12}=0.02053$, the EOS predicts the isobaric VLE correctly.

High Pressure Vapor-Liquid Equilibria (VLE).

For high pressure VLE, the similar equilibrium relation can be applied. In Table 2, the λ_{12} for various types of high pressure distillation phenomena are summarized. As the illustrations, hydrocarbon systems containing CO_2 are chosen. As one can see in Table 2, for most systems, λ_{12} stay in near zero values.

Figure 3 demonstrates the high pressure VLE for CO_2 (1)/ethanol(2) system at 304.2 and 314.2 K ($\lambda_{12}=0.0605$). The model fits the experiment data quantitatively. Similarly, accurately fitted results can be obtained for the CO_2 /butane system at 273.15 and 310.93 K ($\lambda_{12}=0.0964$) (Figure 4) and

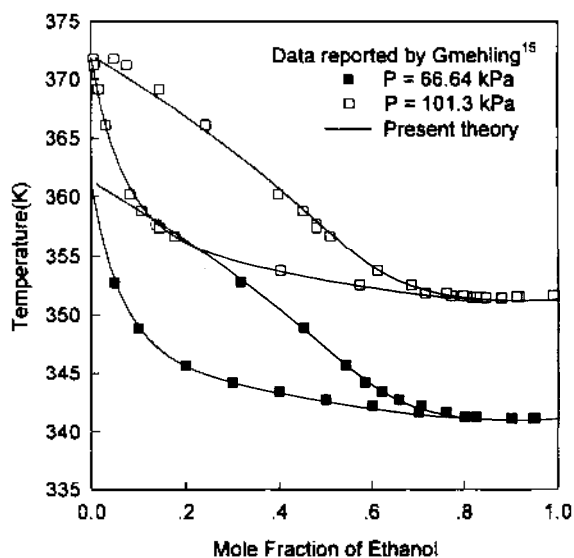


Figure 2. Calculated isobaric VLE of ethanol/water system at 66.64 and 101.3 kPa.

Table 2. Binary interaction parameters and average errors for high pressure VLE

	System	λ_{12}	AADX [%]	T range [K]
CO_2	-Acetone	-.0162	5.476	298.15-313.15
	-Benzene	.076	4.643	313.40-350.
	-Butane	.0964	4.584	273.15-310.93
	-Butene	.0893	3.906	273.15
	-Hexene	.0312	12.493	303.15-313.15
	-Cyclopentane	.0826	8.496	310.86-318.17
	-Ethane	.1041	6.581	244.26-288.71
	-Hexane	.0955	6.247	303.15-313.15
	-Heptane	.0932	5.587	310.65
	-Octane	.0813	7.793	313.15
	-Isobutane	.0991	10.372	273.15
	-Isopentane	.0876	9.247	277.59-310.93
	-Methanol	.0141	16.419	290.00-310.
Ethane	-Ethanol	.0605	8.086	304.20-314.50
	-Toluene	.0799	9.141	308.16-323.17
	-Benzene	.0205	4.865	298.15-313.15
	-Hexane	-.0010	8.183	298.15-338.71
	-Heptane	.0350	7.903	338.15-366.48
	-Octane	.0170	2.817	313.15-323.15

CO_2 /methanol system at 290 K ($\lambda_{12}=0.0141$) (Figure 5). These results demonstrated that the present theory fits correctly the various experimental high pressure VLE.

Vapor-Solid Phase Equilibria (VSE). In VSE calculation, the solid phase is usually assumed to be a pure solid. Then the simplified equilibrium relations can be modified by

$$\mu_i^V(T, P, \{y\}) = \mu_i^S(T, P) \quad (25)$$

The chemical potential in the solid phase causes difficulty in practice since it cannot be directly used. As discussed by

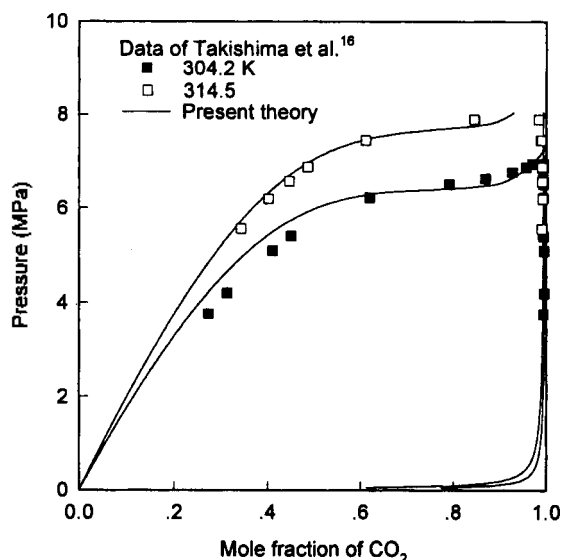


Figure 3. Calculated high pressure vapor-liquid equilibria of CO_2 /ethanol system at 304.2 and 314.2K.

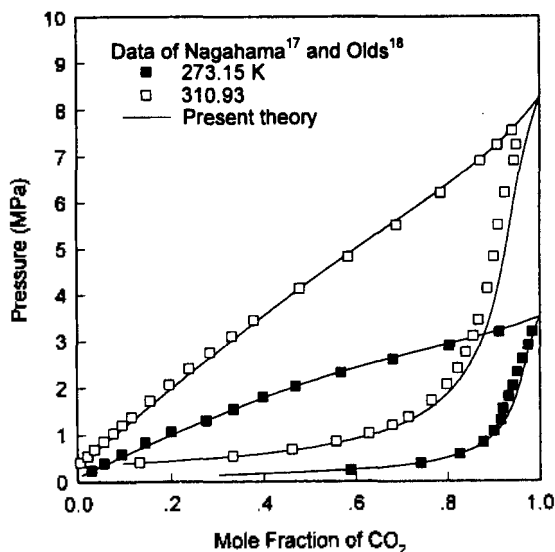


Figure 4. Calculated isothermal high pressure VLE of CO₂/butane system at 273.15 and 310.93 K.

the authors,¹⁴ if both sides of Eq. (25) are replaced by the chemical potential of a pure subcooled liquid, we have

$$\mu_i^V(T, P, \{y\}) = \Delta\mu_{i,pure}(T, P) + \mu_{i,pure}^L(T, P) \quad (26)$$

$$\begin{aligned} \Delta\mu_{i,pure}(T, P) &= \mu_{i,pure}^S(T, P) - \mu_{i,pure}^L(T, P) = RT \ln \left(\frac{f_i^S}{f_i^L} \right)_{pure} \\ &= V_i^{sat} S_i(P - P_i^{sat}, S_i) + RT \ln \left(\frac{P_i^{sat} S_i \phi_i^{sat,V}}{P \phi_i^L} \right) \end{aligned} \quad (27)$$

In Table 3, the binary interaction parameters λ_{12} and errors for representative vapor/solid systems are listed. In Figure 6, fitted results by the EOS with the experimental data for naphthalene/CO₂ system at 318.15 K ($\lambda_{12}=0.07534$) are

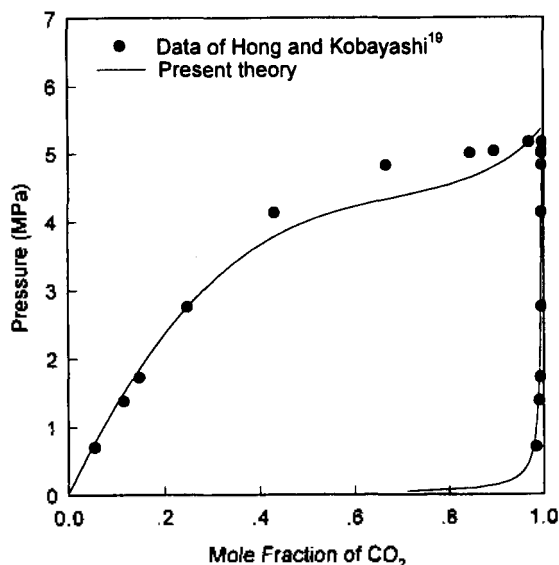


Figure 5. Calculated isothermal high pressure VLE of CO₂/methanol system at 290 K.

Table 3. Binary interaction parameters and error for vapor-solid equilibria

System	λ_{12}	AADY (%)	T range [K]	
Carbon	-Anthracene	.07053	16.342	303.15-328.
	-Biphenyl	.08863	5.584	308.95-322.
	-Benzoic Acid	.05018	9.867	308.15-318.
	-Naphthalene	.07534	14.117	308.15-328.
	-Phenathrene	.08351	1.445	308.15
Ethane	-Anthracene	.01075	4.116	303.15-323.
	-Biphenyl	.02589	5.257	308.15-318.
	-Benzoic Acid	.03153	15.155	308.15-318.
	-Naphthalene	.01448	6.731	308.15-318.
	-Phenathrene	.02900	13.002	303.15-318.

shown. Also, similar results for naphthalene/ethane system at 318.15 K ($\lambda_{12}=0.01448$) are shown in Figure 7. These illustrations are based on the use of the temperature-independent binary parameters in Table 3. In general, the EOS fits better the experimental values than the cubic Peng-Robinson EOS.²²

Activities of solvents in Polymer Solutions. For molecular species, vapor pressure is not well known and usually negligible. Thus the activity of solvents is determined from the VLE of the solvents.

$$\mu_{i,pure}^V(T, P) = \mu_i^L(T, P, \{x\}) \quad \text{for solvents} \quad (28)$$

$$\mu_i^L(T, P, \{x\}) = \mu_{i,pure}^L(T, P) + RT \ln a_i \quad (29)$$

The activity of solvent species i in polymer solutions can be fitted by the present theory. Densities of coexisting phases are calculated and the evaluation of chemical potentials of both phases of solvents by Eq. (28). The binary interaction parameters and errors for some polymer/solvent systems are listed in Table 4.

In Figure 8, calculated activity data for cyclohexane in polyisobutylene at 298.15 K ($\lambda_{12}=0.00766$)^{23,24} are shown. Also, the results compared with other models, such as ran-

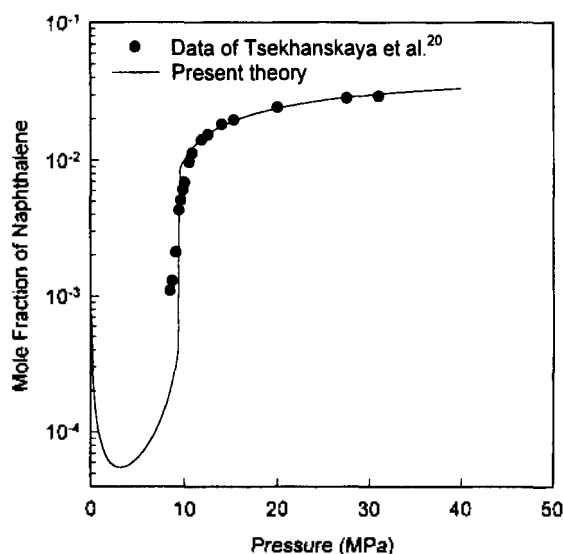


Figure 6. Calculated isothermal high pressure vapor-solid equilibria of naphthalene/CO₂ system at 318.15 K.

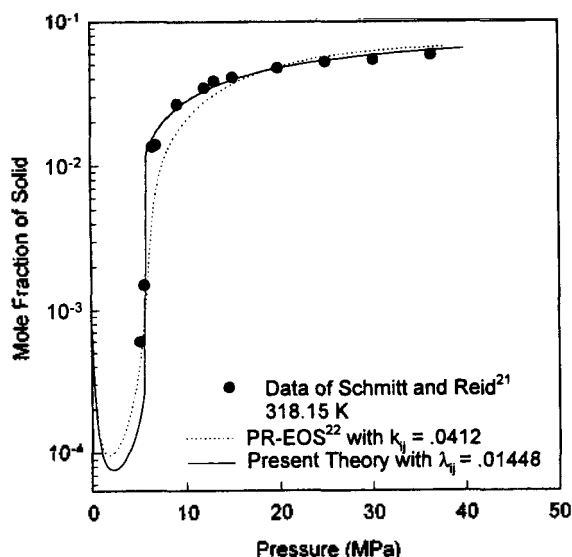


Figure 7. Calculated isothermal high pressure solid-vapor equilibria of naphthalene/ethane system at 318.15 K.

Table 4. Binary interaction parameters and errors for VLE of common polymer solutions

System	T range [%]	λ_{12}	AAD [%]	
Polystyrene	-Benzene	288.15-333.15	.00362	8.663
	-Chloroform	298.15-323.15	-.00074	3.385
	-Toluene	298.15-353.15	-.00081	1.198
Polypropylene oxide	-Benzene	318.15-347.85	-.02956	1.054
	-Chloroform	278.68	-.11028	16.03
	-Acetone	303.15	.02875	5.185
	-Benzene	303.15	.01158	5.626
Polyisobutylene	-Benzene	283.15-353.15	.03036	3.695
	-Butane	298.15-319.65	.01050	1.553
	-Cyclohexane	283.15-338.15	.00766	10.48
	-Pentane	298.15-308.15	.00668	4.706
	-Isobutane	298.15-319.65	.00832	2.277

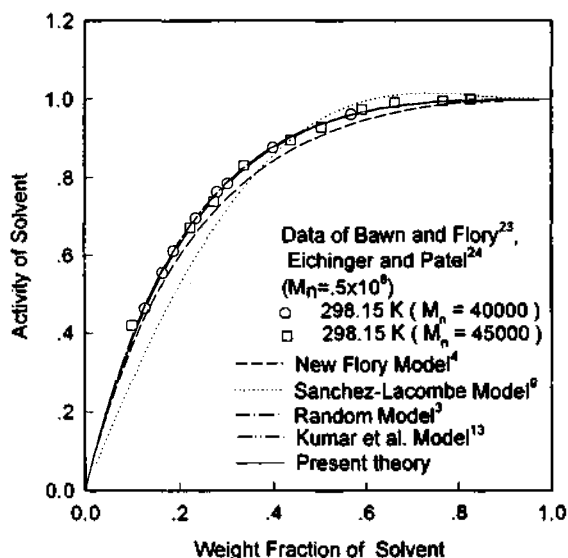


Figure 8. A comparison of calculated activities of solvent by several lattice-theory-based models for cyclohexane(1)/polyisobutylene(2) system at 298.15 K.

dom lattice-hole theory,¹¹ the new Flory's theory,⁴ Sanchez and Lacombe,⁹ and Kumar *et al.*¹³ Most of these models use two binary interaction parameters, while we use only one binary interaction parameter. Similar results are obtained for chloroform in the polypropylene oxide system²⁵ at 278.68K with $\lambda_{12} = -0.11028$ in Figure 9. One important feature of the present theory is its simplicity with favorable versatility and accuracy over existing theories in the same genre. In Figure 9, one can see that the present model and the theory by Kumar *et al.*¹³ fit the experiment with similar accuracy. However, the present theory is much simpler than the extremely complex expression of Kumar *et al.*¹³ Also, since the present theory is based on the statistical mechanical treatment of the r-mers, it has a great potential for use in macromolecular systems.

Liquid-Liquid Equilibria (LLE). The calculation of phase equilibrium properties of liquid mixtures from EOS requires a large computational effort, however, the major disadvantage of this type of calculation is not computational, but the theoretical aspect of the EOSs. To date, we do not have a satisfactory EOS applicable to mixtures over a density range from zero to liquid densities. It is a crucial deficiency of mostly the EOS theories that the phase equilibrium calculations based on EOS alone are often doubtful in LLE. For this reason it is interesting to see how well the present theory correlates LLE. Since even the well-known excess solution models²⁶ usually introduce quadratic temperature interaction parameters to calculate LLE, we employed the temperature dependent λ_{12} for only the case of LLE as

$$\lambda_{12} = a_1^{(0)} + a_1^{(1)}T + a_1^{(2)}T^2 \quad (30)$$

The calculation of LLE can readily be carried out by the following phase equilibrium criterion,

$$\mu_i^{L'}(T, P, \{x'\}) = \mu_i^{L''}(T, P, \{x''\}) \quad i = 1, \dots, C \quad (31)$$

where superscript L' and L'' represent the coexisting liquid phases. At the UCST of a partially miscible mixture, the

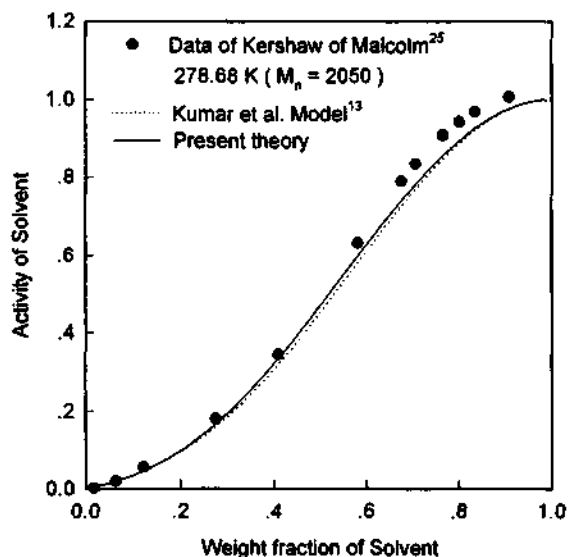


Figure 9. Calculated activities of solvent for chloroform/polypropylene oxide system at 278.68 K.

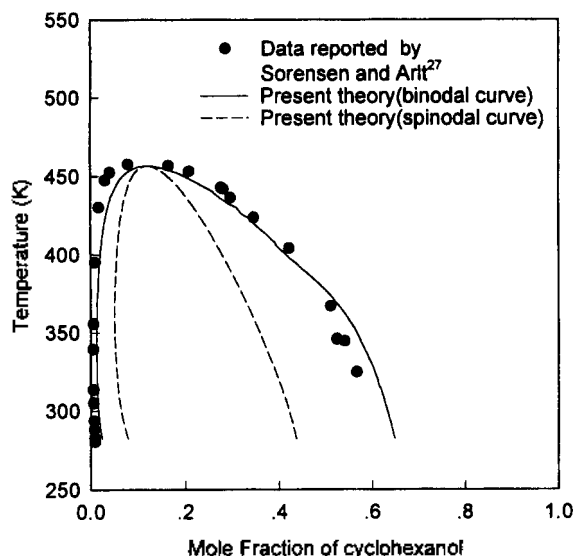


Figure 10. Calculated isobaric liquid-liquid equilibria for cyclohexanol/water system with $\lambda_{12} = -.238586 + .00142552 - 1.64078 \times 10^{-6} T^2$.

compositions of coexisting phases become identical.

In Figure 10, the calculated LLE of cyclohexanol/water system²⁷ is shown with the temperature-dependent $\lambda_{12}(T)$. Obviously the present theory fit correctly the LLE, including the UCST. If the prediction of LLE and UCST is a sensitive criteria to test an EOS theory, it seems that the present theory is remarkable quantitative one.

In Figure 11, the calculated closed-loop critical solution temperatures of tetrahydrofuran/water system is illustrated. Since this mixture exhibit, both the UCST as well as the LCST, it is an excellent candidate for testing the theoretical soundness of the theory.

Critical loci. In general it is extremely difficult to model the complicated phase behavior such as critical loci

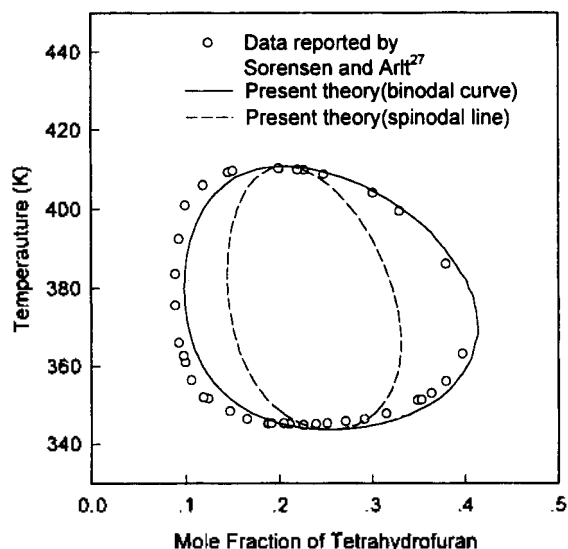


Figure 11. Calculated closed-loop liquid-liquid equilibria for tetrahydrofuran/water system with $\lambda_{12} = -1.04483 + .00519758T - 6.25788 \times 10^{-6} T^2$.

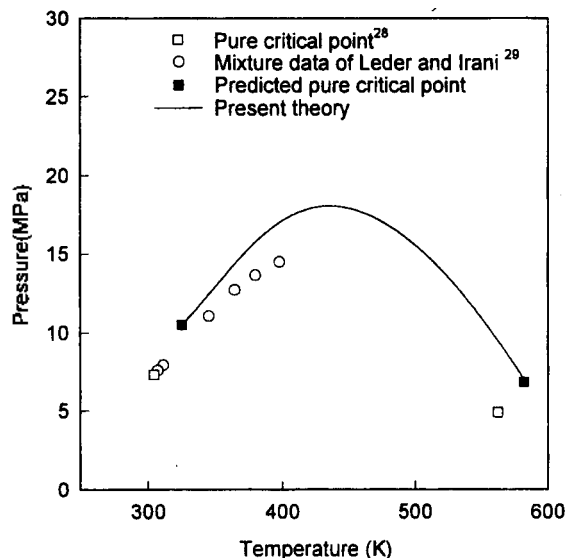


Figure 12. Calculated pressure-temperature locus in the critical region for CO₂/benzene system.

of mixtures using a simple EOS. Therefore quantitative agreements between experimental data of critical phenomena and an EOS are seldom reported to date even for simple systems. Using the expressions in Eqs. (20)-(22) and related equations in the Appendix, we tested the applicability of the present theory to the critical loci of liquid mixtures. We used the value of λ_{12} which was determined from the VLE data. In Figure 12, the predicted P-T projected loci of critical behavior (*i.e.*, L=V) for CO₂/Benzene²⁸ is shown. Predicted values of critical points for pure CO₂ and benzene by the present theory are higher than the experiment. If we adjust the numerical value of λ_{12} to fit the experimental data of critical loci, it should be possible to obtain better correlational results.

In summary, a simple molecular theory of fluid mixtures is presented, based on the lattice-hole theory. The simultaneous description of low and high pressure VLE, VSE and LLE, including macromolecular systems, has been achieved using the same value of the interaction parameter. This model also correctly describe the critical solution temperatures such as UCST, LCST and the critical loci of mixtures. The present theory was found to be simple, but versatile and accurate for the description of mixtures than any other existing theories in the same genre. The lattice-hole theories have been criticized due to the imperfections inherent to the lattice statistical-mechanical combinatory. However, the simple improvement of the Guggenheim combinatory is proven to yield an unified theory relevant to practical utilities. Computer program related to this article can be obtained from the authors upon request.

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Appendix A. Critical conditions for general mixtures

Critical conditions for a single component fluid.

The critical conditions of a homogeneous phase in a single component fluid is given by

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0 = \frac{z\varepsilon_{11}}{2V_H} \left\{ \frac{1}{1-\rho} + \frac{z}{2} \left[\frac{q_1/r_1 - 1}{1+(q_1/r_1-1)\rho} \right] + \frac{r_1 z \theta_1^3}{2q_1 \rho^2} \frac{(\tau_{01} - (\theta_1 - \theta_2)\tau_{01} + \theta_1)}{(\theta_0 \tau_{01} + \theta_1)^2} \right\} \quad (A1)$$

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0 = \frac{z\varepsilon_{11}}{2} V_H \left\{ \frac{1}{(1-\rho)^2} - \frac{z}{2} \left[\frac{q_1/r_1 - 1}{1+(q_1/r_1-1)\rho} \right]^2 + \frac{r_1 z (\tau_{01} - 1) \theta_1^3}{2q_1 \rho^3 (\theta_0 \tau_{01} + \theta_1)^2} \left[\left(\frac{3r_1 \theta_1}{q_1} \rho - 2 \right) (2\tau_{01} - \theta_1 \tau_{01} + \theta_1) + \frac{r_1 \theta_1 (\tau_{01} - 1) (3\tau_{01} - \theta_0 \tau_{01} + \theta_1)}{(q_1 \rho (\theta_0 \tau_{01} + \theta_1))} \right] \right\} \quad (A2)$$

Critical conditions for a multicomponent fluid.

The critical condition of a homogeneous phase in a mixture requires in addition to the above two conditions the following.^{14,15}

$$\left(\frac{\partial^2 \bar{A}}{\partial x^3}\right)_{T,V} + \left(\frac{\partial P}{\partial x}\right)_{T,V} Q = 0 \quad (A3)$$

$$\left(\frac{\partial^3 \bar{A}}{\partial x^3}\right)_{T,V} - 3 \left(\frac{\partial^3 \bar{A}}{\partial V \partial x^2}\right)_T Q - 3 \left(\frac{\partial^2 P}{\partial x \partial V}\right)_T Q^2 + \left(\frac{\partial^2 P}{\partial V}\right)_{T,x} Q^3 = 0 \quad (A4)$$

where, $\bar{A}_C = \beta A_C / n_T$, $\bar{A}_R = \beta A_R / n_T$, $\bar{A}_R = \beta A_R / n_q$

$$\left(\frac{\partial \beta P}{\partial x}\right)_{T,V} = \left(\frac{\partial \beta P_C}{\partial x}\right)_{T,V} + \frac{q_1 \rho \{1 + (q_2 - r_2) \rho / r_M\}}{r_M \{1 + (q_M / r_M - 1) \rho\}^2} \left(\frac{\partial \beta P_R}{\partial \theta_1}\right)_{T,V} \quad (A5)$$

$$\left(\frac{\partial \beta P_C}{\partial x}\right)_{T,V} = \frac{(r_1 - r_2) \rho}{r_M V_H} \left[\frac{1}{1-\rho} - \frac{1}{1+(q_M/r_M-1)\rho} \right] \quad (A6)$$

$$\left(\frac{\partial \beta P_R}{\partial \theta_1}\right)_{T,V} = \frac{z}{2V_H} \left[\left(\frac{\tau_{01}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} - 1 \right) - \theta_1 \frac{\tau_{01}(-1-\alpha)\tau_{01} + 1 + \alpha\tau_{21}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} \right] + \alpha \left[\frac{\tau_{02}}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} + 1 \right] - \theta_2 \frac{\tau_{02}(-1-\alpha)\tau_{02} + \tau_{12} + \alpha}{(\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2)^2} \quad (A7)$$

where $\alpha = \frac{q_2 \{1 + (q_1 - r_1) \rho / r_M\}}{q_1 \{1 + (q_2 - r_2) \rho / r_M\}}$ (A8)

$$\left(\frac{\partial \beta P_C}{\partial C}\right)_{T,x} = -\frac{\rho^2}{r_M V_H^2} \left\{ \frac{1}{1-\rho} + \left(\frac{z}{2}\right) \frac{q_M/r_M - 1}{1+(q_M/r_M-1)\rho} \right\} \quad (A9)$$

$$\left(\frac{\partial \beta P_R}{\partial V}\right)_{T,x} = \frac{z\rho}{2r_M V_H^2 [1+(q_M/r_M-1)\rho]} \left[\theta_1 \left(\frac{\tau_{01}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} - 1 \right) - \theta_1 \frac{\tau_{01}(-\theta_1 - \theta_2)\tau_{01} + \theta_1 + \theta_2 \tau_{21}}{(\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21})^2} + \theta_2 \left(\frac{\tau_{02}}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} - 1 \right) - \theta_2 \frac{\tau_{02}(-\theta_1 - \theta_2)\tau_{02} + \theta_1 \tau_{12} + \theta_2}{(\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2)^2} \right] \quad (A10)$$

$$Q = \frac{(\partial P / \partial x)_{T,V}}{\partial P / \partial V}_{T,x} \quad (A11)$$

$$\left(\frac{\partial^2 \bar{A}}{\partial x^2}\right)_{T,V} = \left(\frac{\partial^2 \bar{A}_C}{\partial x^2}\right)_{T,V} + \frac{q_1^2 \rho^2 \{1 + (q_2 - r_2) \rho / r_M\}^2}{\{1 + (q_M / r_M - 1) \rho\}^3} \left(\frac{\partial^2 \bar{A}_R}{\partial \theta_1^2}\right)_{T,V} \quad (A12)$$

$$\left(\frac{\partial^2 \bar{A}_C}{\partial x^3}\right)_{T,V} = \frac{(r_1 - r_2)^2}{r_M} \frac{\rho}{1-\rho} + \frac{1}{x_1 x_2} - \frac{2(r_1 - r_2)^2 \rho}{r_M \{1 + (q_M / r_M - 1) \rho\}} \quad (A13)$$

$$\left(\frac{\partial^2 \bar{A}}{\partial \theta_1^2}\right)_{T,V} = -\frac{z}{2} \left[\frac{2(-1-\alpha)\tau_{01} + 1 + \alpha\tau_{21}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} - \theta_1 \left(\frac{(-1-\alpha)\tau_{01} + 1 + \alpha\tau_{21}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} \right)^2 \right] = \frac{2\alpha(-1-\alpha)\tau_{02} + \tau_{12} + \alpha}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} - \theta_2 \left(\frac{(-1-\alpha)\tau_{02} + \tau_{12} + \alpha}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} \right)^2 \quad (A14)$$

$$\left(\frac{\partial^2 \beta P}{\partial x \partial V}\right)_T = \left(\frac{\partial^2 \beta P_C}{\partial V \partial x}\right)_T + \frac{q_1 \rho}{r_M \{1 + (q_M / r_M - 1) \rho\}^2} \left[\left(1 + \frac{q_2 - r_2}{r_M} \rho \right) \left(\frac{\partial^2 \beta P_R}{\partial V \partial \theta}\right)_T + \left(\frac{\rho}{r_M V_H} \right) \left(\frac{(q_M / r_M - 1) \rho - 2(q_2 - r_2) \rho / r_M - 1}{(1 + (q_M / r_M - 1) \rho)} \right) \left(\frac{\partial \beta P_R}{\partial \theta_1}\right)_{T,V} \right] \quad (A15)$$

$$\left(\frac{\partial^2 \beta P_R}{\partial V \partial x}\right)_T = \frac{z\rho}{2r_M V_H^2 [1+(q_M/r_M-1)\rho]} \left[\frac{\tau_{01} \theta_1 \{(-2\theta_1 - \theta_2 - \alpha\theta_2)\tau_{01} + 2\theta_1 + (\theta_2 + \alpha\theta_1)\tau_{21}\}}{(\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21})^2} + \frac{\tau_{01} \theta_1}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} \{ \alpha_V (\tau_{01} - \tau_{21}) (\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}) - 2((1-\alpha)\tau_{01} + 1 + \alpha\tau_{21})(-\theta_1 - \theta_2)\tau_{01} + \theta_1 + \theta_2 \tau_{21} \} \right]$$

$$\begin{aligned}
 & + \alpha_V \left(\frac{\tau_{02}}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} - 1 \right) + \\
 & \alpha \frac{\tau_{02} \{ (-\alpha \theta_1 + \theta_2 + 2\alpha \theta_2) \tau_{02} + (\theta_1 + \theta_2) \tau_{12} + \theta_2 + \alpha \theta_2 \}}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} \\
 & + \frac{\tau_{02} \theta_2}{\theta_0 \tau_{01} + \theta_1 \tau_{12} + \theta_2} \times \left[\alpha_V (\tau_{02} - 1) (\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2) \right. \\
 & \left. - 2 \{ (1 - \alpha) \tau_{02} + \tau_{12} + \alpha \} (-\theta_1 + \theta_2) \tau_{02} + \theta_2 \tau_{12} + \theta_2 \right] \quad (A16)
 \end{aligned}$$

where, $\alpha_V = \frac{2q_2(r_2 - r_1)\rho[1 + (q_M/r_M - 1)\rho]}{r_M z q_1 [1 + (q_2 - r_2)\rho/r_M]^2}$

$$\left(\frac{\partial^2 \beta P}{\partial V^2} \right)_{T,x} = \left(\frac{\partial^2 \beta P_C}{\partial V^2} \right)_{T,x} + \left(\frac{\partial^2 \beta P_R}{\partial V^2} \right)_{T,x} \quad (A17)$$

$$\left(\frac{\partial^2 \beta P_C}{\partial V^2} \right)_{T,x} = \frac{\rho^3}{r_M^2 V_H^3} \left[\frac{2 - \rho}{(1 - \rho)^2} + \frac{z}{2} \frac{(q_M/r_M - 1) \{ 2 + (q_M/r_M - 1) \rho \}}{\{ 1 + (q_M/r_M - 1) \rho \}^2} \right] \quad (A18)$$

$$\begin{aligned}
 & \left(\frac{\partial^2 \beta P_R}{\partial V^2} \right)_{T,x} = \frac{z \rho^2}{2r_M^2 V_H^3 [1 + (q_M/r_M - 1)\rho]^2} \\
 & \left[2\theta_1 \left(\frac{\tau_{01}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} - 1 \right) - 4\theta_1 \frac{\tau_{01} \{ (-\theta_1 - \theta_2) \tau_{01} + \theta_1 + \theta_2 \tau_{21} \}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} \right. \\
 & + 2\theta_1 \frac{\tau_{01} \{ (-\theta_1 - \theta_2) \tau_{01} + \theta_1 + \theta_2 \tau_{21} \}^2}{(\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21})^3} + 2\theta_2 \left(\frac{\tau_{02}}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} - 1 \right) \\
 & - 4\theta_2 \frac{\tau_{02} \{ (-\theta_1 - \theta_2) \tau_{02} + \theta_1 \tau_{12} + \theta_2 \}}{(\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2)^2} \\
 & \left. + 2\theta_2 \frac{\tau_{02} \{ (-\theta_1 - \theta_2) \tau_{02} + \theta_1 \tau_{12} + \theta_2 \}^2}{\theta_2 \tau_{02} + \theta_1 \tau_{12} + \theta_2} \right] \quad (A19)
 \end{aligned}$$

$$\left(\frac{\partial^3 \bar{A}}{\partial x^3} \right)_{T,V} = \left(\frac{\partial^3 \bar{A}_C}{\partial x^3} \right)_{T,V} + \frac{q_1^2 \rho^2}{r_M^2} \frac{\{ 1 + (q_2 - r_2) \rho / r_M \}^2}{\{ 1 + (q_M / r_M - 1) \rho \}^4} \left[\frac{q_1 \{ 1 + (q_2 - r_2) \rho / r_M \}}{1 + (q_M / r_M - 1) \rho} \times \left(\frac{\partial^3 \bar{A}_R}{\partial \theta_1^3} \right)_{T,V} - 3(q_1 - q_2 + r_2 - r_1) \left(\frac{\partial^2 \bar{A}_R}{\partial \theta_1^2} \right)_{T,V} \right] \quad (A20)$$

$$\left(\frac{\partial^2 \bar{A}_C}{\partial x^2} \right)_{T,V} = \frac{(r_1 - r_2)^3}{r_M^2} \frac{\rho^2}{(1 - \rho)^2} \frac{1}{x_1^2} + \frac{1}{x_2^2} \frac{4(r_1 - r_2)^3 \rho^2}{z^2 r_M^3 \{ 1 + (q_M / r_M - 1) \rho \}^2} \quad (A21)$$

$$\begin{aligned}
 & \left(\frac{\partial^3 \bar{A}_R}{\partial \theta^3} \right)_{T,V} = -\frac{z}{2} \left[-3 \left(\frac{(-1 - \alpha) \tau_{01} + 1 + \alpha \tau_{21}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} \right)^2 \right. \\
 & \left. = 2\theta_1 \left(\frac{(-1 - \alpha) \tau_{01} + 1 + \alpha \tau_{21}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} \right)^3 \right]
 \end{aligned}$$

$$-3\alpha \left(\frac{(-1 - \alpha) \tau_{02} + \tau_{12} + \alpha}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} \right)^2 + 2\theta_2 \left(\frac{(-1 - \alpha) \tau_{02} + \tau_{12} + \alpha}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} \right)^3 \quad (A22)$$

$$\begin{aligned}
 & \left(\frac{\partial^2 \bar{A}}{\partial V \partial x^2} \right)_T = \left(\frac{\partial^2 \bar{A}_C}{\partial V \partial x^2} \right)_T + \frac{q_1^2 \rho}{r_M} \frac{\{ 1 + (q_2 - r_2) \rho / r_M \}^2}{\{ 1 + (q_M / r_M - 1) \rho \}^3} \\
 & \left(\frac{\partial^3 \bar{A}_R}{\partial V \partial \theta_1^2} \right)_T - \frac{q_1^2 \rho^2}{r_M^2 V_H} \\
 & \frac{\{ 1 + (q_2 - r_2) \rho / r_M \} \{ 1 - 2(q_M / r_M - 1) \rho + 3(q_2 - r_2) \rho / r_M \}}{\{ 1 + (q_M / r_M - 1) \rho \}^4} \\
 & \left(\frac{\partial^2 \bar{A}_R}{\partial \theta_1^2} \right)_{T,V} \quad (A23)
 \end{aligned}$$

$$\left(\frac{\partial^3 \bar{A}_C}{\partial V \partial x^2} \right)_T = -\frac{(r_1 - r_2)^2 \rho^2}{r_M^2 V_H} \left[\frac{1}{1 - \rho)^2} - \frac{2}{z} \frac{1}{\{ 1 + (q_M / r_M - 1) \rho \}^2} \right] \quad (A24)$$

$$\begin{aligned}
 & \left(\frac{\partial^3 \bar{A}_R}{\partial V \partial \theta^2} \right)_T = \frac{z \rho}{2r_M V_H [1 + (q_M / r_M - 1) \rho]} \\
 & \left[2 \frac{\alpha_V (\tau_{01} - \tau_{21})}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} - 2 \frac{\{ (-1 - \alpha) \tau_{01} + 1 + \alpha \tau_{21} \}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} \times \right. \\
 & \left. \{ (-\theta_1 - \theta_2) \tau_{01} + \theta_1 + \theta_2 \tau_{21} \} - \theta_1 \left(\frac{(-1 - \alpha) \tau_{01} + 1 + \alpha \tau_{21}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} \right)^2 \right. \\
 & - 2\theta_1 \frac{\alpha_V (\tau_{01} - \tau_{21})}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} \times \{ (-1 - \alpha) \tau_{01} + 1 + \alpha \tau_{21} - \\
 & \frac{\{ (-1 - \alpha) \tau_{01} + 1 + \alpha \tau_{21} \}^2 \{ (-\theta_1 - \theta_2) \tau_{01} + \theta_1 + \theta_2 \tau_{21} \}}{\theta_0 \tau_{01} + \theta_1 + \theta_2 \tau_{21}} - \\
 & 2\alpha_V \frac{\{ (-1 - \alpha) \tau_{02} + \tau_{12} + \alpha \}}{(\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2)} + 2\alpha \frac{\alpha_V (\tau_{02} - 1)}{(\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2)} \\
 & \left. \frac{\{ (-1 - \alpha) \tau_{02} + \tau_{12} + \alpha \}}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} \times \{ (-\theta_1 - \theta_2) \tau_{02} + \theta_1 \tau_{12} + \theta_2 \} \right. \\
 & \left. - \theta_2 \left(\frac{(-1 - \alpha) \tau_{02} + \tau_{12} + \alpha}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} \right)^2 - 2\theta_2 \frac{\{ (-1 - \alpha) \tau_{02} + \tau_{12} + \alpha \}}{\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2} \times \right. \\
 & \left. \alpha_V (\tau_{02} - 1) + 2\theta_2 \frac{\{ (\alpha \theta_1 + \theta_2) \tau_{12} + 3\alpha \theta_2 \} \{ (-1 - \alpha) \tau_{02} + \tau_{12} + \alpha \}^2}{(\theta_0 \tau_{02} + \theta_1 \tau_{12} + \theta_2)^3} \right] \quad (A25)
 \end{aligned}$$

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Synthesis and Electrochemical Studies of Cu(II) and Ni(II) Complexes with Tetradentate Schiff Base Ligands

Ki-Hyung Chjo, Byeong-Goo Jeong[†], Jung-Hee Kim, Seungwon Jeon, Chae-Pyung Rim, and Yong-Kook Choi*

Department of Chemistry, Chonnam National University, Kwang-Ju 500-757, Korea

[†]*Department of Electrical Engineering, Seonghwa College, Kangjin, Korea*

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A series of tetradentate Schiff-base ligands; 1,3-bis(salicylideneimino) propane, 1,4-bis(salicylideneimino)butane, and 1,5-bis(salicylideneimino)pentane, and their Cu(II) and Ni(II) complexes have been synthesized. The properties of ligands and complexes have been characterized by elemental analysis, IR, NMR, UV-Vis spectra, molar conductance, and thermogravimetric analysis. The mole ratio of Schiff base to metal at complexes was found to be 1:1. All complexes were four-coordinated configuration and non-ionic compound. The electrochemical redox processes of the ligands and their complexes in DMF solution containing 0.1 M TEAP as supporting electrolyte have been investigated by cyclic voltammetry, chronoamperometry, differential pulse voltammetry at glassy carbon electrode, and by controlled potential coulometry at platinum gauze electrode. The redox process of the ligands was highly irreversible, whereas redox process of Cu(II) and Ni(II) complexes was observed as one electron transfer process of quasi-reversible and diffusion-controlled reaction. Also the electrochemical redox potentials of complexes were affected by chelate ring size of ligands. The diffusion coefficients of Cu(II) and Ni(II) complexes in DMF solution were determined to be $4.2\text{--}6.6 \times 10^{-6}$ cm²/sec. Also the exchange rate constants were determined to be $3.6\text{--}9.7 \times 10^{-2}$ cm/sec.

Introduction

Investigations involving reversible dioxygen complexation

to Schiff base cobalt(II) compounds employing tetradentate ligands have yielded numerous significant findings.¹ There has been considerable interest in Schiff base metal com-