Prediction of Configurational Properties of Pure Fluids and Mixtures From Molecular Structures Based on Lattice-Hole Theory[1]

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ABSTRACT

In a previous article elsewhere[1], a new concept of unified group contribution(GC) lattice equation of state(EOS) was formulated by the present authors for predicting configurational properties of pure fluids and mixtures. As a further refinement, the effect of end groups was taken into account on the previous GC scheme in the present study. The refined GC scheme still requires two parameters reflecting size of groups and energetic interaction between groups. The approach quantitatively describes pVT behaviors, phase transition, and phase equilibria of single- and multicomponent fluids in general. The practical utility of the approach was demonstrated by predicting various configurational pure properties and phase equilibria of mixtures.

KEY WORDS: lattice-hole theory, group contribution approach, pure fluids and mixtures, phase equilibria, hydrocarbons.

1. INTRODUCTION

To estimate thermophysical properties of fluids where experimental data are severely limited or even not available, one may consider a predictive method based on a concept of functional group contribution(GC). The GC approach has been used separately for pure fluid properties[2] and for excess properties of liquid mixtures[3-5]. Implementation of a single GC frame for both pure fluids and mixtures remains to be realized.

The recent success of an elementary quasilattice equation of state(EOS) description of fluids by the present authors[6-8] encouraged them to look into GC extension of the EOS. As a result, they proposed a unified GC framework which is applicable to both pure fluids and mixtures in general. The basic idea of the GC-EOS scheme was reported elsewhere with some preliminary applications[1,9,10]. However, some predictive inaccuracy was found in the previous GC formulation when it was applied to low carbon number systems such as $C_1 \sim C_3$ substances since the EOS was based on the lattice theory of r-mer fluids. Thus in recent years the present authors have concentrated on the elimination of such inaccuracies.

When the effect of end-group branching in r-mers was considered in relation to the GC scheme for determining parameters reflecting group segment size and the group-group energetic interaction, it was possible to improve the original GC scheme. We report here the improved GC prediction results obtained to date.

2. APPROXIMATE LATTICE-HOLE THEORY

Since we presented in detail elsewhere on the EOS[6-8], we write here only the essential expressions of the EOS. It is given by,

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

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

where ε_{ij} is the interaction energy between species i and j. $q_M = \Sigma x_i q_i$, $r_M = \Sigma x_i r_i$ and q_i and r_i are the surface area and segment number. ρ is the density and the overall surface area fraction is defined by $\theta = \Sigma\theta_i$ where $\theta_i = N_{ii}q_i / N_q$ and $N_q = N_0 + \Sigma N_i q_i$. N_0 and N_i are the number of holes and molecules of species i. z is the coordination number fixed by 10 and V_H is the unit cell volume fixed by 9.75 cm^3mol^{-1}. The characteristic volume is defined by $V_i^* = N_A V_H r_i$ where N_A is Avogadro's number. Thus the molar volume $V = V_i^* / \rho$. We need to determine two independent molecular parameters, r_i and ε_{ii}. We omit here other equations such as chemical potential[6-8].

3. GROUP CONTRIBUTION SCHEME

The basic GC concept was based on an assumption that group parameters should be identical whether molecules are in pure fluids or in mixtures. This GC idea is applied to determine the molecular parameters r_i and ε_{ij} from group characteristics r_i^G and ε_{ij}^G.

$$r_i = \sum_{j=1}^{g}\nu_{ij}r_j^G \quad (3)$$

$$\varepsilon_{ij} = \sum_{k=1}^{g}\sum_{l=1}^{g}\theta_{ik}^G\theta_{jl}^G\varepsilon_{kl}^G = \sum_{k=1}^{g}\sum_{j=1}^{g}\nu_{ik}\nu_{jl}q_k^G q_l^G\varepsilon_{kl}^G / \sum_{k=1}^{g}\sum_{j=1}^{g}\nu_{ik}\nu_{jl}q_k^G q_l^G \quad (4)$$

where ν_{ij} is the number of group *j* in species *i*. θ_{ik}^G is the surface area fraction of group

k in species i.

When the effect of molecular bulkness factor is not considered[11], the lattice theories require that r_i and q_i satisfy the relation

$$zq_i = (z-2)r_i + 2 \tag{5}$$

In our previous work[1], we simply set $q_j^G = r_j^G$ to avoid the complexity associated with the bulkness factor. However, this condition defined by Eq. (5) can be satisfied by setting q_i^G for linear or branched chains as

$$zq_i^G = (z-2)r_i^G + (2 - n_{e,i}) \tag{6}$$

where $n_{e,i}$ is the number of branches in a group i. Thus, for example $n_{e,i}$ =1 for end group. Other investigators[5] separately determined r_i^G and q_i^G for each group. This leads to a difficulty that the resulting r_i and q_i as a sum of group properties does not satisfy the relation given by Eq. 6. The freedom in choosing r_i^G and q_i^G are allowed only with the introduction of the bulkness factor[12]. Although the argument here is not exact for groups in aromatics and cyclic compounds, the idea was extended empirically to such compounds.

The two group parameters r_i^G and q_i^G are intrinsically a function of temperature and they are related by[13]

$$r_j^G = w_j^G + h_j^G (T - T_0) + c_j^G \left(T \ln \frac{T_0}{T} + T - T_0 \right) \tag{7}$$

$$\mathrm{e}_{ij}^G / k = a_{ij}^G + b_{ij}^G (T - T_0) + d_{ij}^G \left(T \ln \frac{T_0}{T} + T - T_0 \right) \tag{8}$$

where T_0 is set as 298.15 K. The numerical GC parameters in Eq. (8) and (9) obtained previously[1,9,10] were revised in this work by satisfying Eq. (6) from existing data

resources[14,15].

4. RESULTS AND DISCUSSION

The revised numerical values in Eq. (7) and (8) are summarized in Tables ¥ åand¥ ±A unique feature of the method is that the single set of group parameters given in Tables ¥ åand ¥ ±are used for both pure fluids and mixtures in general. With emphasis on practical utility of the present approach, limited prediction results are illustrated due to limited space of this article. The predicted vapor pressure and saturated liquid density of pure alkanes(C_3~C_8) are shown in Fig. 1 and 2, respectively. Also, the vapor pressure of pure eithers is shown in Fig. 3. The revised GC parameters predicts these pure properties data quantitatively well.

As we expected when the effect of end groups was taken into account in the relation of r_i^G and q_i^G, the GC-EOS works quantitatively better than the previous case for mixtures containing low carbon number hydrocarbons(i.e., C_1~C_3)[1]. One example is shown in Fig. 4 for propane/*n*-decane system where the prediction results by the previous[1] and the revised GC parameters are compared. For this system, the revised GC parameters predict the experiment better than the previous one.

In Fig. 5, the predicted isobaric T-x-y data of 1-hexadecene/dodecane system[15] are shown. With a single set of parameters in Tables ¥ åand ¥ ±the EOS predicts data of nonpolar/nonpolar system quantitatively. In Fig. 6, the predicted result for 1-pentanol/*n*-pentane system[15] is shown. As is well known, this system is a nonpolar/polar system and the vapor-phase mole fraction in this system changes drastically with respect to the small variation of pressure. However the model predicts this system reasonably well. In

the next illustration, low pressure T-x-y equilibria of 1-hexanol/1-pentanol system are shown in Fig. 7. The GC parameters obtained to date predict quantitatively the nonpolar/ nonpolar(Fig. 5) and polar/polar(Fig. 7) and show some inaccuracy for nonpolar/polar system(Fig. 6). Finally, the isobaric isothermal x-y equilibria of 2-butanone/*n*-hexane system are shown in Fig. 8. Even with an azeotropic system, the revised GC parameters work relatively well.

In summary, a simple GC scheme in which the effect of end groups was taken into account was implemented to an EOS formulated recently by the present authors. The revised numerical group parameters were based on a limited set of experimental data. Further compilation of these parameters from various collections of experimental data would improve further the reliability of the approach.

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REFERENCES

1. S.J. Yoo, K.-P. Yoo and C.S. Lee, *J. Phys. Chem. B.* **101**:1072 (1977).
2. I. Langmuir, *The distribution and orientation of molecules*, 3rd Colloid Symp. Monograph, (The Chem. Catalog Co. Inc. New York, 1925).
3. E.L. Derr and C.H. Deal Jr, *Inst. Chem. Eng. Symp. Ser.*: London. **3**:40 (1969).
4. A. Fredenslund, R.L. Jones and J.M. Prausnitz, *AIChE. J.* **21**:1086 (1975).
5. High, M. S. and Danner, R. P., *AIChE J.* **36**:1625 (1990).
6. You, S. S., Yoo, K. -P. and Lee, C. S., *Fluid Phase Equilibria.* **93**:193 (1994).
7. You, S. S., Yoo, K. -P. and Lee, C. S., *Fluid Phase Equilibria.* **93**:215 (1994).
8. You, S. S., Lee, C. S., Yoo, S. J. and Yoo, K. -P., *J. Supercrit. Fluids.* **7**: 251 (1994).
9. K.-P. Yoo and C.S. Lee, *Fluid Phase Equilibria.* **117**:48 (1996).
10. S.J. Yoo, K.-P. Yoo, H.Y. Kim and C.S. Lee, *Fluid Phase Equilibria.* **125**: 21 (1996).
11. A.J. Staverman, *Rec. Trav. Chim. Pays-Bas*. **69**:163 (1950).
12. N.A. Smirnova and A.I. Victorov, *Fluid Phase Equilibria.* **34**:235 (1987).
13. H.V. Kehiaian, J.P.E. Grolier and G.C. Bebson, *J. Chem. Phys.* **75**:1031(1978).
14. J. Timmermans, *Physicochemical Constants of Pure Organic Compounds, Vol. 1.* (Elsevier, Amsterdam, 1950).
15. J. Gmehling, U. Onken, and W. Arlt, Vapor-liquid equilibrium data collection,DECHEMA (Chemistry Data Series). Vol. 1. Part 1-7. (Frankfurt a/m, 1990)
16. R.C. Reid, J.M. Prausnitz and B.E. Poling, *The Properties of Gases and Liquids*, 3rd ed. (McGraw-Hill Book Co. 1986).

Table ¥ .°Temperature coefficients for the group size parameter defined by Eq. (7)

Group	w_j^G	h_j^G	c_j^G	Range (K)
CH_3-	2.5718	-0.0002716	0.002181	250-550
-CH_2-	1.5721	-0.0002531	0.000182	250-550
CH_2CH-	3.6887	-0.0003520	0.002024	250-550
OH-	1.0237	0.006175	0.008315	250-550
-CH_2- (alcoholic)	1.7037	-0.0006369	0.0006194	250-550
CH_3COCH_2-	5.7414	0.002418	0.003990	280-510
-CH_2COCH_2-	4.6687	0.001233	0.0005835	330-540
CH_3OCH_2-	4.8392	0.0002767	0.0008777	260-490
-CH_2OCH_2-	3.9596	0.0003899	0.002218	250-570
-CH<	0.4646	-0.0001526	-0.0000553	280-540

Table ¥ ±Temperature coefficients for the group-group interaction energy defined by Eq. (8)

Group-Group	a_{ij}G	b_{ij}G	d_{ij}G	Range (K)
CH_3-CH_3-	72.0002	0.0605	0.2353	250-550
CH_3-CH_2-	103.5676	-0.0449	-0.2455	250-550
CH_3-CH_2CH-	83.3604	0.1663	1.2005	250-550
CH_3-OH-	145.1020	-0.3984	1.0499	250-550
CH_3-CH_3COCH_2-	110.6718	-0.0439	-0.1011	250-510
CH_3-CH_2COCH_2-	131.0306	-0.0261	-0.1009	330-540
CH_3-CH_3OCH_2-	106.1215	-0.0238	-0.0372	280-510
CH_3-CH_2OCH_2-	100.8041	-0.0318	-0.1728	330-540
CH_3-CH<	267.6021	-0.0334	-1.6012	240-560
-CH_2-CH_2-	105.2091	0.1517	0.2598	250-550
-CH_2-CH_2CH-	105.8167	-0.0619	-0.4234	250-550
-CH_2-OH-	247.6686	-2.0408	-5.9744	250-550
-CH_2-CH_3COCH_2-	111.2109	0.0023	-0.0062	280-410
-CH_2-CH_2COCH_2-	109.0029	0.1262	0.3102	330-430
-CH_2-CH_3OCH_2-	103.4076	0.0954	0.1453	280-510
-CH_2-CH_2OCH_2-	98.9180	0.1734	0.3692	330-540
-CH_2-CH<	115.4852	0.8807	1.6680	240-560
CH_2CH-CH_2CH-	102.1526	0.0227	-0.9038	250-550
OH-OH-	1068.1043	-3.9862	-3.5600	250-550
CH_3COCH_2-CH_3COCH_2-	140.4363	-0.0480	-0.1099	250-510
-CH_2COCH_2-CH_2COCH_2-	145.6958	-0.0153	-0.0537	330-540
CH_3OCH_2-CH_3OCH_2-	101.5714	-0.0226	-0.0989	280-510
-CH_2OCH_2-CH_2OCH_2-	143.4861	-0.0089	-0.0552	330-540
CH-CH-	281.5604	0.0543	-0.8205	240-560

FIGURE CAPTIONS

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

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

Fig. 3. Predicted vapor pressures of pure ethers

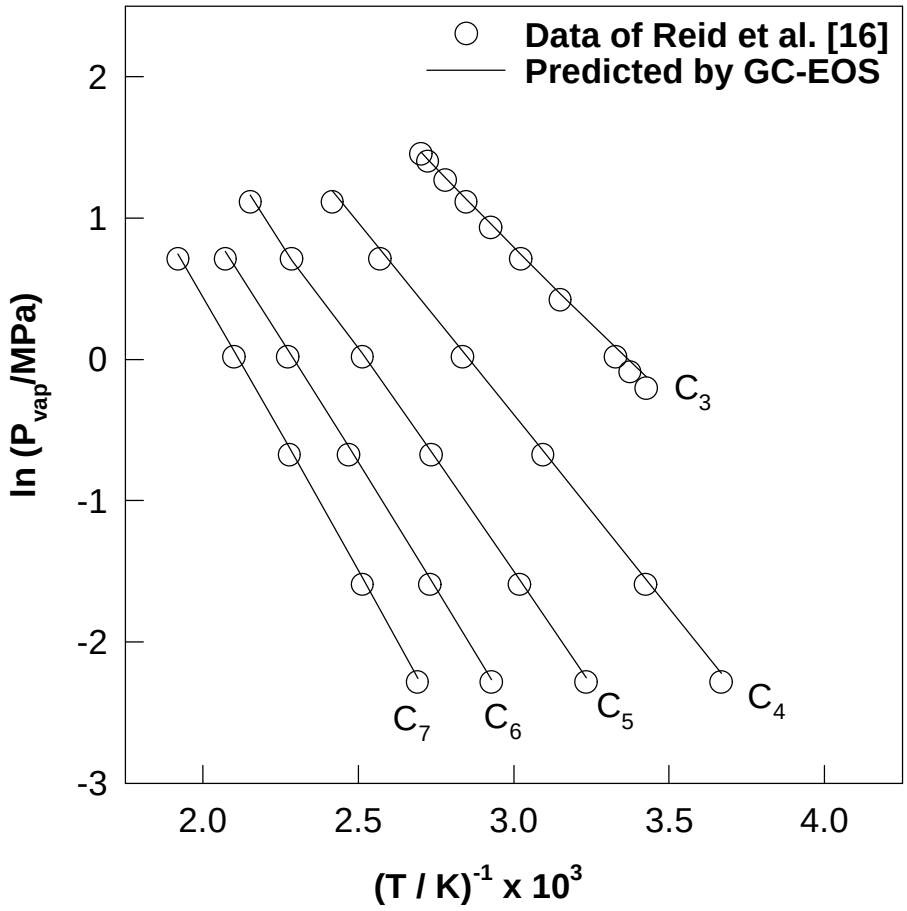
Fig. 4. Predicted isothermal P-x-y data by the previous and present revised GC parameters for propane/*n*-decane system

Fig. 5. Predicted isobaric T-x-y equilibria of 1-hexadecene/dodecane system

Fig. 6. Predicted isothermal P-x-y equilibria of 1-pentanol/n-pentane system at 303.15 K

Fig. 7. Predicted isobaric T-x-y equilibria of 1-hexanol / 1-pentanol system

Fig. 8. Predicted x-y equilibrium of 2-butanone / n-hexane system



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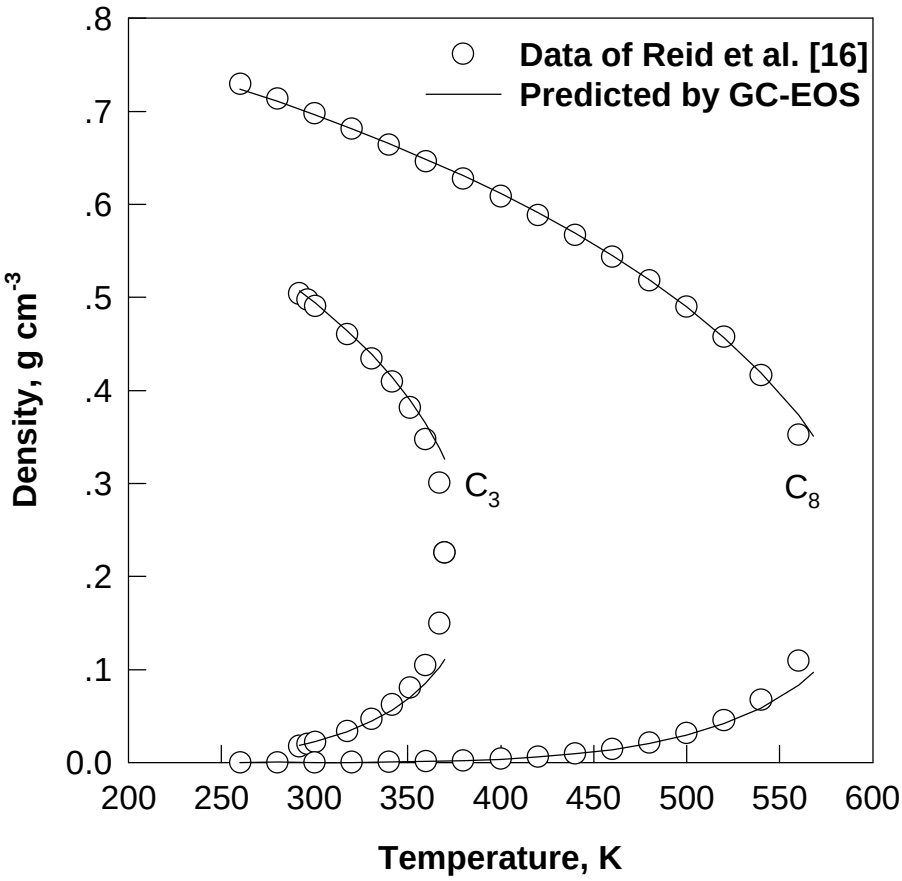
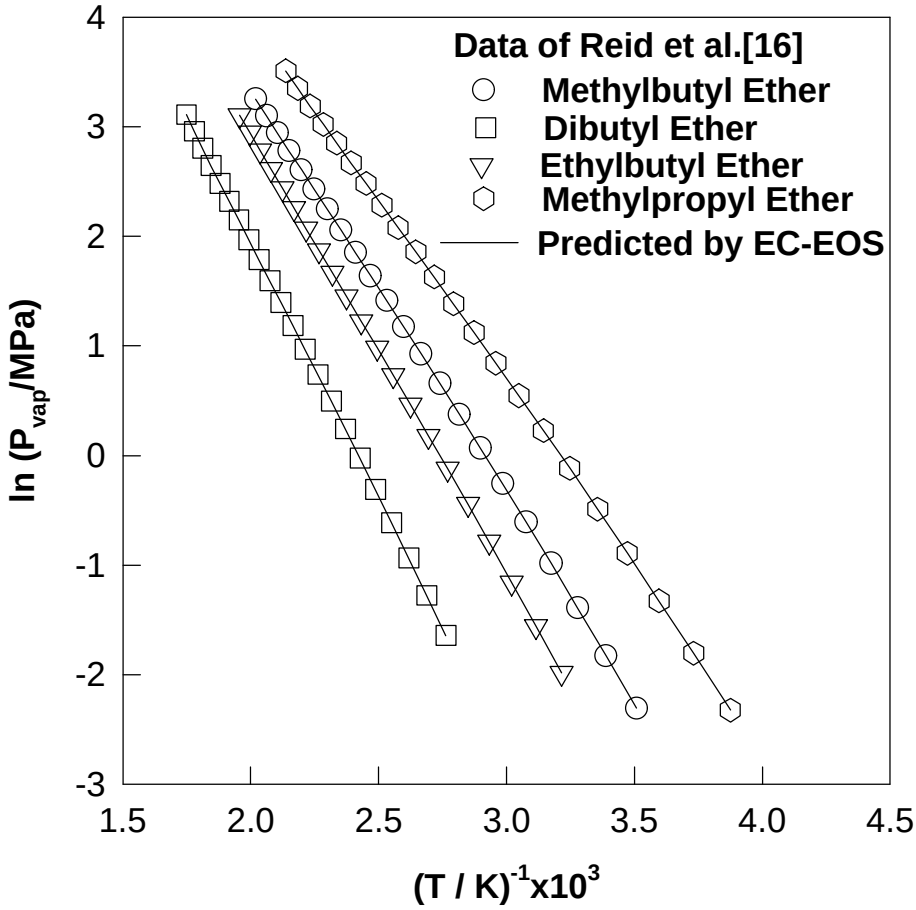


Fig. 2. Predicted saturated densities of pure *n*-alkanes



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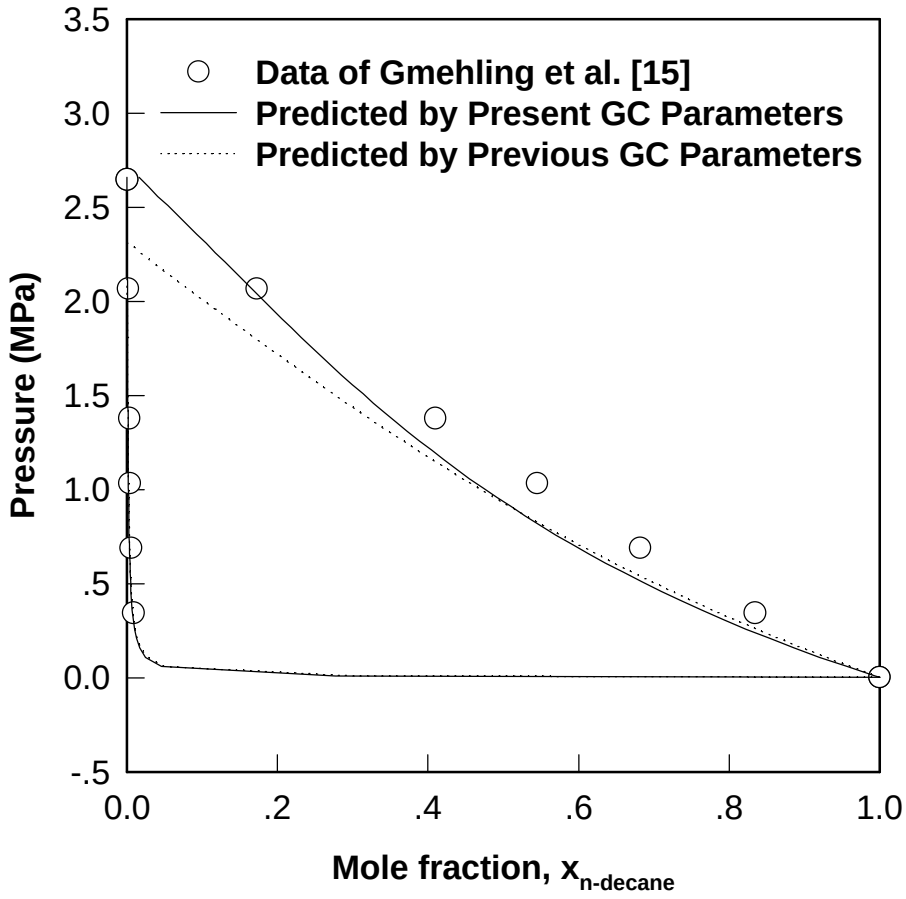

Fig. 4. Predicted isothermal P-x-y data by the previous and present revised GC parameters for propane/*n*-decane system

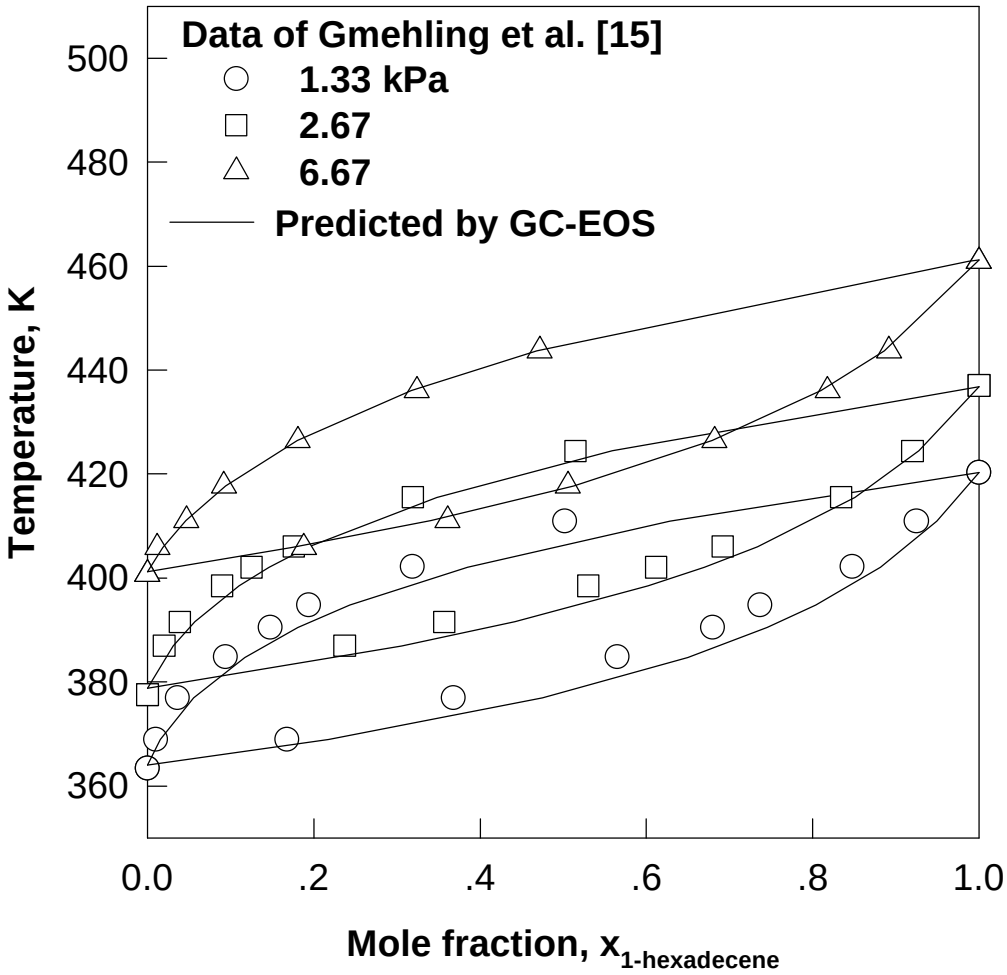

Fig. 5. Predicted isobaric T-x-y equilibria of 1-hexadecene/dodecane system

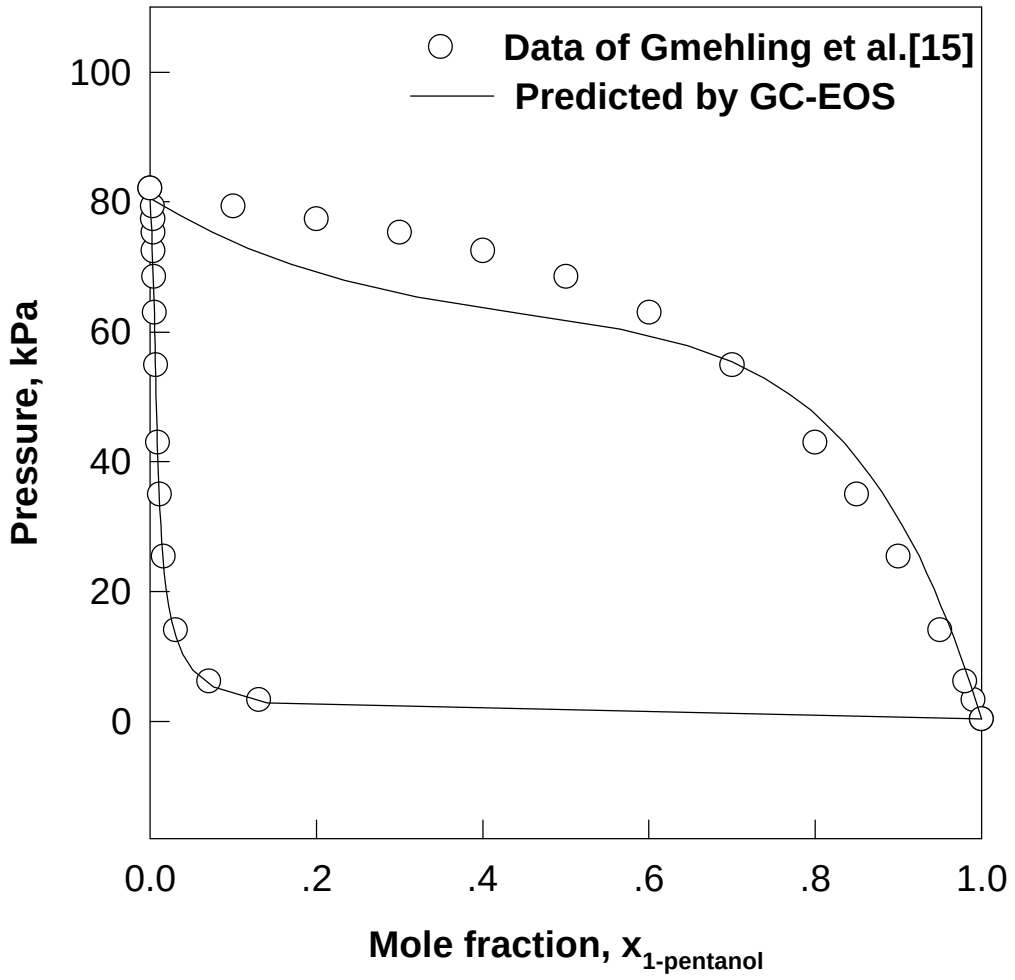

Fig. 6. Predicted isothermal P-x-y equilibria of 1-pentanol/n-pentane system at 303.15 K

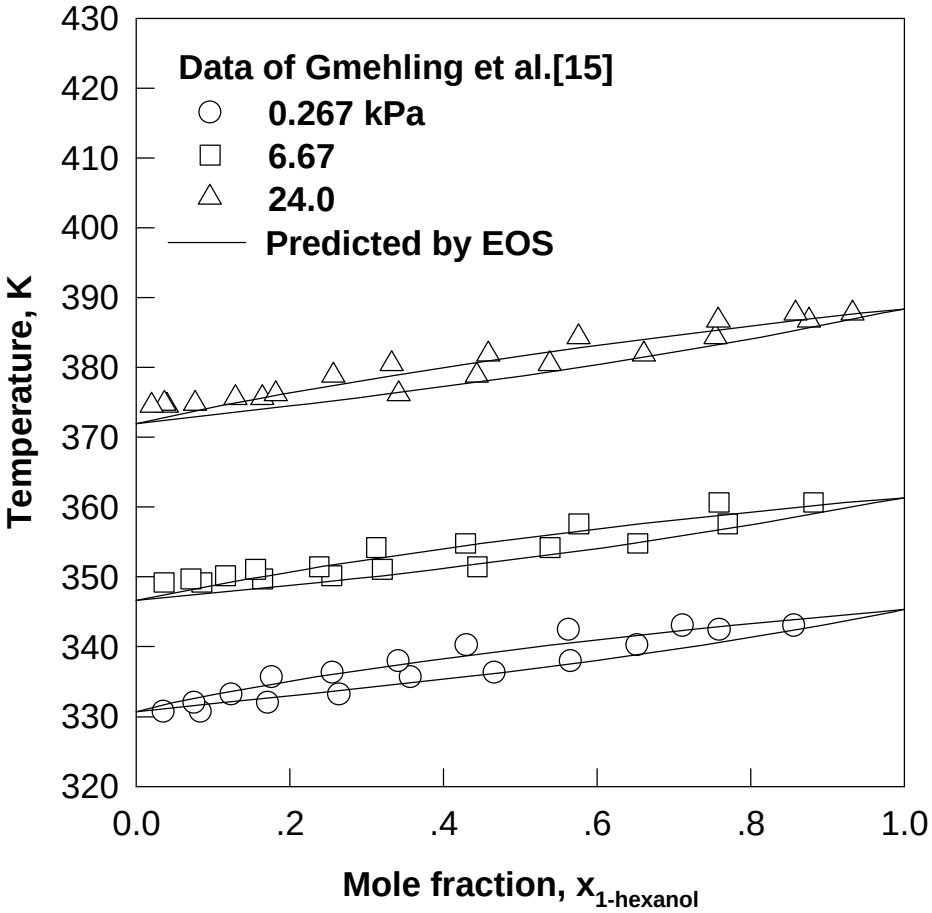

Fig. 7. Predicted isobaric T-x-y equilibria of 1-hexanol / 1-pentanol system

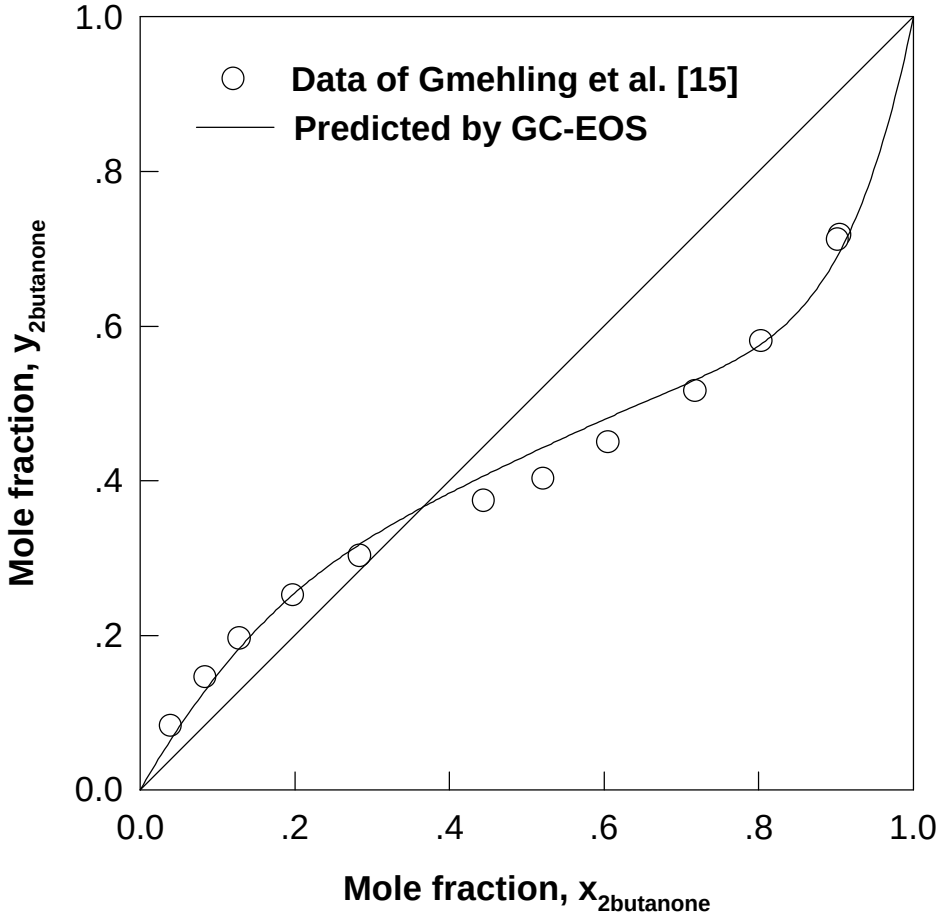

Fig. 8. Predicted x-y equilibrium of 2-butanone / n-hexane system