A GROUP CONTRIBUTION METHOD BASED ON NONRANDOM LATTICE-HOLE THEORY WITH MOLECULAR BULKINESS

Byung Heung Park, Min Sun Yeom*, Ki-Pung Yoo* and Chul Soo Lee[†]

Department of Chemical Engineering, Korea University, Seoul 136-701, Korea
*Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea

Abstract – The Guggenheim nonrandom lattice-hole theory for open chain molecules was extensively studied recently and a new rigorous equation of state (EOS) was proposed by the present authors. A method was also proposed for the estimation of EOS parameters based on a group contribution (GC) applicable to large molecules. In the present study, the formalism was extended to closed chain molecules and small molecules based on the Staverman combinatory. Using the new method properties of alkanes, ethers, ketons, alcohols and their mixtures were predicted. Since the present method is an EOS method, it applies to pure systems as well as mixtures and to high pressure systems. Flash calculation results indicate that the present method is as accurate as the UNIFAC method.

Key words: Lattice-Hole Theory, Bulkiness Factor, Group Contribution, Prediction, Physical Properties, Phase Equilibria, Pure Fluids, Mixtures

INTRODUCTION

Although some limited success has been achieved, it is still difficult to predict thermophysical properties of mixtures solely in terms of intermolecular forces and the molecular structure of pure components. Taking a step forward, the present authors recently formulated a fundamental concept of a group contribution method for thermodynamic properties of single- and multi-component real fluids [Yoo and Lee, 1996; Yoo et al., 1996, 1997]. The approach is based on a recent rigorous model for general r-mer fluids [You et al., 1993, 1994a,b,c]. The authors introduced a postulate that functional group interactions between molecules should be identical whether the groups are in pure fluids or in multi-component mixtures. The approach was found predictive for simultaneously estimating various physical properties of pure substances, and vapor-liquid, liquid-liquid and vapor-solid equilibria of real mixtures.

The basic scheme of the group contribution method involves the determination of molecular parameters from group parameters. The intermolecular interaction energy is an average of inter-group interactions. The molecular size and surface area are the sum of corresponding group properties. However, the previous approach [Yoo and Lee, 1996; Yoo et al., 1996, 1997] satisfied the summation conditions only approximately. Subsequently Lee and Yoo [1997] proposed a more general scheme involving the group bulkiness factor. The present study explores the consequences of the generalization.

APPROXIMATE LATTICE-HOLE THEORY

As we discussed in detail elsewhere [You et al., 1993,

1994a,b,c, 1995a,b], the lattice-hole description of fluids is developed for a lattice space of the coordination number z and of the unit cell size, V_H. Molecules of component i occupy r_i sites and interact with a neighboring segment of molecules or holes. The effective surface area of species i for interaction is q_i so that zq_i is the number of external contacts. The r_i values for holes are assumed unity.

The configurational lattice-hole partition function of Guggenheim [1952] for linear or branched chain r-mers is based on the relation,

$$zq_i = (z-2)r_i + 2 \tag{1}$$

The present authors [You et al., 1994b] recently derived a new approximate configurational Helmholtz free energy by expanding the full Guggenheim partition function. The resulting equation of state (EOS) from the approximate Helmholtz free energy was found adequate in calculating various phase equilibrium properties of pure fluids and complex mixtures [You et al., 1993, 1994 a,b,c].

In the general scheme of Lee and Yoo [1997] the open chain assumption was relaxed using the Staverman formula [Staverman, 1950; Smirnova and Victorov, 1987]. In the method relation Eq. (1) is extended by introducing the 'the bulkiness factor', l_i,

$$zq_i = (z-2)r_i + 2(1 - l_i) \tag{2}$$

Following the similar derivation for the Guggenheim combinatory without the bulkiness factor [You et al., 1994b], a new expression of Helmholtz free energy stemming from the Staverman formula can be obtained. After some algebra, the Helmholtz free energy expression is obtained,

$$\beta A^c = \sum_{i=1}^{c} N_i \lambda_i + \sum_{i=0}^{c} N_i \ln N_i - \sum_{i=0}^{c} N_i - N_r \ln N_r + N_r + \sum_{j=1}^{c} N_j l_j \ln N_r$$

$$-\left(\frac{\beta z N_q}{2}\right)\left[\sum_{i=1}^{g}\sum_{j=1}^{g}\theta_i\,\theta_j\,\varepsilon_{ij} + \frac{\beta}{2}\sum_{i=1}^{g}\sum_{j=1}^{g}\sum_{k=1}^{g}\sum_{l=1}^{g}\theta_i\,\theta_j\,\theta_k\,\theta_l\,\varepsilon_{ij}\right.$$

$$\left.(\varepsilon_{ij}+\varepsilon_{kl}-\varepsilon_{ik}-\varepsilon_{jk})\right] \tag{3}$$

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

$$-\left(\frac{z}{2}\right)\theta^2\left(\frac{\varepsilon_M}{V_H}\right) \tag{4}$$

$$\varepsilon_M = \left(\frac{1}{\theta^2}\right)\left[\Sigma\Sigma\theta_i\,\theta_j\,\varepsilon_{ij} + \left(\frac{\beta}{2}\right)\Sigma\Sigma\Sigma\Sigma\theta_i\,\theta_j\,\theta_k\,\theta_l\,\varepsilon_{ij}\right.$$

$$\left.(\varepsilon_{ij}+3\varepsilon_{kl}-2\varepsilon_{ik}-2\varepsilon_{jk})\right] \tag{5}$$

where $\beta=1/kT$, and N_0 and N_i ($i>0$) are the number of holes and molecular species. q_M $(=\Sigma x_i q_i)$, r_M $(=\Sigma x_i r_i)$ and l_M $(=\Sigma x_i l_i)$ are mole fraction averages of relevant properties for the molecular species. The θ $(=\Sigma\theta_i)$ is the total surface area fraction of molecules and ρ $(=\Sigma r_i N_i/[N_0+\Sigma r_i N_i])$ is a reduced density. Expressions for other thermodynamic properties may also be obtained. We set $z=10$ and $N_A V_H=9.75$ cm^{3}mol^{-1} where N_A is Avogadro's number. Thus parameters for pure subtances are r_i, ε_{ii} and l_i. For binary mixtures an adjustable binary interaction parameter, λ_{ij}, is defined by $\varepsilon_{ij}=(\varepsilon_{ii}\varepsilon_{jj})^{0.5}(1-\lambda_{ij})$.

GROUP CONTRIBUTION METHODS BASED ON EOS

1. Basic Framework

The basic framework for determining molecular parameters from corresponding group parameters is that the intermolecular interaction energy is an average of inter-group interactions and that molecular size and surface area are the sum of corresponding group properties. Thus r_i and ε_{ij} are expressed in terms of the group characteristics r_i^G and r_{ij}^G [Yoo and Lee, 1996; Yoo et al., 1996, 1997].

$$r_i = \sum_{j=1}^{g} v_{ij} r_i^G \tag{6}$$

$$\varepsilon_{ij} = \sum_{k=1}^{g}\sum_{l=1}^{g}\theta_{ik}^G\theta_{jl}^G\varepsilon_{kl}^G = \sum_{k=1}^{g}\sum_{l=1}^{g}v_{ik}v_{jl}q_k^G q_l^G\varepsilon_{kl}^G \Big/ \sum_{k=1}^{g}\sum_{l=1}^{g}v_{ik}v_{jl}q_k^G q_l^G \tag{7}$$

where v_{ij} is the number of group j in species i. r_i^G and q_j^G are the segment number and the surface area parameter of group j. θ_{ik}^G is the surface area fraction of group k in species i. ε_{kl}^G is the interaction energy parameter between group k and l.

The temperature dependence of these parameters r_i^G and ε_{ij}^G is represented by

$$r_j^G = d_j^G + e_j^G(T-T_0) + f_j^G\left(T\ln\frac{T_0}{T}+T-T_0\right) \tag{8}$$

$$\varepsilon_{ij}^G/k = a_{ij}^G + b_{ij}^G(T-T_0) + c_{ij}^G\left(T\ln\frac{T_0}{T}+T-T_0\right) \tag{9}$$

where T_0 is a reference temperature (298.15 K). The functional form defined above is adopted from the theory proposed by a previous investigator [Kehiaian et al., 1978]. In principle, the numerical parameters can be determined from experimental pVT and vapor pressure data of pure substances, and the phase equilibrium data of mixtures. λ_{ij} is no longer required in the group contribution method.

In the determination of group parameters, r_i^G and ε_{ij}^G, lattice theories require that r_i and q_i satisfy Eq. (1) if the bulkiness factor is set to zero. High and Danner [1990] separately determined r_i^G and q_i^G for each group without introducing the molecular bulkiness factor. Yoo and Lee [1996] assumed q_i^G is proportional to r_i^G. This approach leads to a violation that the resulting r_i and q_i as a sum of group properties do not satisfy Eq. (1). The summation condition for q_i may be written as,

$$q_i = \sum_{j=1}^{g} v_{ij} q_j^G \tag{10}$$

The freedom in choosing both r_i^G and q_i^G is allowed only with the nozero bulkiness factor as in Smirnova and Victorov [1987].

2. Case I: $q_j^G=r_j^G$ and $l_i=0$

This condition requires that Eqs. (1), (6) and (10) be satisfied simultaneously. Since the effect of the molecular bulkiness factor is not significant for a large chain molecule, $q_j^G= r_j^G$ becomes an approximate solution, which is convenient. This assumption also avoids the complexity associated with the bulkiness factor. This relation was the basis for previous works [Yoo and Lee, 1996; Yoo et al., 1996] and was tested extensively [Yoo et al., 1997]. Various experimental phase equilibria behaviors were predicited. However, they produced large errors for the hydrocarbons of low carbon number (i.e., C_3 and lower) as expected.

3. Case II: $l_i=0$ and $l_i^G=n_{e,i}$

Instead of case I, a new relation was established to satisfy Eq. (1) on the molecular level. On the group level Eq. (2) is written for q_i^G for linear or branched chains as

$$zq_i^G = (z-2)r_i^G + (2-n_{e,i}) \tag{11}$$

where $n_{e,i}$ is the number of branches in a group i [Lee and Yoo, 1997]. Thus, for example, $n_{e,i}=1$ for end groups and $n_{e,i}=2$ for internal groups in a linear chain. Although the argument here is not exact for groups in aromatics and cyclic compounds, the idea was extended empirically to such compounds. Based on this relation, new sets of parameters were determined from existing data resources [Timmermans, 1950; Gmehling et al., 1980] and presented in Tables 1 and 2.

4. Case III: $l_i\neq0$

In the present case we have the freedom of chosing two out of three parameters, r_i^G, q_i^G and l_i^G. Case II may be regarded as a special case for open chains. Abusleme and Vera [1985] proposed a method to predetermine l_i^G. Then q_i^G is calculated by the relation,

$$zq_i^G = (z-2)r_i^G + (2-l_i^G) \tag{12}$$

The summation condition also applies to l_i^G. The consequences of this case have yet to be explored.

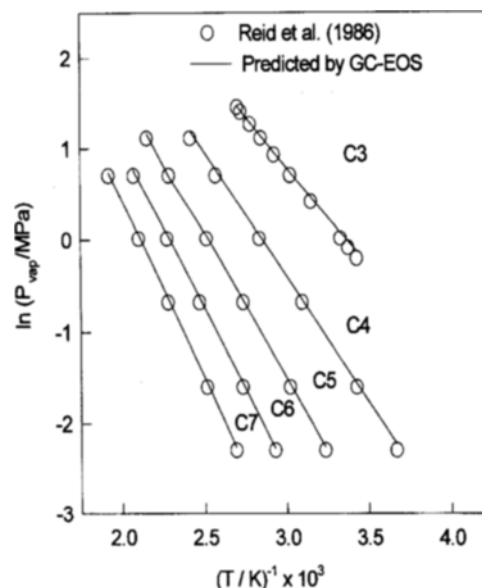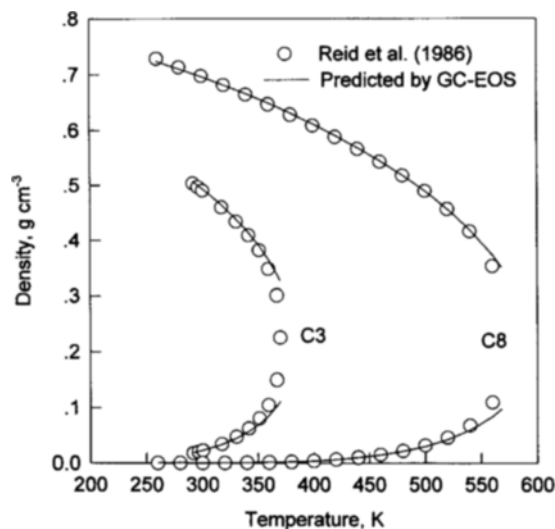**Table 1. Temperature coefficients for the group size parameter defined by Eq. (8)**

Group	d_j^G	e_j^G	f_j^G	Range (K)
CH₃-	2.5718	-0.0002716	0.002181	250-550
-CH₂-	1.5721	-0.0002531	0.000182	250-550
-CH₂CH-	3.6887	-0.0003520	0.002024	250-550
OH-	1.0237	0.006175	0.008315	250-550
-CH₂- (alcoholic)	1.7037	-0.0006369	0.0006194	250-550
CH₃COCH₂-	5.7414	0.002418	0.003990	280-510
-CH₂COCH₂-	4.6687	0.001233	0.0005835	330-540
CH₃OCH₂-	4.8392	0.0002767	0.0008777	260-490
-CH₂OCH₂-	3.9596	0.0003899	0.002218	250-570
-CH<	0.4646	-0.0001526	-0.0000553	280-540

Table 2. Temperature coefficients for the group-group interaction energy defined by Eq. (9)

Group-Group		a_{ij}^G	b_{ij}^G	c_{ij}^G	Range (K)
CH₃-	-CH₃	72.0002	0.0605	0.2353	250-550
CH₃-	-CH₂-	103.5676	-0.0449	-0.2455	250-550
CH₃-	-CH₂CH-	83.3604	0.1663	1.2005	250-550
CH₃-	-OH-	145.1020	-0.3984	1.0499	250-550
CH₃-	CH₃COCH₂-	110.6718	-0.0439	-0.1011	250-510
CH₃-	-CH₂COCH₂-	131.0306	-0.0261	-0.1009	330-540
CH₃-	CH₃OCH₂-	106.1215	-0.0238	-0.0372	280-510
CH₃-	-CH₂OCH₂-	100.8041	-0.0318	-0.1728	330-540
CH₃-	-CH<	267.6021	-0.0334	-1.6012	240-560
-CH₂-	-CH₂-	105.2091	0.1517	0.2598	250-550
-CH₂-	-CH₂CH-	105.8167	-0.0619	-0.4234	250-550
-CH₂-	-OH-	247.6686	-2.0408	-5.9744	250-550
-CH₂-	CH₃COCH₂-	111.2109	0.0023	-0.0062	280-410
-CH₂-	-CH₂COCH₂-	109.0029	0.1262	0.3102	330-430
-CH₂-	CH₃OCH₂-	103.4076	0.0954	0.1453	280-510
-CH₂-	-CH₂OCH₂-	98.9180	0.1734	0.3692	330-540
-CH₂-	-CH<	115.4852	0.8807	1.6680	240-560
-CH₂CH-	-CH₂CH-	102.1526	0.0227	-0.9038	250-550
-OH-	-OH-	1068.1043	-3.9862	-3.5600	250-550
CH₃COCH₂-	CH₃COCH₂-	140.4363	-0.0480	-0.1099	250-510
-CH₂COCH₂-	-CH₂COCH₂-	145.6958	-0.0153	-0.0537	330-540
CH₃OCH₂-	CH₃OCH₂-	101.5714	-0.0226	-0.0989	280-510
-CH₂OCH₂-	-CH₂OCH₂-	143.4861	-0.0089	-0.0552	330-540
>CH-	-CH<	281.5604	0.0543	-0.8205	240-560

Fig. 1. Predicted vapor pressure of pure n-alkanes.

Fig. 2. Predicted saturated densities of pure n-alkanes.

RESULTS AND DISCUSSION

Among three cases discussed, the applicability of the case II ($l_i \neq 0$ and $l_i = n_{e,i}$) is presented in this study. Fitted values of temperature coefficients for Eqs. (8) and (9) are listed in Table 1 and 2. Using these parameters, we predicted the vapor pressure and saturated densities of vapor and liquid phases of n-alkanes (C₃-C₈). An expert system based approach was proposed by Lee et al. [1993] for division of molecules into groups. We found a larger group gives better results for molecules with double bond, ethers, and ketones. The predicted results were compared with the experimental data [Reid et al., 1986] in Figs. 1 and 2. Except for the critical region the method is seen to yield quantitative agreement. The saturated liq-

uid-phase densities of four pure ethers (i.e., dibutyl-, diethyl-, ethylbuthyl- and ethylpropyl-ethers) were predicted by the model and compared with the experimental data [Reid et al., 1986] in Fig. 3.

In general, the traditional group contribution approaches including the present method cannot differentiate isomers composed of the same functional groups. For four dimethylhexane isomers (i.e., 2,3-, 2,4-, 2,5-, and 3,4-dimethylhexanes), the vapor pressures [Reid et al., 1986] were illustratively predicted. As shown in Fig. 4 the vapor pressures of these dimethylhexanes are not much different; therefore predicted values show reasonable agreement.

Results for cases I and II are compared in Fig. 5 for propane/n-decane system [Gmehling et al., 1980]. It was noted that case I corresponds to the large molecule limit. Therefore, properties of a small molecule like propane are not adequately represented. Such difficulties are seen to have been remov-

ed in case II.

The applicability of the present method is illustrated for different types of mixtures. Average absolute errors are summarized in Table 3. The 1-butanol-*n*-heptane system is seen to show large errors for liquid composition. The trend is expect-
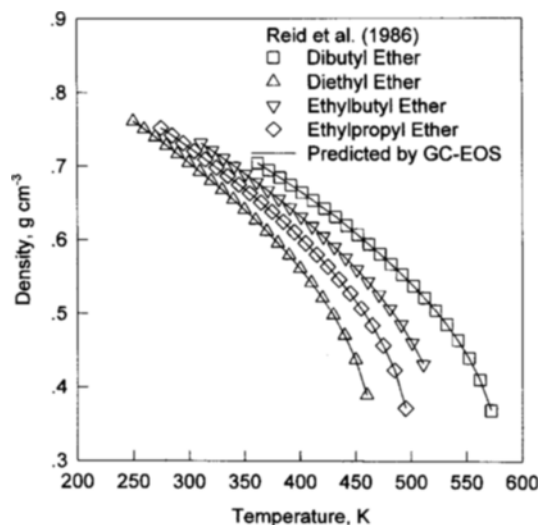

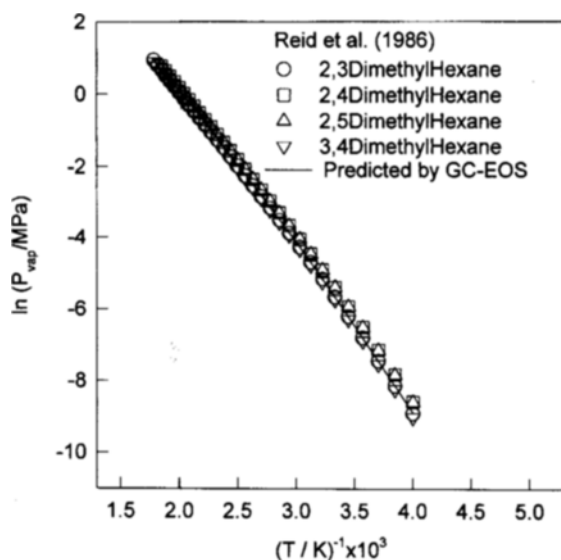Fig. 3. Predicted saturated liquid densities of pure ethers.

Fig. 4. Predicted vapor pressure of pure dimethylhexanes.

ed for strongly polar/nonpolar systems due to the neglect of specific interactions in the present method. For other systems the results are better. The errors in vapor mole fraction are comparable with those by UNIFAC [Sandler, 1993]. It should be noted that the present method applies to pure systems and mixtures while the UNIFAC method applies to mixtures only.

As an example of nonpolar/nonpolar systems, results for isothermal P-x-y data [Gmehling et al., 1980] of *n*-octane/*n*-heptane system are shown in Fig. 6. The prediction result is based on parameters given in Tables 1 and 2. As a polar/polar system, prediction was made for isobaric T-x-y data of a 1-decanol/1-octanol system [Gmehling et al., 1980] as shown in Fig. 7. The present GC-EOS predicts accurately the polar/polar systems. The method is also applicable to polar/nonpolar systems as shown by Fig. 8. The predicted and experimental isothermal P-x-y data of an n-dibutylether/n-heptane system [Gmehling et al., 1980] show close agreement.

For isomers made up by the same group bonded at a different position, different numerical values are given for the group was bonded to end in a molecule and bonded to inside skeletal position as shown in Table 1 and 2. In case of dibutylether, numerical value of ether group was the case of inside
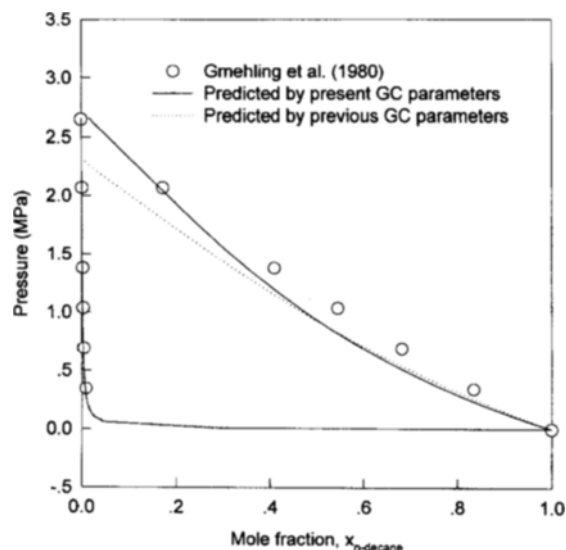

Fig. 5. Predicted isothermal P-x-y data by the previous and present revised GC parameters for propane/*n*-decane system at 344.26 K.

Table 3. Errors for flash calculation by the present method

System	T/K	P/kPa	AADX	AADY	Ref.
n-pentane-propane	344.26	292.3-2663.4	.021	.012	a
n-octane-*n*-heptane	328.15	8.5-23.1	.020	.023	b
isopentane-propane	273.15	50.7-48.1	.051	.037	a
n-hexane-2.3-dibutylbutane	298.15	20.2-31.3	.013	.012	b
1-hexadecene-*n*-heptane	377.15-437.15	2.7	.050	.023	b
1-butanol-*n*-heptane	303.15	4.6-80.5	.135	.002	b
1-hexanol-1-octanol	370.15-400.15	2.7	.039	.014	b
2-butanone-*n*-hexane	333.15	66.7-80.2	.073	.049	b
dibuthylether-*n*-heptane	363.15	26.5-68.4	.002	.024	b

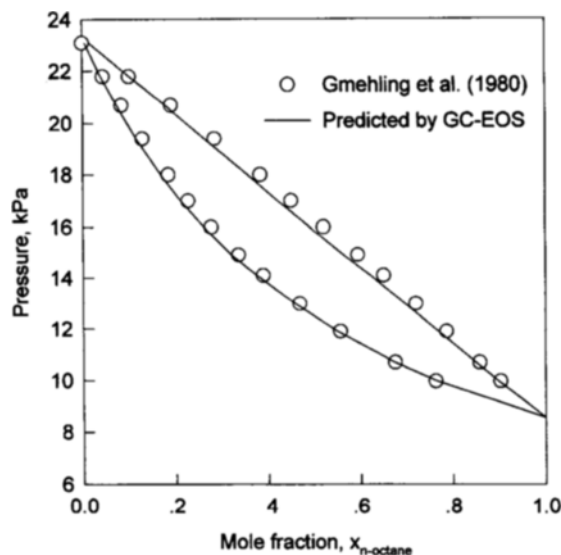a: Knapp et al. [1982], b: Gmehling et al. [1980]

Fig. 6. Predicted isothermal P-x-y equilibrium of n-octane/n-heptane system at 328 K.
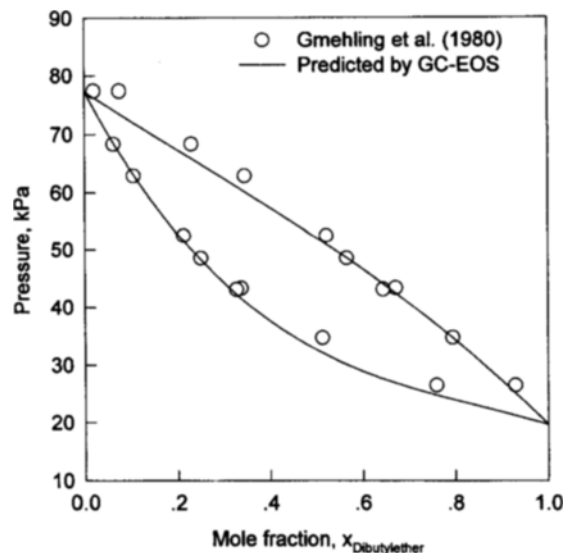

Fig. 8. Predicted isothermal P-x-y equilibrium of dibutylether/n-heptane system at 363.15 K.
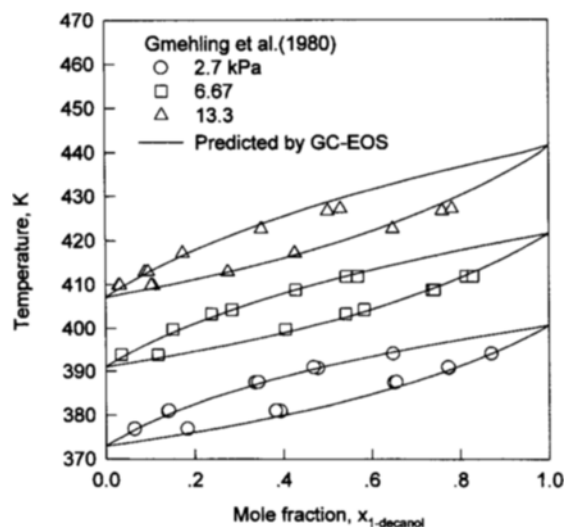

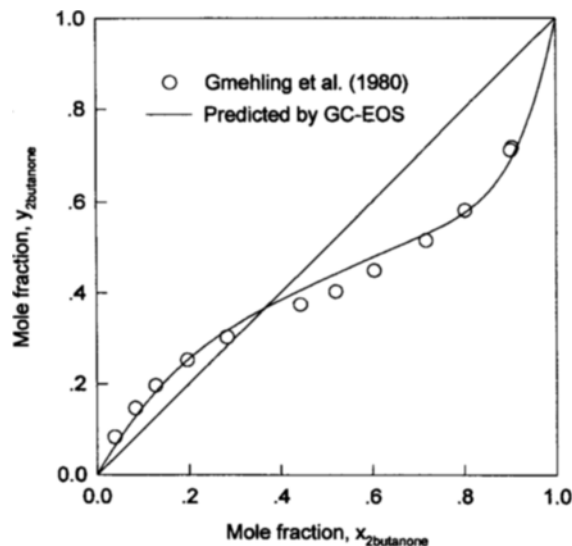**Fig. 7. Predicted isobaric T-x-y equilibria of 1-decanol/1-octanol system.**

Fig. 9. Predicted x-y equilibrium of 2-butanone/n-hexane system at 333.15 K.

bonding. By this way, it was possible to predict more accurately then the case of present work [Yoo et al., 1996]. As a final example, the isothermal x-y equilibrium of 2-butanone/n-hexane system was shown in Fig. 9. Even for an azeotropic system, the model is seen to give good results.

CONCLUSION

The previously proposed group contribution method for EOS parameters of large open chain molecules was extended to accommodate small molecules and closed chain molecules. The summation condition that segment numbers and surface area parameters for groups should correctly add up to give corresponding properties for molecules can be met by introducing bulkiness factors. A method for predetermine the group bulkiness factor was proposed for open chain molecules. Us-

ing the new method, we predicted properties of alkanes, ethers, ketons, alcohols and their mixtures. Flash calculation results indicate that the present method is as accurate as the UNIFAC method.

ACKNOWLEDGMENT

REFERENCES

Abusleme, J. A. and Vera, J. H., "The Quasi-Chemical Group Solution Theory for Organic Mixtures", *Fluid Phase Equilibria*, **22**, 123 (1985).

Guggenheim, E. A., "Mixtures", Oxford Press, London, 1952.

Gmehling, J., Onken, U. and Arlt, W., "Vapor-liquid Equilibrium Data Collection", DECHEMA (Chemistry Data Series), Vol. 1, Frankfurt a/m, 1980.

High, M. S. and Danner, R. P., "Application of the Group Contribution Lattice-Fluid EOS to Polymer Solutions", AIChE J., 36, 1625 (1990).

Kehiaian, H. V., Grolier, J. P. E. and Bebson, G. C., "Thermodynamics of Organic mixtures. A Generalized Quasi-chemical Theory in Terms of Group Surface Interactions", J. Chem. Phys., 75, 1031 (1978).

Knapp, H., Döring, R., Oellrich, L., Plöcker, U. and Prausnitz, J. M., "Vapor-Liquid Equilibria for Mixtures of Low Boiling Subtances", DECHEMA, Frankfurt a/m, 1982.

Lee, C. S. and Yoo, K.-P., "Developments in Lattice-Hole Based Equations of State and Their Applications to Complex Fluids", Fluid Phase Equilibria, in press (1998).

Reid, R. C., Prausnitz, J. M. and Poling, B. E., "The Properties of Gases and Liquids", 3rd ed. McGraw-Hill Book Co., 1986.

Sandler, S. I., "Models for Thermodynamic and Phase Equilibria Calculations", Dekker, New York, 1993.

Smirnova, N. A. and Victorov, A. I., "Thermodynamic Properties of Pure Fluids and Solutions from the Hole Group-Contribution Model", Fluid Phase Equilibria, 34, 235 (1987).

Staverman, A. J., "The Entropy of High Polymer Solutions. Generalization of Formula", Rec. Trav. Chim. Pays-Bas., 69, 163 (1950).

Timmermans, J., "Physicochemical Constants of Pure Organic Compounds", Vol. 1, Elsevier, Amsterdam, 1950.

Yoo, K.-P., Kim, H. and Lee, C. S., "Unified Equation of State Based on the Lattice Fluid Theory for Phase Equilibria of Complex Mixtures Part I. Molecular Thermodynamic Framework", Korean J. Chem. Eng., 12, 277 (1995a).

Yoo, K.-P., Kim, H. and Lee, C. S., "Unified Equation of State Based on the Lattice Fluid Theory for Phase Equilibria of Complex Mixtures Part II. Application to Complex Mixtures", Korean J. Chem. Eng., 12, 289 (1995b).

Yoo, K.-P. and Lee, C. S., "A New Lattice-Fluid Equation of State and Its Group Contribution Application for Predicting Phase Equilibria of Mixtures", Fluid Phase Equilibria, 117, 48 (1996).

Yoo, S. J., Yoo, K.-P., Kim, H. and Lee, C. S., "A New Predictive Quasi-Lattice Equation of State for High-Pressure Phase Equilibria of Pure Fluids and Mixtures", Fluid Phase Equilibria, 125, 21 (1996).

Yoo, S. J., Yoo, K.-P. and Lee, C. S., "Unified Description of Real Fluids and Their Mixtures by Group-Contribution Lattice-Hole Theory", J. Phys. Chem. B., 101, 1072 (1997).

You, S. S., Lee, C. S. and Yoo, K.-P., "Modeling of Supercritical-Fluid Phase-Equilibria Using a New Nonrandom Lattice-Fluid Theory", J. Supercritical Fluids, 6, 69 (1993).

You, S. S., Lee, C. S., Yoo, S. J. and Yoo, K.-P., "Multiphase Behavior and Critical Loci in Binary Mixtues using a New Equation of State Based on the Nonrandom Lattice-fluid Theory", J. Supercritical Fluids, 7, 251 (1994a).

You, S. S., Yoo, K.-P. and Lee, C. S., "An Approximate Nonrandom Lattice Theory of Fluids. General Derivation and Application to Pure Fluids", Fluid Phase Equilibria, 93, 193 (1994b).

You, S. S., Yoo, K.-P. and Lee, C. S., "An Approximate Nonrandom Lattice Theory of Fluids. Mixtures", Fluid Phase Equilibria, 93, 215 (1994c).