Unified Description of Real Fluids and Their Mixtures by Group-Contribution Lattice-Hole Theory

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Based on a rigorous solution derived by the quasichemical approximation to the lattice-hole statistical−mechanical theory, a unified group contribution equation of state was formulated. The model was found to be quantitatively applicable for the calculation and prediction of thermodynamic properties of real pure fluids and mixtures in general. The approach requires segment size and interaction energy parameter from functional group characteristics. The unique feature of the method is that a single set of temperature-dependent group parameters are used for both pure fluids and mixtures. The group parameters were determined and tabulated for various functional groups. Its applicability was demonstrated for vapor pressures, binodals, and critical properties of pure fluids including polymeric substances and phase-equilibrium properties of mixtures.

I. Introduction

Rigorous statistical−mechanical theories have been developed to express thermodynamic properties of real fluids in terms of intermolecular forces. Yet practical use of statistical mechanics has been limited to simple pure fluids. Nowadays with the increasing computing capability, molecular simulation becomes less time consuming and partially substitutes for statistical mechanics. However, simple solutions of general applicability from statistical mechanics would be more than welcome. One way of obtaining such a solution is via lattice-hole theories. Sanchez and Lacombe[1] proposed a solution by a gross simplification of Guggenheim's lattice combinatory[2] of the nonrandom lattice theory. However, the first order solution or the quasichemical approximation of the Guggenheim combinatory yields the exact solution only for pure fluid systems. Therefore, one has to resort to numerical procedures to find the solution that is analytically applicable to real mixtures. In this study we present an elementary theory that can be quantitatively applicable to the description of thermodynamic properties of simple or complex molecules in pure or mixed states. The approach involves two steps: in the first place we derive a general approximation to the quasichemical solution of the Guggenheim's lattice-hole combinatory, and in the second step the molecular parameters in the approximate solution is obtained by employing the functional group contribution method. Thus, both single- and multi-component real fluids are described by functional group characteristics. One important advantage of the approach presented here is that the configurational properties of both pure fluids and mixtures can simultaneously be predicted by a unique set of functional group parameters.

II. Partition Function and Helmholtz Free Energy

In a three-dimensional lattice of the coordination number z and of the unit cell size, V_H, molecules of component i occupies r_i sites and interact with a neighboring segment of molecules with effective surface area q_i so that the number of external contacts, zq_i equals to $zr_i - 2r_i + 2$ for molecules which are not cyclic. The configurational part of the lattice partition function away from the critical point may be written as follows,[3,4]

$$\Omega^c = g_R g_{NR} \exp(-\beta U^c) \tag{1}$$

and the random contribution, g_R, and nonrandom contribution, g_{NR}, are written in the Guggenheim's lattice-hole combinatory by

$$g_R = [N_r!/(\Pi N_i!)](N_q!/N_r!)^{z/2} \tag{2}$$

$$g_{NR} = (\Pi N_{ii}^0!\Pi[(N_{ij}^0/2)!]^2)/(\Pi N_{ii}!\Pi[(N_{ij}/2)!]^2) \tag{3}$$

where $\beta = 1/kT$, $N_r = N_0 + \Sigma_i N_i r_i$ and $N_q = N_0 + \Sigma_i N_i q_i$. N_0 is the number of vacant sites (or holes) and N_{ij} is the number of i−j segment contacts. N_{ij}^0 denotes the same for random mixing. N_{ij} satisfies the mass balance relations, $2N_{ii} + \Sigma N_{ij} = N_i z q_i$, $2N_{ii}^0 + \Sigma N_{ij}^0 = N_i z q_i$ for all i including holes. $N_{ii}^0 = z N_i q_i \theta_i$, $N_{ij}^0 = z N_i q_i \theta_j$ and $\theta_i = N_i q_i/N_q$ and N_{ij} is related to N_{ij}^0 in the quasichemical approximation[5] as $N_{ij} = \Gamma_{ij} N_{ij}^0$, where $\Gamma_{ij}^2 = \Gamma_{ii}\Gamma_{jj} \exp(-\beta\Delta\epsilon_{ij})$ and $\Delta\epsilon_{ii} = \epsilon_{ii} + \epsilon_{jj} - 2\epsilon_{ij}$.

The configurational part of potential energy in eq 1 is written as

$$U^c = \sum_i N_{ii}(-\epsilon_{ii}) + \sum_{i>j}\sum N_{ij}(-\epsilon_{ij}) \tag{4}$$

where ϵ_{ij} is the absolute value of interaction energy between segments i and j.

"Athermal solution" corresponds to taking $U^c = 0$ and for this solution $g_{NR} = 1$ or $\Gamma_{ij} = 1$. One difficulty in the first order solution or the quasichemical approximation of Guggenheim's combinatory of nonrandom lattice theory has been that it yields the exact solution only for hole-single molecular species systems. Therefore the solution for real mixtures has to resort to numerical procedures. The authors recently proposed a rigorous approximation to the quasichemical approximation for general mixtures.[3] The configurational Helmholtz free energy obtained by the relation $\beta A^c = -\ln \Omega^c$, is expanded around the reference athermal solution to give the first order approximation,

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$$\beta A^c = \beta A^{c0} + \beta \sum_{i \geq j} \sum \left(\frac{\partial A^c}{\partial \epsilon_{ij}}\right)^0 \epsilon_{ij} +$$

$$\left(\frac{\beta}{2}\right) \sum_{i \geq j} \sum \sum_{k \geq l} \sum \left(\frac{\partial^2 A^c}{\partial \epsilon_{kl} \partial \epsilon_{ij}}\right)^0 \epsilon_{ij} \epsilon_{kl} + \dots \quad (5)$$

where superscript 0 indicates that the expression is evaluated at the reference athermal solution. When the algebra is done, eq 5 is rewritten as

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

$$\left(\frac{\beta z N_q}{2}\right)\left[\sum_{i=1}^{c}\sum_{j=1}^{c} \theta_i \theta_j \epsilon_{ij} +\right.$$

$$\left.\left(\frac{\beta}{2}\right)\sum_{i=1}^{c}\sum_{j=1}^{c}\sum_{k=1}^{c}\sum_{l=1}^{c} \theta_i \theta_j \theta_k \theta_l \epsilon_{ij}(\epsilon_{ij} + \epsilon_{kl} - \epsilon_{ik} - \epsilon_{jk})\right] + \dots \quad (6)$$

Expressions for configurational properties follow from the Helmholtz free energy using standard thermodynamic methods.

III. Equation of State and Other Configurational Properties

Since the system volume V is represented by $V = V_H(N_0 + \sum N_i r_i)$, the equation of state is obtained from eq 6,

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

$$\left(\frac{z}{2}\right)\theta^2 \left(\frac{\epsilon_M}{V_H}\right) \quad (7)$$

$$\epsilon_M = \left(\frac{1}{\theta^2}\right)\left[\sum\sum \theta_i \theta_j \epsilon_{ij} +\right.$$

$$\left.\left(\frac{\beta}{2}\right)\sum\sum\sum\sum \theta_i \theta_j \theta_k \theta_l \epsilon_{ij}(\epsilon_{ij} + 3\epsilon_{kl} - 2\epsilon_{ik} - 2\epsilon_{jk})\right] \quad (8)$$

where q_M and r_M are given as mole fraction averages of relevant properties for molecular species, $q_M = \sum x_i q_i$ and $r_M = \sum x_i r_i$. Summations are sums over all molecular species unless otherwise specified.

The chemical potential of component i in a multicomponent mixture and other configurational properties are obtained and given elsewhere.[3] For pure component fluids we need to consider only ϵ_{11}. There are apparently four molecular parameters in the equation of state for pure fluids, z, V_H, r_1, and ϵ_{11}. We set $z = 10$ and $N_A V_H = 9.75$ cm^3 mol^{-1} as used in the lattice-hole theories in the same genre.[1,5] Here N_A is Avogadro's number. We found that the specific choice of the lattice parameter (z and V_H) has no significant effect on the capability of the equation of state. Thus to model real pure fluids, we need to determine two molecular parameters r_1 and ϵ_{11}. Also, for binary mixtures, we need one additional adjustable interaction parameter λ_{ij} in the combining rule defined by

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{0.5}(1 - \lambda_{ij}) \quad (9)$$

Away from the immediate vicinity of critical point, the model was found to describe quantitatively *pVT* behavior, phase transition, and (multi)phase equilibria of pure fluids and mixtures. We also found that the model is especially relevant to r-mer fluids.[3,4] One possible extension on the use of present author's solution is to apply the concepts of the

TABLE 1: Coefficients in the Temperature-Dependent Segment Number Correlation Defined by Eq 12

group	w_j^G	$h_j^G \times 10^{-3}$	$c_j^G \times 10^{-3}$	temp range (K)
CH$_3$	2.655	0.203	1.786	270–450
CH$_2$	1.540	−0.201	1.218	270–450
CH	0.454	−2.425	−0.593	270–450
OH	1.480	4.273	6.132	270–450
O	0.682	0.024	1.242	270–450
ACCH$_3^a$	2.975	0.146	1.625	270–450
ACCH$_2$	1.860	−0.405	−0.372	270–450
ACCH	0.708	−1.187	−1.252	270–450
ACH	1.401	0.188	1.062	270–450
CO	1.377	1.917	1.526	270–450
CO$_2$	3.782	4.755	4.512	270–450
CYCH$_2^b$	1.652	−0.004	1.141	270–450

^{a} AC denotes aromatic carbons. ^{b} CY denotes cyclic carbon.

TABLE 2: Coefficients in the Temperature-Dependent Group–Group Interaction Parameter Defined by Eq 13

group–group	a_{ij}^G	b_{ij}^G	d_{ij}^G	temp range (K)
CH$_3$–ACH	97.354	8.643×10^{-3}	-6.058×10^{-2}	270–450
CH$_2$–ACH	114.758	1.490×10^{-2}	-3.528×10^{-2}	270–450
CH$_3$–CH$_3$	78.174	5.046×10^{-2}	3.880×10^{-1}	270–450
CH$_3$–CH$_2$	96.050	1.135×10^{-2}	-2.735×10^{-1}	270–450
CH$_2$–CH$_2$	112.776	4.973×10^{-2}	7.032×10^{-2}	270–450
CH$_3$–OH	104.468	-2.301×10^{-1}	-6.164×10^{-2}	270–450
CH$_2$–OH	204.269	-7.072×10^{-1}	-1.514×10^{-0}	270–450
CH$_3$–ACCH$_3$	86.120	6.235×10^{-2}	2.617×10^{-1}	270–450
CH$_2$–ACCH$_3$	121.178	3.610×10^{-2}	-1.888×10^{-1}	270–450
CH$_3$–CYCH$_2$	92.544	2.308×10^{-2}	-9.809×10^{-3}	270–450
CH$_2$–CYCH$_2$	112.142	2.450×10^{-2}	-9.319×10^{-2}	270–450
OH–OH	756.626	-4.031×10^{-0}	-8.787×10^{-0}	270–450
OH–CYCH$_2$	168.824	-5.501×10^{-1}	-1.059×10^{-0}	270–450
ACH–ACH	119.958	-1.189×10^{-2}	-1.042×10^{-1}	270–450
CO$_2$–ACH	93.859	-6.006×10^{-2}	-2.324×10^{-1}	270–450
CO$_2$–ACCH$_3$	84.698	-2.388×10^{-2}	-1.947×10^{-1}	270–450
CO$_2$–CH$_3$	73.677	-3.112×10^{-2}	-1.489×10^{-1}	270–450
CO$_2$–CH$_2$	89.951	-3.028×10^{-2}	-1.442×10^{-1}	270–450
CO$_2$–CO$_2$	84.920	-9.950×10^{-2}	-3.455×10^{-1}	270–450
CO$_2$–OH	170.711	-6.611×10^{-1}	-1.526×10^{-0}	270–450
CO$_2$–CYCH$_2$	86.804	-4.461×10^{-2}	-2.062×10^{-1}	270–450
CYCH$_2$–CYCH$_2$	109.776	1.705×10^{-2}	-7.497×10^{-2}	270–450
ACH–CYCH$_2$	112.929	3.416×10^{-3}	-8.616×10^{-2}	270–450
ACH–ACCH$_3$	117.764	1.247×10^{-2}	-7.735×10^{-2}	270–450
ACCH$_3$–ACCH$_3$	113.005	3.916×10^{-3}	-1.303×10^{-3}	270–450

functional group contribution. We discuss the new scheme in the next section.

IV. Scheme of Functional Group Contribution

The group contribution application[6–9] of the solution involves the calculation of molecular parameters r_i and ϵ_{ij} from group characteristics r_i^G and ϵ_{ij}^G. The fundamental concept of group contribution has long history and have been powerful tools for estimating properties of pure fluids or mixtures from experimental data on related substances. The lattice theory-based group contribution methods have widely been used in engineering to describe the departure from ideal solution are "excess properties". However, no such formulations are known to the authors for estimating configurational properties. Thus, it is interesting to see if configurational properties of complex or large molecular species and mixtures with such molecular species can be calculated using group segment number and group–group interaction parameter.

The group contribution method is based on the assumption that each group is physically identical regardless of its environment. Indeed the environmental effect or the proximity effect can be averaged to give mean group characteristics for a large collection of molecules.[10] Thus the sum of segment numbers
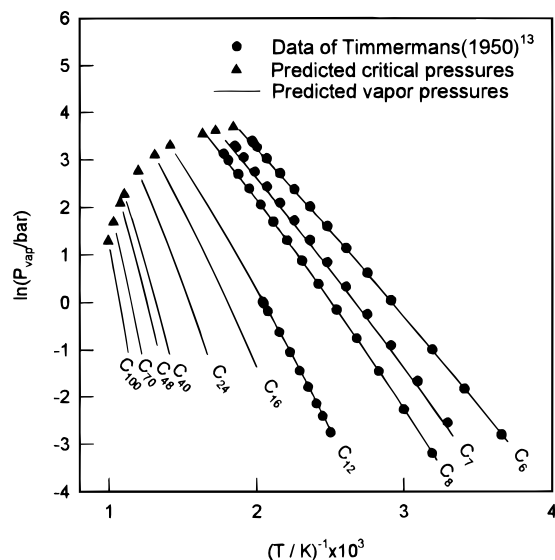
Figure 1. Predicted vapor pressures of pure alkanes by the unique set of parameters r_{CH3}^G and r_{CH2}^G given in Table 1 and $\epsilon_{CH3-CH3}^G$, $\epsilon_{CH3-CH2}^G$ and $\epsilon_{CH2-CH2}^G$ in Table 2.
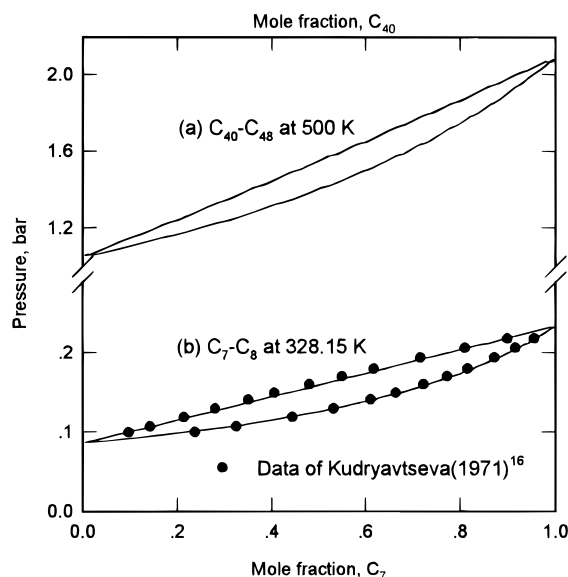

Figure 2. Predicted vapor-liquid equilibria for C_7-C_8 at 328.15 K and $C_{40}-C_{48}$ at 500 K by the same set of parameters used in Figure 1.
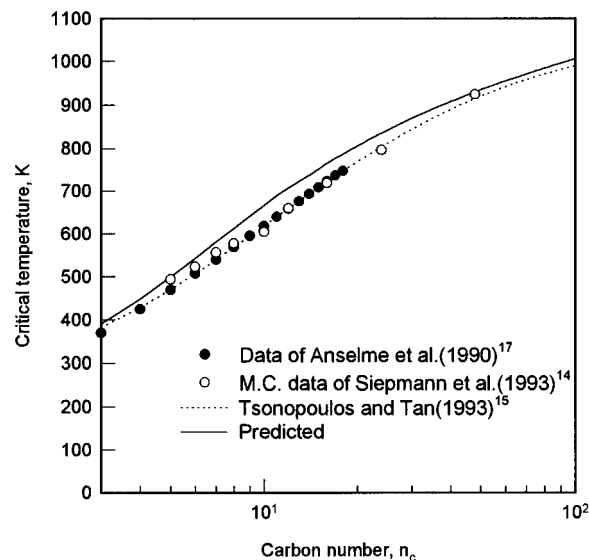

Figure 3. Predicted critical temperatures as a function of carbon number of alkanes by the same set of parameters used in Figure 1.

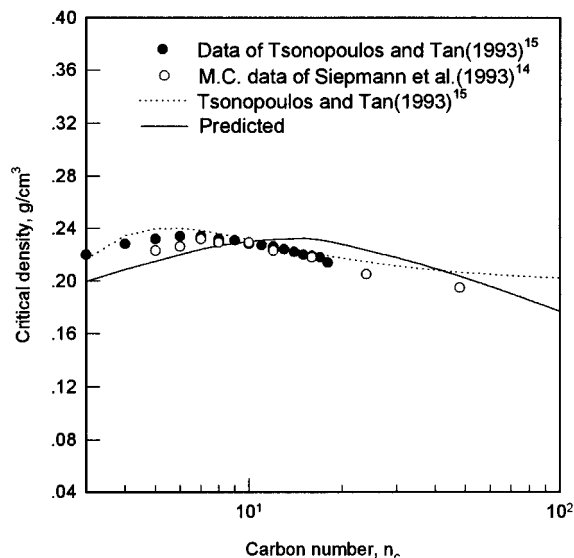**Figure 4.** Predicted critical densities as a function of carbon number of alkanes by the same set of parameters used in Figure 1.

gives the molecular segment number,

$$r_i = \sum_{j=1}^{g} \nu_{ij} r_j^G \tag{10}$$

where ν_{ij} is the number of group j in species i. r_j^G is the segment number of group j.

The molecular interaction energy is an average value of mean group interaction energy. The possible weighting factors for the average are the group surface area fraction and the Boltzmann factor. If the temperature dependence of the Boltzmann factor is lumped into the energy parameter, we have

$$\epsilon_{ij} = \sum_{k=1}^{g}\sum_{l=1}^{g} \theta_{ik}^G \theta_{jl}^G \epsilon_{kl}^G = \sum_{k=1}^{g}\sum_{j=1}^{g} \nu_{ik}\nu_{jl}q_k^G q_l^G \epsilon_{kl}^G \Big/ \sum_{k=1}^{g}\sum_{j=1}^{g} \nu_{ik}\nu_{jl}q_k^G q_l^G \tag{11}$$

where θ_{ik}^G is the surface area fraction of group k in species i. q_k^G is the surface area parameter of group k and ϵ_{kl}^G is the

interaction energy parameter between group k and l. This relation implies that the group interactions should be identical whether groups are in pure fluids or in mixtures. Since the effect of molecular bulkness factor is not significant, we set $q_j^G = r_j^G$ to avoid the complexity associated with the bulkness factor.[11] The temperature dependence of these parameters are represented by

$$r_j^G = w_j^G + h_j^G(T - T_0) + c_j^G\left(T \ln\frac{T_0}{T} + T - T_0\right) \tag{12}$$

$$\epsilon_{ij}^G/k = a_{ij}^G + b_{ij}^G(T - T_0) + d_{ij}^G\left(T \ln\frac{T_0}{T} + T - T_0\right) \tag{13}$$

where T_0 is an arbitrarily chosen reference temperature (298.15 K). The functional form defined in eqs 12 and 13 are adopted from the theory proposed by a previous investigator.[9] In eq 13, the numerical parameters are determined from pVT and vapor pressure data of pure substances and phase equilibrium data for mixtures. In Tables 1 and 2, numerical parameters in

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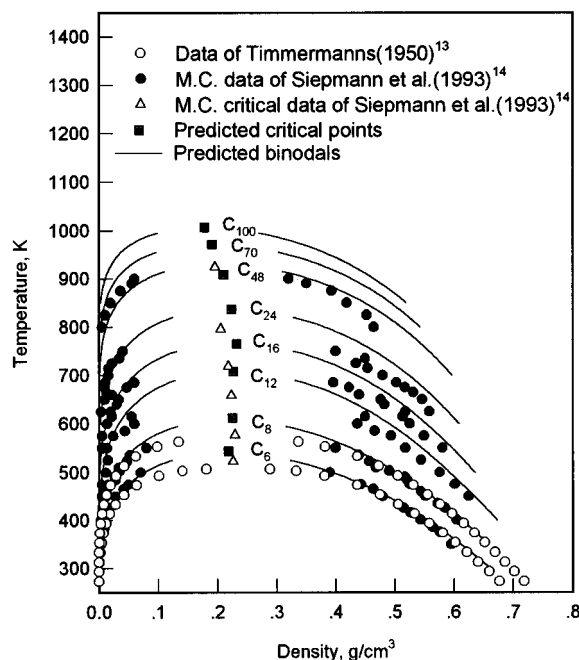
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Figure 5. Predicted binodal curves including critical points of alkanes plotted as temperature vs density by the same set of parameters used in Figure 1.
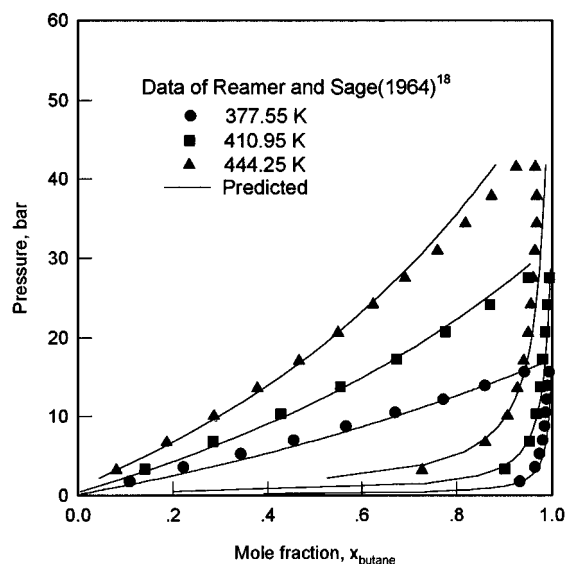

Figure 6. Predicted P-x-y equilibria for butane−decane system at three isotherms by the same set of parameters used in Figure 1.

eqs 12 and 13 determined from experimental data are shown for some illustrative functional groups.[12]

V. Prediction of Configurational Properties of Real Fluid Systems

The unique feature of the method is that a single set of group parameters given in Tables 1 and 2 are used for both pure fluids and mixtures. Indeed, one needs not introduce an adjustable binary interaction energy parameter, λ_{ij}, defined in eq 9. Thus, the description of configurational properties of real world fluids is reduced to functional group characteristics which are the group segment number and the group−group interaction energy parameter.

We can expect that, as long as the numerical parameters are reliable, the present approach should estimate various configurational properties of single component and multicomponent real fluids. In this article, we consider two functional groups, CH_3
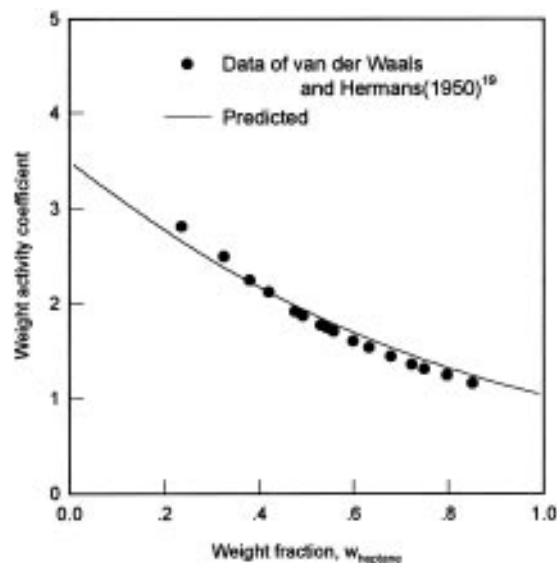

Figure 7. Predicted weight activity coefficients of heptane in polyethylene ($M_v = 26\,300$) solution at 382 K by the same set of parameters used in Figure 1.

and CH_2, to illustrate the approach. Alkanes are the most typical species which are composed of such groups. We have chosen alkanes since extensive experimental data,[13] molecular simulation results,[14] and empirical models[15] are available for them.

An interesting application of the concept is in the prediction capability. As molecular simulations do, the present group contribution method can be utilized to calculate binodals, critical properties, and mixture phase equilibria of systems for which no experimental data are available or even not accessible experimentally. Predicted vapor pressures of pure alkanes with experimental data[13] are shown in Figure 1. All the predicted results are based on the same set of parameters given in Table 1 and 2. In Figure 2, predicted vapor−liquid equilibrium properties of alkane−alkane mixtures are shown where the same set of group parameters are used. Thus, the description of configurational properties of real world fluids is reduced to functional group characteristics.

Predicted critical temperatures and critical densities for pure alkanes are shown in Figures 3 and 4, respectively, as a function of the carbon number. In Figures 3 and 4, we also show the comparison of calculated densities with data[11,12] and molecular simulation.[13] Two difficulties are noted in the present approach. One is that the classical approach including the present approach is not rigorous in the vicinity of critical points due to nonclassical characteristics of real fluids. The other is that group characteristics determined in the temperature range where data are available may become unrealistic at high temperatures. Thus we took molecular simulation results into consideration at high temperatures when available. When compared with the Flory−Huggins prediction[15] for very large alkanes, critical pressure almost exactly scales to their value. Critical temperature changes vary slowly around 1200 K which is somewhat higher than their value. In spite of these difficulties, the results are seen to follow the results of molecular simulation and the correlation[15] closely. Molecular simulations also have their difficulties, but we will not elaborate on them here.

Figure 5 shows binodals for pure alkanes. Predicted vapor−liquid equilibria of the butane−decane system at three different isotherms are also illustrated in Figure 6. Finally, the predicted weight fraction activities of heptane in polyethylene solution ($M_v = 26\,300$) are shown in Figure 7. Close agreements are observed using the same set of group parameters given in Tables 1 and 2.

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VI. Conclusion and Future Direction

Based on a rigorous approximation to the quasichemical solution derived by the present authors, a group contribution method was proposed for the calculation and the prediction of configurational properties of real fluids and mixtures. Its applicability was demonstrated for critical properties and vapor−liquid equilibria of pure or mixed r-mer fluids, and polymer solutions. In this study, the numerical parameters in eqs 12 and 13 were determined from the relatively limited set of experimental data. The refinement of the parameters from an extensive collection of experimental data would improve the results. The approach should be extended to other functional groups. Future work will be focused on the refinement of the approach to the level of practical tools in engineering.

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