수소결합 격자 상태 방정식을 이용한 혼합물의 상평형 및 과잉 물성 묘사

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Description of Equilibrium and Excess Properties of Mixtures by NLF-HB EOS

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Introduction

Excess property data have been widely correlated by the empirical Redlich-Kister type equation. Excess Gibbs energy (G^E) models which were developed to describe equilibrium properties also have been used to reproduce low-pressure excess enthalpies (H^E) and VLE by fitting temperature dependent model parameters to data of H^E and VLE. Since all residual thermodynamic properties are calculated from an equation of state (EOS), an accurate EOS may be used for the computation of excess properties and VLE simultaneously.

Simple cubic EOSs combined with conventional or G^E-mixing rules have been applied to phase equilibrium and excess property calculations. Orbey and Sandler [1] compared calculated results of cubic EOSs with various mixing rules. The researches for H^E calculations by means of EOS have shown that a G^E-mixing rule with temperature dependent parameters is required for mixtures with associating species and the temperature dependence is not suitable for the extrapolation over wide ranges of temperatures.

Recently, complex EOSs such as SAFT [2], APACT [3], and NLF-HB [4] have been proposed to treat associating chemical species by accounting for the specific interactions between molecules explicitly. However, the usage of the complex EOSs have been focused on equilibrium calculations. One of notable applications to H^E calculation was done by Kang et al. [5]. They used a lattice based EOS of You et al. [6,7] in correlating H^E and VLE simultaneously and obtained satisfactory results for nonpolar-nonpolar systems. In this study, the applicability of NLF-HB EOS [4] to mixtures representing association is studied for simultaneous description of H^E and VLE.

Hydrogen-bonding nonrandom lattice fluid (NLF-HB) model

The configurational partition function of NLF-HB model consists of two parts. The physical contribution is derived by expanding the Guggenheim combinatory around the reference athermal solution and the extended Veytsman statistics [8] is adopted as the chemical part. Then, the Helmholtz free energy expression is obtained after doing some algebra following well-known thermodynamic relations. In this paper we will present the resulting equations for calculation briefly since the detail derivation can be found elsewhere [4,8].

The pressure, chemical potential, and enthalpy expressions are derived as following equations.

$$\frac{PV_H}{RT} = \frac{z}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] - \ln(1-\rho) - \frac{z\beta}{2}\varepsilon_M\theta^2 - (\nu-\nu^0)\rho \tag{1}$$

$$\beta\mu_i = r_i \ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] - r_i \ln(1-\rho) + \ln\left(\frac{\theta_i}{q_i}\right) - D_i \ln\frac{N^{10}_{D}}{N^{10}_{D0}} - \sum_k d^k_i \ln\frac{N^{k0}_{0}}{N_{k0}} - \sum_l a^l_i \ln\frac{N^{0l}_{0}}{N_{0l}}$$
$$+\left(\frac{z\beta}{2}\right) q_i \varepsilon_M \theta^2 \left[1-\frac{r_i}{q_i} - \frac{2\sum\theta_k\varepsilon_{ik} + \beta\sum\sum\sum\theta_j\theta_k\theta_k\varepsilon_{ij}(\varepsilon_{ij}+2\varepsilon_{kl}-2\varepsilon_{jk}-\varepsilon_{ik})}{\varepsilon_M\theta^2}\right] \tag{2}$$

$$\frac{H^c}{RT} = \frac{PV}{RT} - \frac{z}{z-2} q'_M \frac{PV_H}{RT} - r'_M \rho(\nu-\nu^0) + r_M \sum_k\sum_l (\nu_{kl} - \nu^0_{kl})\beta U_{kl} + \frac{zq_M}{2} \ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]$$
$$+\frac{zq_M\beta}{2\theta}\Bigg[\sum\sum\theta_i\theta_j\varepsilon_{ij}\left(\frac{q'_i}{q_i}+\frac{q'_j}{q_j}-\frac{q'_M}{q_M}\theta+\frac{\varepsilon'_{ij}}{\varepsilon_{ij}}-1\right)+\frac{\beta}{2}\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}\{(\varepsilon_{ij}+\varepsilon_{kl}-\varepsilon_{ik}-\varepsilon_{jk})$$
$$\times\left(\frac{q'_i}{q_i}+\frac{q'_j}{q_j}+\frac{q'_M}{q_M}\theta+\frac{\varepsilon'_{ij}}{\varepsilon_{ij}}-2\right)-\frac{q'_M}{q_M}\theta(2\varepsilon_{ij}+4\varepsilon_{kl}-3\varepsilon_{ik}-3\varepsilon_{jk})+\varepsilon'_{ij}+\varepsilon'_{kl}-\varepsilon'_{ik}-\varepsilon'_{jk}$$
$$+\frac{q'_k}{q_k}(\varepsilon_{kl}-\varepsilon_{ik}-\varepsilon_{jk})+\frac{q'_l}{q_l}\varepsilon_{kl}\}\Bigg] \tag{3}$$

where primed quantities denote derivatives with respect to *ln*T.

The surface area parameter (q_i) is obtained using the relation zqi = zr_i-2r_i+2 given r_i. The total number of site (N_r) and surface area (N_q) of system with N_0 vacant sites are evaluated by following equations.

$$N_r = N_0 + \sum N_i r_i, \quad N_q = N_0 + \sum N_i q_i \tag{4}$$

r_M and q_M are mole fraction averages of r_i and q_i. θ and ρ are defined below.

$$\theta = \sum\theta_i = \sum N_i q_i / N_q, \quad \rho = \sum N_i r_i / N_r \tag{5}$$

We also have

$$\varepsilon_M = \frac{1}{\theta^2}\left[\sum\sum\theta_i\theta_j\varepsilon_{ij} + \left(\frac{\beta}{2}\right)\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij}+3\varepsilon_{kl}-2\varepsilon_{ik}-2\varepsilon_{jk})\right] \tag{6}$$

with

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{0.5}(1-\lambda_{ij}) \tag{7}$$

where λ_{ij} is a binary interaction parameter.

For the association contribution, numbers of dimerizing sites, D_1^i, donor type k, d_k^i, and acceptor type l, a_l^i, in molecules of species i and association free energy, A_{kl}, are required. The number of undimerized sites, N^D_{10}, unpaired donor (N_{10}) and acceptor (N_{01}) from dimerizing groups are given by following equations.

$$N^D_{10} = N^D_{01} = \sum_i N_i D^i_1 - 2N_{11} \tag{8}$$

$$N_{10} = N^D_{10} - \sum_{l>1} N_{1l}, \quad N_{01} = N^D_{01} - \sum_{k>1} N_{k1} \tag{9}$$

For numbers of unpaired donor type k>1, and acceptor type l>1, following mass balance relations are used.

$$N_{k0} = \sum_i N_i d^i_k - \sum_{j\geq 1} N_{kj}, \quad N_{0l} = \sum_i N_i a^i_l - \sum_{j\geq 1} N_{jl} \tag{10}$$

N_{11} and N_{kl} are obtained by the simultaneous solution from the constrained maximization conditions of

$$(2N_{11})(N^D_{10}N^D_{01}) = (N_{10}N_{01})^2(r_H/N_r)\exp(-\beta A_{11}) \tag{11}$$

$$N_{kl} = N_{k0}N_{0l}(r_H/N_r)\exp(-\beta A_{kl}) \qquad \text{(for kl} \neq 11) \tag{12}$$

N_{kl}^0 are solutions of the same equations with $A_{ij}=0$. Also defined are ν and ν^0.

$$\nu = \sum_k\sum_l \nu_{kl} = \sum_k\sum_l N_{kl} / \sum_i N_i r_i, \quad \nu^0 = \sum_k\sum_l \nu^0_{kl} = \sum_k\sum_l N^0_{kl} / \sum_i N_i r_i \tag{13}$$

Parameter determination

Two temperature dependent molecular parameters for physical contribution are the segment interaction energy, ε_{ii}, and the segment number, r_i, that are fitted to the saturated liquid density and the vapor pressure data. Then they are correlated as functions of temperature using following equations.

$$r_i = r_a + r_b(T - T_0) + r_c[T\ln(T_0/T) + T - T_0] \quad (14)$$

$$\varepsilon_{ii}/k = e_a + e_b(T - T_0) + e_c[T\ln(T_0/T) + T - T_0] \quad (15)$$

where the reference temperature T_0 is 298.15K.

For associating components ε_{ii} and r_i are also dependent on the association free energy represented in the form,

$$A_{kl} = U_{kl} - TS_{kl} \quad (16)$$

The free energy and the binary interaction parameters are fitted to data of VLE and H^E simultaneously then the binary interaction parameter is correlated by following equation.

$$\lambda_{ij} = a + b/T \quad (17)$$

The segment number of donor or acceptor sites, r_H, is set to 0.05.

Results and discussion

The temperature dependence of the binary interaction parameter was found very sensitive to H^E. Thus by fitting VLE and H^E data at a temperature we can predict VLE at a high temperature accurately as shown in Fig 1 for n-pentane + ethanol mixture at around the room temperature. The extrapolated enthalpy calculation is less accurate. However, with slight losses of accuracy the simultaneous fitting of VLE and H^E was found feasible when the temperature dependence of the binary interaction parameter became more realistic.

In Table 1, calculated results are compared with experimental data from electronic version of Dortmund Data Bank (DDB). The temperature coefficients of a binary parameter were determined at the room temperature and they were used for extrapolation to other temperatures. VLE and H^E calculations including those with extrapolated parameters are generally good.

Conclusion

The applicability of the hydrogen-bonding lattice fluid model (NLF-HB) to describe VLE and H^E were studied for associating mixtures. Parameter optimizations were found feasible for VLE with H^E. The allowing range for the temperature extrapolation of the binary parameter was wide for VLE than for H^E.

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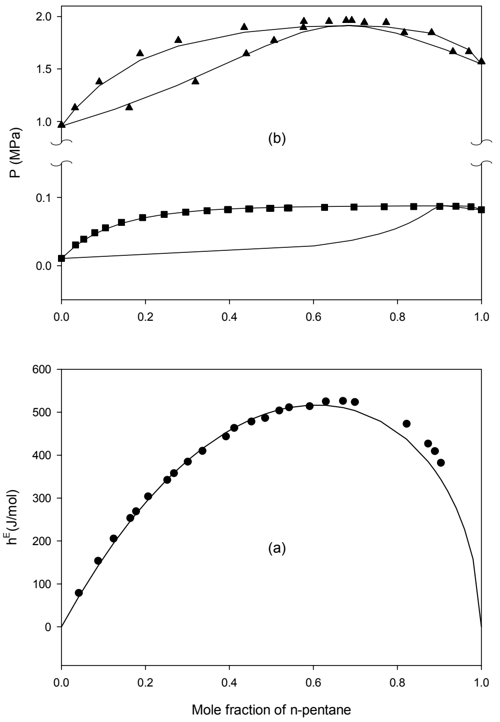

Figure 1. Comparison of calculated properties (----) using extrapolated binary parameter determined from excess enthalpy data at 298.15K and VLE data at 303.15K to VLE calculation at other temperatures for n-pentane + ethanol system: (a) excess enthalpy at 298.15K (●) (b) VLE at 303.15K (■) and 422.6K (▲).

Table 1. Comparisons of calculation results with experimental data

System	λ_{12}		T(K)	VLE		Δh^E(%)
	a	b		ΔP(%)	Δy	
n-butane + ethanol	0.0602	-9.004	298.15	1.18	-	6.60
			323.15*	1.64	-	5.75
n-pentane + ethanol	0.0408	-5.993	298.15	1.54	-	3.61
			422.60*	2.01	0.0151	-
n-hexane + ethanol	0.0350	-5.665	283.15*	2.97	0.0340	8.75
			298.15	0.47	0.0239	4.83
			308.15*	1.43	0.0268	22.60
n-hexane + 1-propanol	0.0196	-1.073	298.15	1.56	0.0024	10.13
			308.15*	2.51	-	8.91
n-hexane + 1-butanol	0.0199	-0.865	298.15	2.50	0.0064	8.88
n-hexane + 1-pentanol	0.0063	1.099	298.15	1.38	0.0036	5.57
Avg.				2.20	0.0145	9.07