빈자리를 포함한 격자 상태방정식의 그룹기여 방식에 의한 순수, 혼합 유체의 상평형물성 예측

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Prediction of Pure and Mixture Fluid Phase Equilibria Properties by Group Contribution Application of New Lattice-Hole EOS

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Introduction

Group contribution methods, for instances UNIFAC and ASOG, are developed for the thermodynamic properties of various fluids and their mixtures. And these methods are capable of making prediction of properties for which only the molecular structure may be known

The present method is based on a new lattice-hole equation of state derived by expanding the Helmholtz free energy from the full Guggenheim combinatory with vacant sites around the reference athermal solution.

The main object of this work is to calculate group interaction and size parameters of EOS and show applicabilities in predicting phase equilibria properties of pure n-alkanes, pure olefins, pure alchols, pure ketones and their mixtures.

Equation of State

Considering the lattice which has a coordination number z and unit cell volume V_H, we derived an approximate configurational Helmholtz energy function from the quasichemical theory.

$$\begin{aligned}\beta A^c = & \sum_{i=0}^{c} N_i(\ln N_i - 1) - N_r(\ln N_r - 1) \\ & - (\frac{z}{2})[N_q \ln N_q - N_q - N_r \ln N_r + N_r] - (\frac{zN_q}{2})\beta [\sum\sum \theta_i\theta_j\varepsilon_{ij} \\ & + (\frac{\beta}{2}) \sum\sum\sum\sum \theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk})] + \cdots \end{aligned} \quad (1)$$

where $\beta = 1/kT$ and

$$\theta_i = N_i q_i / N_q, \quad N_q = N_0 + \sum N_i q_i, \quad N_r = N_0 + \sum N_i r_i \quad (2),(3),(4)$$

ε_{ij} is the interaction energy between species i and j and assumed as follows

$$\varepsilon_{ij}=(\varepsilon_{ii}\varepsilon_{jj})^{\frac{1}{2}}(1-\lambda_{ij}) \tag{5}$$

where λ_{ij} is the binary interaction parameter. There are no interactions between holes and species.

At each molecule of species i segment number r_i and surface area parameter q_i have a relation in lattice theory.

$$zq_i=(z-2)r_i+2 \tag{6}$$

The equation of state and the chemical potential of component i can be obtained from A^c .

$$P=(\frac{1}{\beta V_H})\left\{(\frac{z}{2})\ln[1+(\frac{q_M}{r_M}-1)\rho]-\ln(1-\rho)\right\}-(\frac{z}{2})\theta^2(\frac{\varepsilon_M}{V_H}) \tag{7}$$

$$\frac{\mu_i}{RT}=\gamma_i(T)-r_i\ln(1-\rho)+\ln(\frac{\theta_i}{q_i})+r_i\ln[1+(\frac{q_i}{r_M}-1)\rho]+\frac{zq_i\beta\varepsilon_M\theta^2}{2} \times[1-\frac{r_i}{q_i}-\frac{2\sum\theta_j\varepsilon_{ij}+\beta\sum\sum\sum\theta_k\theta_l\theta_m\varepsilon_{ik}(\varepsilon_{ik}+2\varepsilon_{lm}-2\varepsilon_{kl}-\varepsilon_{il})}{\theta^2\varepsilon_M}] \tag{8}$$

where,

$$q_M=\sum x_iq_i\ ,\quad r_M=\sum x_ir_i \tag{9), (10}$$

and reduced density ρ, ε_M and θ are defined as,

$$\rho=\sum V_i^*/V=\sum r_iN_i\ /\ (N_0+\sum r_iN_i) \tag{11}$$

$$\varepsilon_M=\frac{1}{\theta^2}[\sum\sum\theta_i\theta_j\varepsilon_{ij}+(\frac{\beta}{2})\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij}+3\varepsilon_{kl}-2\varepsilon_{ik}-2\varepsilon_{jk})] \tag{12}$$

$$\theta=\sum N_iq_i\ /\ (N_0+\sum N_iq_i) \tag{13}$$

Group contribution application

We are able to apply to group contribution method in calculating required characteristic volume, V_i^*, and interaction energy parameter, ε_{ij}. V_i^* is related to the segment number, r_i, by the relation

$$V_i^*=N_aV_Hr_i=N_aV_H\sum\nu_{ij}r_i^G=\sum\nu_{ij}V_j^* \tag{14}$$

where ν_{ij} is the number of group j in a molecule of species i, r_i^G is the segment number of group i and V_j^* is the characteristic volume of group

j, N_a is the Avogadro's number. The energy parameter ε_{ij} is assumed

$$\varepsilon_{ij}=\sum_k\sum_l \nu_{ik}\nu_{jl}q_k^G q_l^G \varepsilon_{kl}^G \;/\; \sum_k\sum_l \nu_{ik}\nu_{jl}q_k^G q_l^G \tag{15}$$

where superscript G means group values. The most noticeable implication is that the interaction between identical groups do not change whether in pure fluids or in mixtures.

We suggest to distinguish two kinds of groups, internal and end groups.

$$zq_i^G=(z-2)r_i^G \qquad \text{for internal groups} \tag{16a}$$

$$zq_i^G=(z-2)r_i^G+1 \qquad \text{for end groups} \tag{16b}$$

The group parameters r_j^G and ε_{ij}^G are determined from experimental data. Lattice parameters are set to $z=10$ and $N_aV_H=9.75$ cm³/mol .

The temperature dependence of these parameters are

$$V_i^{*G}=V_a+V_bT+V_c\ln T \tag{17}$$

$$\varepsilon_{ij}^G/k=E_a+E_bT+E_c\ln T \tag{18}$$

Results and Discussion

We can calculate properties of pure fluids and mixtures by using the same set of parameters which is determined from saturated liquid volume, vapor pressure and isothermal VLE data fittings.

Table 1. Coefficients for the group volume parameter

Groups	V_a	V_b	V_c
CH3	-12.2276	-0.02944	8.090
CH2	12.8760	-0.00471	0.677
CH2=CH	1.6323	-0.02830	7.509
OH	-153.2154	-0.04196	30.848
CH2 (alcholic)	7.6420	-0.01382	2.298
CH3COCH2	-21.0099	-0.02548	14.914
CH2COCH2	30.4253	0.00426	2.425

Parameters for selected group characteristic volume and interaction energy temperature coefficients are given in table 1 and 2 respectively. Phase equilibria properties are presented figure 1 and 2.

As shown by figures, results have good agreement with the experimental data.

Table 2. Coefficients for the group group interaction energy parameters.

Group - group	E_a^G	E_b^G	E_c^G
CH3 - CH3	-367.6360	-0.23606	89.5412
CH3 - CH2	556.8128	0.26448	-93.4181
CH3 - CH2=CH	-2116.9508	-1.34640	456.7744
CH3 - OH	-1617.0744	-1.72138	399.4815
CH3 - CH3COCH2	286.2419	0.04605	-28.1594
CH3 - CH2COCH2	379.4457	0.12270	-46.4998
CH2 - CH2	-405.4151	-0.17563	98.8410
CH2 - CH2=CH	882.8690	0.47164	-161.1110
CH2 - OH	11559.6204	5.48760	-2273.2296
CH2 - CH3COCH2	612.7469	0.34038	-106.0253
CH2 - CH2COCH2	138.3475	0.07917	-8.7089
CH2=CH - CH2=CH	1714.5884	1.11616	-343.8887
OH - OH	8634.6063	0.49982	-1354.5754
CH3COCH2 -CH3COCH2	359.2045	0.13484	-50.1012
CH2COCH2 - CH2COCH2	380.7958	0.16908	-58.0746

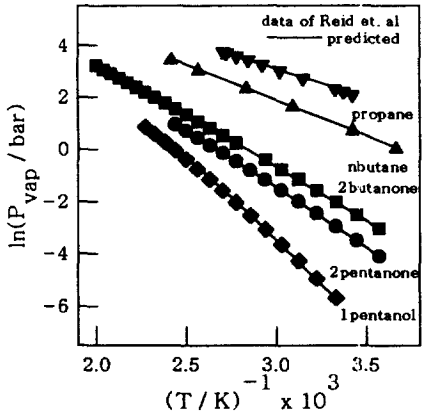

Figure 1. Comparison of vapor pressure

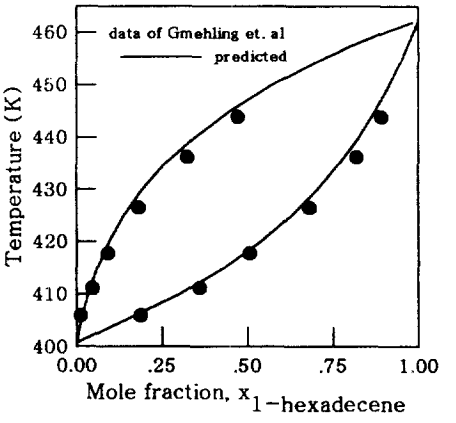

Figure 2. T-x-y equilibria at 0.0667bar for 1-hexadecene - n-dodecane system.

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