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AN IMPROVED CONFORMAL SOLUTION METHOD BASED ON HARD SPHERE EXPANSION TO PREDICT VAPOR-LIQUID EQUILIBRIA

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Abstract – The conformal solution method based on the hard sphere expansion (HSE) theory predicts thermodynamic properties of mixtures by separating the mixture properties into a contribution from repulsion and other contributions from various types of intermolecular attraction. The original HSE, however, has a tendency to show increasing relative error in the prediction of thermodynamics properties as the difference of molecular sizes in mixtures increases since the radial distribution functions of a mixture are represented by that of a pure reference in the mean density approximation (MDA). When the hard convex body (HCB) equation of state was substituted for the hard sphere equation of state in the repulsion term to overcome the shortcoming of the original HSE, better results on the K-value in binary hydrocarbon mixtures were obtained.

Key words : Hard Sphere Expansion, Conformal Solution Theory, Hard Convex Body, Spherocylinder, K-value

INTRODUCTION

There has been a great need for accurate thermodynamic data in the petroleum and many other industries. Since all the necessary thermodynamic properties cannot be obtained from direct measurements alone, it becomes very important to investigate some theoretical methods for the accurate prediction of those properties. Many empirical methods have been developed to correlate experimental data available; the simplest way is the application of the semi-empirical or empirical equations of state.

However, these equations are accurate only in the temperature and pressure ranges where experimental values are used in the curve fitting or regression. Another difficulty is that this method usually requires empirical mixing rules in the calculation of mixture properties. The empirical mixing rules are known not to properly describe the composition dependence of thermodynamic properties of mixtures which are particularly important in the phase equilibrium predictions. Some theoretically based methods have been suggested to calculate the mixture properties with minimum assumptions and without the empirical mixing rules.

It is a good example to apply the corresponding states principle (CSP) based on statistical thermodynamics. An essential method is also known as the conformal solution theory, which predicts thermodynamic properties from one or more reference fluids whose thermodynamic properties are well described. Also, the perturbation method expresses an intermolecular potential function by a repulsion contribution and other contributions from attraction. The HSE procedure is known as one of the most successful methods making use of the CSP and perturbation method.

The HSE theory predicts thermodynamic properties of a mixture by separating its properties into the repulsion and attraction contributions. While the attraction contribution is obtained by the corresponding states procedure from a similar contribution in a pure reference fluid, the repulsion contribution is calculated directly from an appropriate equation of state for hard sphere mixtures. A variational procedure is also applied to the determination of the effective diameter for the reference fluid.

The advantage of the HSE conformal solution theory is to avoid the use of empirical mixing rules involved in mixture calculations and to represent better composition dependence. The original HSE theory, however, has a tendency to show increasing relative error on the prediction of thermodynamics properties as the difference of molecular sizes in the mixture increases, which may be due to the fact that the radial distribution function of the mixture is represented by that of a pure reference in the mean density approximation (MDA).

This work substitutes the hard convex body (HCB) equation of state for the hard sphere (HS) equation of state in the repulsion term to improve the original HSE under the assumption that the molecules in mixtures can be described as a hard convex body model. The prolate spherocylinder model among the various HCB models is adopted to predict K-values in several binary hydrocarbon systems in this work.

HSE CONFORMAL SOLUTION THEORY

The description of thermodynamic behavior from statistical mechanics gives a better understanding of the physical properties of mixtures in equilibrium. The entire problem of predicting equilibrium thermodynamic properties of a fluid from molecular characteristics involves coupling two types of information, that describing the potential between molecules and that de-

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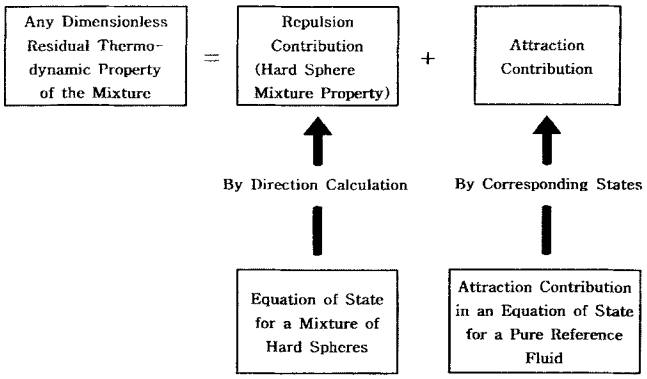

Fig. 1. The HSE corresponding states procedure for mixture properties.

scribing the structure of the fluid with regard to the location of molecules relative to each other.

The HSE conformal solution theory developed a new type of corresponding states method with the strongest theoretical basis for prediction of mixture properties. This procedure separates thermodynamic properties into a contribution arising from intermolecular hard sphere repulsion and other contributions resulting from various types of intermolecular attraction where the CSP is embedded. The HSE method avoids the use of the empirical mixing rules involved in mixture calculations and has been known to represent better composition dependence than the empirical mixing rules. This type of the CSP was originally proposed by Mansoori and Leland [1972] and developed further by Chen et al. [1982] and Hang [1985].

As shown in Fig. 1, any dimensionless residual property in the HSE method can be divided into two parts when asymmetrical attraction contributions resulting from the long range forces are neglected. One is the repulsion contribution of mixture which can be obtained directly from the Mansoori-Carnahan-Starling-Leland (MCSL) hard sphere mixture equation [1971]. Hang [1985] gave an alternate and more convenient form for the compressibility factor Z as follows:

$$Z^{HSM} = \frac{1+\eta_m(3\alpha-2)+\eta_m^2(3\gamma-3\alpha+1)-\gamma\eta_m^3}{(1-\eta_m)^3} \tag{1}$$

where η_m is the packing fraction related to the mixture density (ρ_m) and diameter (d_i) of constituent i as in Eq. (2):

$$\eta_m = \frac{\pi}{6} N_A \rho_m \sum_i x_i d_i^3 \tag{2}$$

In Eq. (2), N_A is the Avogadro number. Also, the two dimensionless parameters in Eq. (1) are defined as:

$$\alpha = \frac{<d><d^2>}{<d^3>} \tag{3}$$

$$\gamma = \frac{<d^2>^3}{<d^3>^2} \tag{4}$$

with

$$<d^k> = \sum_i x_i d_i^k \tag{5}$$

Eq. (1) is just another expression of the hard convex body (HCB) equation of state proposed by Boublik [1974], which will be discussed later. For pure components, the MCSL equation as well as Eq. (1) reduces to the Carnahan-Starling equation of state [1969] given by

$$Z^{HS} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{6}$$

where η is also the packing fraction and corresponds to η_m as in Eq. (2) in the case of mixture.

The description of the repulsion contribution by means of an accurate rigid body equation of state presents some serious difficulties which result from high sensitivity of the repulsion contribution to the size of the rigid body. It is, therefore, very important in the HSE calculations to find the effective hard sphere diameter, d_i, of each constituent in the mixture.

In the HSE corresponding states principle method, a precise value of the optimal repulsion must be determined for the compressibility factor and for the dimensionless residual Helmholtz free energy. Hang and Leland [1986] expanded any dimensionless residual properties X with respect to 1/T around a parameter called "characteristic temperature T_o" at constant density and truncated the expansion of X after the $(1/T)^2$ term. The hard sphere property of X can be shown by following equation:

$$X = \left[X_o - \left(\frac{\partial X}{\partial(1/T)} \right)_o \frac{1}{T_o} + \frac{1}{2} \left\{ \frac{\partial^2 X}{(1/T)^2} \right\}_o \frac{1}{T_o^2} \right] \tag{7}$$

By making use of the variational theory and equating Eq. (7) for the compressibility factor to the Carnahan-Starling equation in Eq. (6), the effective diameter of the reference fluid can be evaluated.

The attraction contributions from isotropic interactions and all induction effects in the HSE method, on the other hand, are determined by corresponding states using shape factors evaluated relative to a pure reference fluid. To make use of the CSP, the effective pair potential u(r) is expressed as:

$$u(r) = u^+ + u^- + u^{asym} \tag{8}$$

where u^+ is a positive repulsion of hard spheres of diameter d, u^- is a negative symmetrical attractive potential, and u^{asym} accounts for asymmetric long-range orientation dependent pair interactions which will be omitted in this work. For the conformality of the u^- portion, u^- is assumed to be of the following form:

$$\mu_{eff}^- = \varepsilon f_o^-[r/d] \tag{9}$$

In Eq. (9), f_o^- is a universal function for all constituents of the mixture and the analytical form of f_o^- need not be specified. As a result of the conformality assumption, the following relationships for an individual component i and the reference fluid r are obtained [Leach et al., 1968]:

$$\varepsilon_i = a_o \theta_{ir} T_{ci}, \quad d_i^3 = b_o \phi_{ir} V_{ci} \tag{10}$$

$$\varepsilon_r = a_o T_{cr}, \quad d_r^3 = b_o V_{cr} \tag{11}$$

where the subscript 'c' denotes critical properties, a_o and b_o are parameters which have the same values for all constituents conformal to the reference fluid, and θ_{ir} and ϕ_{ir} are the energy and volume shape factors to establish the conformality between

component i and the reference r by satisfying Eq. (9). From the definitions of diameters in Eqs. (10) and (11), the following relation can be obtained.

$$d_i^3 = \frac{d_r^3}{V_{cr}} \phi_{ir} V_{ci} \tag{12}$$

Eq. (12) will be used for the determination of one molecular dimension needed to represent a hard convex body model.

The CSP is applied to predict the attraction contribution to a dimensionless residual property of the mixture from that of the pure reference fluid as explained above, and thus the attraction contribution to the mixture properties is given by the difference between the value obtained from the equation of state for the reference fluid and the hard sphere repulsion value to the reference property as determined by the Carnahan-Starling equation of state. Because equations of state used in this work are not given in the reduced form, the following equivalent temperature and density conditions are defined, at which any given fluid and the reference exist in corresponding states.

For constituent i:

$$T_i^o = \left(\frac{T_m}{T_C'}\right) T_{Ci}\theta_{ir} = \frac{T_m}{\bar{\varepsilon}}\varepsilon_i, \quad \rho_i^o = \frac{\rho_m V_C'}{V_{Ci}\phi_{ir}} = \frac{\rho_m \bar{d}^3}{d_i^3} \tag{13}$$

For the reference fluid:

$$T_r^o = \left(\frac{T_m}{T_C'}\right) T_{Cr} = \frac{T_m}{\bar{\varepsilon}}\varepsilon_r, \quad \rho_r^o = \frac{\rho_m V_C'}{V_{Cr}} = \frac{\rho_m \bar{d}^3}{d_r^3} \tag{14}$$

In Eqs. (13) and (14), T_i^o and ρ_i^o are the equivalent temperature and density, and T_c' and V_c' are the pseudo-critical temperature and volume which are related to the pseudo-parameters $\bar{\varepsilon}$ and $\bar{d}^3$ as follows:

$$\bar{\varepsilon} = a_o T_C', \quad \bar{d}^3 = b_o V_C' \tag{15}$$

Mansoori and Leland [1972] have derived the pseudo-parameters $\bar{\varepsilon}$ and $\bar{d}^3$ for the attraction term of the HSE theory using the mean density approximation (MDA) and pairwise additivity of a potential. The MDA to give the relationship between the RDF's of mixture and the reference fluid is defined as follows:

$$g_{ij}(r) = g_o(r/\sigma_{ij},\ \rho'\sigma_{ij}^3,\ kT/\varepsilon_{ij}) \tag{16}$$

where g_o is the RDF of the reference fluid and k is the Boltzmann constant. In Eq. (16), ρ' is the mean density given by the relation $\rho' = \rho_m(\sigma_x/\sigma_{ij})^3$ where ρ_m is the mixture density, and σ_x is the effective diameter defined as in Eq. (17) [Chen et al., 1987].

$$\sigma_x = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \tag{17}$$

As seen in Eq. (16), the MDA assumes that the distribution function in the mixture is the same as in a pure component with given pair interaction, but at a density different from that of the mixture. The idea is essentially to replace the true environment around the pair by that of an average, and Eq. (16) is the basic assumption required in the derivation of the van der Waals and HSE conformal solution methods whose effectiveness is indicated to some extent by the success of those theories. Recently, the MDA combined with the Kirkwood-Buff solution theory was successfully used to predict solubility of solutes in supercritical fluids [Kwon and Mansoori, 1993; Kwon et al., 1997].

The form of the pseudo-parameters is chosen so that the attraction terms for the pure reference are conformal to those of the mixture. Equating the two attraction terms in equations for mixture and pure reference yields the following HSE pseudo-parameters [Chen et al., 1987]:

$$\bar{\varepsilon} = \frac{\sum_i \sum_j x_i x_j \varepsilon_{ij}^2 d_{ij}^3}{\sum_i \sum_j x_i x_j \varepsilon_{ij} d_{ij}^3}, \quad \bar{d}^3 = \frac{[\sum_i \sum_j x_i x_j \varepsilon_{ij} d_{ij}^3]^2}{\sum_i \sum_j x_i x_j \varepsilon_{ij}^2 d_{ij}^3} \tag{18}$$

Now using the relationship between potential parameters and critical properties as in Eq. (10), and introducing the modified Lorentz-Berthelot forms of the unlike pair interactions as follows:

$$\varepsilon_{ij} = \xi_{ij}(\varepsilon_i \varepsilon_j)^{1/2}, \quad d_{ij}^3 = \lambda_{ij}(d_i^3 + d_j^3)/2.0 \tag{19}$$

The HSE pseudo-parameter equation (18) then becomes the pseudo-critical equation. Using Eqs. (15), (18), and (19), the following pseudo-criticals can be obtained:

$$T_C' = \frac{\sum_i \sum_j x_i x_j (\theta_{ir} T_{ci}\, \theta_{jr} T_{cj}) \xi_{ij}^2 \lambda_{ij} (\phi_{ir} V_{ci} + \phi_{jr} V_{cj})(1/2)}{\sum_i \sum_j x_i x_j (\theta_{ir} T_{ci}\, \theta_{jr} T_{cj})^{1/2} \xi_{ij} \lambda_{ij} (\phi_{ir} V_{ci} + \phi_{jr} V_{cj})(1/2)}$$

$$V_C' = \frac{[\sum_i \sum_j x_i x_j (\theta_{ir} T_{ci}\, \theta_{jr} T_{cj})^{1/2} \xi_{ij} \lambda_{ij} (\phi_{ir} V_{ci} + \phi_{jr} V_{cj})(1/2)]^2}{\sum_i \sum_j x_i x_j (\theta_{ir} T_{ci}\, \theta_{jr} T_{cj}) \xi_{ij}^2 \lambda_{ij} (\phi_{ir} V_{ci} + \phi_{jr} V_{cj})(1/2)} \tag{20}$$

The conformality between the constituents of the mixture and the reference fluid is made by using the shape factors in Eq. (20), which can be evaluated through the relationship that makes the compressibility and residual Helmholtz free energy of the mixture conformal to those of the reference fluid at equivalent conditions of each component [Chen et al., 1982; Hang, 1985].

The concept of shape factor is utilized in the HSE conformal solution method as well as the STRAPP, a commercial software which was developed at NIST and was proven to predict various thermodynamics properties of mixtures including the K-value in vapor-liquid equilibria very well.

MODIFICATION OF HSE

The original HSE theory yields good agreement with the experimental thermodynamic data for light hydrocarbon mixture systems. However, there is a limit to the molecular size and shape difference in mixtures where the intermolecular repulsion can be represented by a hard-sphere mixture. When the shape of molecules deviates appreciably from sphericity, the hard sphere model that is used in the original HSE could lead to large error in the prediction of phase equilibria. To overcome this drawback, this work replaces the HS equation of state by the HCB equation of state for the repulsion term assuming that the molecules in mixtures can be described as

the hard convex body model.

There has been much interest in developing the molecular models describing nonspherical molecules. One of these models is the convex body (CB) model. A convex body is defined as one in which any straight-line segment connecting two arbitrary points lies entirely within the body. Many researchers [Gibbons, 1969; Boublik, 1974; Naumann and Leland, 1984] have tried to develop the HCB equation of state for improving the role of the repulsion contribution to systems composed of nonspherical molecules.

The HCB equation of state proposed by Boublik [1974], which is based on the Kihara's geometry and is expressed in simpler form than Naumann and Leland's equation [1984], has the same form as Eq. (1) except the packing fraction defined as:

$$\eta = \rho \Sigma x_i V_i \tag{21}$$

In Eq. (21), x_i is the mole fraction of component i and V_i is its molecular volume. In the case of convex body, the dimensionless geometrical parameters α and γ in Eq. (21) are defined as:

$$\alpha = \frac{\bar{R}\bar{S}}{3\bar{V}} \tag{22}$$

and

$$\gamma = \frac{\bar{R}^2\bar{S}^2}{9\bar{V}^2} \tag{23}$$

with

$$\bar{R} = \sum_{n=1}^{n} x_i R_i \tag{24}$$

$$\bar{R}^2 = \sum_{n=1}^{n} x_i R_i^2 \tag{25}$$

$$\bar{S} = \sum_{n=1}^{n} x_i S_i \tag{26}$$

$$\bar{V} = \sum_{n=1}^{n} x_i V_i \tag{27}$$

where R_i, S_i, and V_i are the mean radius, surface area, and volume of a molecule i, respectively, and are called three molecular dimensions. It can be shown easily that the parameters α and γ in Eqs. (22) and (23) reduce to those in Eqs. (3) and (4) in the case of hard sphere mixture.

For a pure component, the dimensionless geometrical parameter α, measuring the degree of nonsphericity of molecules, is always greater than unity for nonspherical molecules and is equal to unity for spherical ones. The prolate spherocylinder model among the various kinds of the HCB models, which is geometrically well-defined and simple, is considered to express nonspherical molecules in this work. The prolate spherocylinder model is shown in Fig. 2 where the dotted line denotes the axis of rotation. The length-width ratio σ in the spherocylinder model is defined as follows:

$$\sigma = L/W \tag{28}$$

where L and W are the length and width of a spherocylinder, respectively.

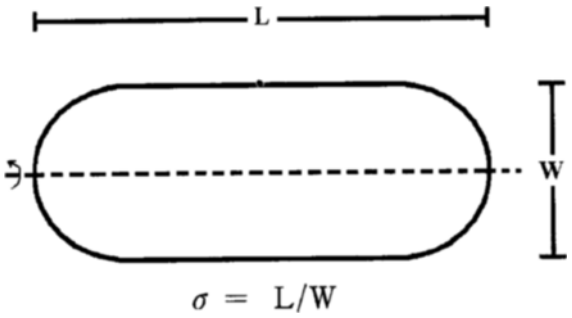

Fig. 2. Prolate spherocylinder.

Three molecular dimensions of a spherocylinder are, then, expressed in terms of σ and W as follows:

$$R = W(\sigma + 1)/4 \tag{29}$$

$$S = \pi W^2 \sigma \tag{30}$$

$$V = \pi W^3(3\sigma - 1)/12 \tag{31}$$

As shown in Eqs. (28)-(31), three molecular dimensions needed to evaluate the parameters α and γ for a spherocylinder can be determined if the values of a molecular dimension W and σ are given.

As pointed out by Pitzer [1955], the acentric factor, ω, represents both molecular geometry and polarity. For nonpolar or slightly polar hydrocarbon molecules, the acentric factor is assumed to represent only molecular geometry, that is, how much its geometry deviates from sphere. With such an assumption, the acentric factor for a component i can be considered to be the function of its length-width ratio only, i.e.,

$$\sigma_i = f(\omega_i) \tag{32}$$

With the known value of ω_i for a pure component, therefore, the length-width ratio can be evaluated from Eq. (32) and such a relationship will be obtained in order for the better prediction of the K-values in this work.

While the length-width ratio is determined from the acentric factor, another molecular dimension W in Eqs. (29)-(30) is still left to be determined. Once the diameter of the reference fluid (d_r) is evaluated using the variational method in the HSE method as explained before, the diameter of a component i (d_i) in the mixture is computed using Eq. (12). Under the assumption that the volume of a hard convex body, V_i, is equal to that of a hard sphere, the volume can be calculated from the hard sphere diameter of a component i, i.e.,

$$V_i = \pi d_i^3/6 \tag{33}$$

V_i in Eq. (33) is referred to as the equivalent volume of the convex body in this work and used for the molecular dimension V in Eq. (21). With the known values of σ_i and V_i, the width W and two other molecular dimensions R and S can also be determined from Eqs. (29)-(31).

The method to get the thermodynamic properties of mixtures according to an improved HSE in this work, therefore, can be summarized as follows:

$$X_m(T_m, \rho_m, \{x_i\}) = X^+ + X^-$$
$$= X^{HCBM}(\rho_m, \{d_i\}, \{\omega_i\}, \{x_i\})$$
$$+ [X^{ES}(\rho_r^o, T_r^o) - X_r^{HCB}(\rho_r^o d_r^3, \omega_r)] \quad (34)$$

where X represents any dimensionless residual property, subscripts m and r indicate the mixture with mole fraction $\{x_i\}$ and reference fluid, respectively. Also, the superscript ES in Eq. (34) denotes an equation of state, that is, the total property determined from the equivalent temperature and density conditions for the reference fluid. It can be known that the attraction contribution of the mixture is replaced by that of the reference fluid by the CSP with the shape factors that are used in defining the equivalent conditions as in Eq. (14).

As in Eq. (34), any dimensionless residual property of mixture can be computed from the repulsion and attraction contributions through the perturbation method. While the repulsion part is determined directly from the equation of state for the hard convex body, the attraction one of the mixture is evaluated from that of the reference fluid where the concept of CSP is used. Compared with the original HSE as in Fig. 1, it can be shown that the repulsion contribution term of the mixture and that of the reference fluid in the attraction term are obtained by replacing the HS terms with the corresponding HCB terms.

For vapor-liquid equilibrium calculations, fugacities of components in each phase are obtained from:

$$\ln\left(\frac{f_i}{x_i P}\right) = -\ln z + (z-1) + \left(\frac{A-A^*}{RT}\right)$$
$$+ n\frac{\partial}{\partial n_i}\left(\frac{A-A^*}{RT}\right)_{T,\rho,n_{j\neq i}} \quad (35)$$

In Eq. (35), f_i represents the fugacity of component i, n the total moles and n_i the moles of component i in the phase. The vapor-liquid equilibrium constant K_i of each component is calculated from the partial fugacities of both phases.

$$K_i = \frac{(f_i^L/x_i P)}{(f_i^V/y_i P)} \quad (36)$$

where x_i and y_i are the mole fractions of component i in liquid phase and vapor phase, respectively.

RESULTS AND DISCUSSION

As explained above, the method of determining the diameters of the reference and each component in the mixture is very important in this work. The procedure to evaluate the diameter of the reference fluid requires an equation of state for the pure reference fluid with the capability of predicting accurate second derivatives of P-V-T properties and accurate residual constant volume heat capacities. In this work, the MBWR equation proposed by Jacobsen and Stewart [1973] with 32 constants was used for that purpose.

The original HSE is modified by replacing the HS equation of state in the repulsion term by the HCB equation of state in order to overcome its shortcoming. This work calculates the K-values in the binary hydrocarbon system under the assumption that molecules in the mixture are described as the prolate spherocylinder model among the various hard convex bodies. In the vapor-liquid equilibria calculation, thermodynamic properties are extremely sensitive to the unlike-pair interaction factor ξ_{ij} in Eqs. (19) and (20). While λ_{ij} is always set to unity in this work as in the original HSE theory, ξ_{ij} is adjusted to give better prediction of the K-value results.

To test the improved HSE method in this work, six binary systems containing methane and another hydrocarbon up to n-hexane were employed: methane-ethane, methane-propane, methane-n-butane, methane-n-pentane, methane-n-hexane, whose dissimilarities between two molecules are as large as possible.

Considering the length-width ratio an adjustable parameter for each component, the length-width ratio for each component was optimized to fit the experimental data on the K-values. Fig. 3 shows the results of the K-value of the methane-n-butane system at 277.6 K and this work gave a slightly better prediction of the K-value than the original HSE.

When the length-width ratio of each component for a system was optimized, the results were always better than the original HSE. Since the length-width ratio should be assumed to be independent of temperature just as the acentric factor, it is necessary to express its values of all components tested in this work in terms of the acentric factor. Fig. 4 shows the values of the length-width ratio for methane through n-hexane; the length-width ratio becomes larger as the number of carbon of a component increases, as expected. The regression of those values gives the following relationship between the acentric factor and the value of length-width ratio:

$$\sigma_i = 1.003 - 1.318\omega_i + 14.262\omega_i^2 - 13.482\omega_i^3 \quad (37)$$

Using the values of the length-width ratio from Eq. (37),

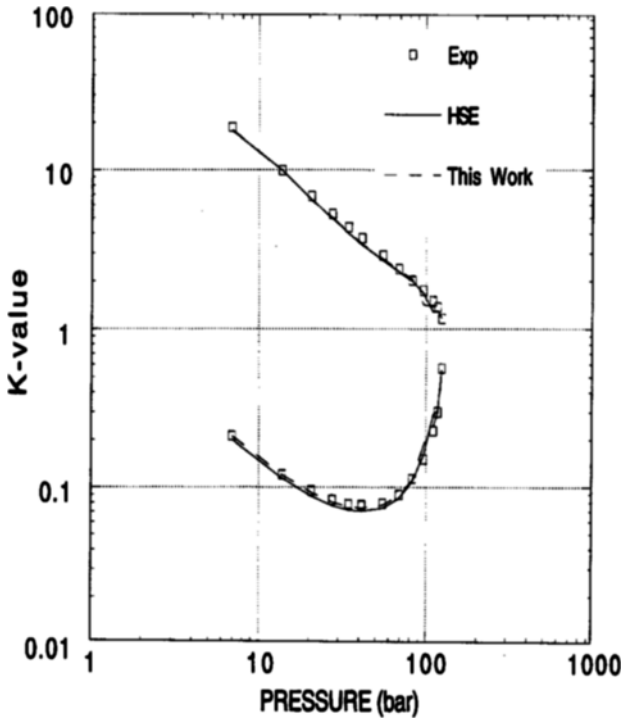

Fig. 3. The results of the K-value of methane-n-butane system at 277.6 K.

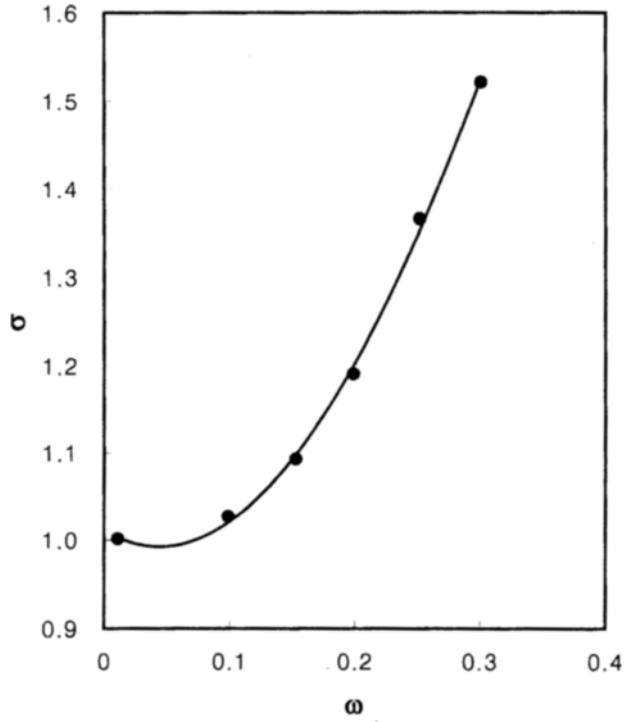

Fig. 4. The relationship between the length-width ratio (σ) and the acentric factor (ω) for methane to n-hexane.

the K values for the binary mixtures tested in this work were calculated and listed in Table 1. As shown in Table 1, the results by this method for methane-ethane, methane-propane system, which are composed of relatively spherical molecules, were not much better than the original HSE method. For methane pentane, methane-hexane systems, this method provided significant improvement in prediction of K-values as expected.

However, there is a limit to molecular size and shape difference in mixtures where the intermolecular repulsion can be represented by hard convex body mixtures in this work. The nonspherical component which can be treated as in this work might be n-octane. In the case of mixtures containing highly dissimilar molecules, the hard convex body expansion (HCBE) conformal solution method [Kwon and Leland, 1989] can be used.

CONCLUSION

The original HSE theory calculates thermodynamic properties of a mixture by separating its properties into contributions from molecular repulsion, which are calculated directly from a hard sphere mixture equation of state, and other contributions from various types of intermolecular attraction, which are obtained by the CSP from the known values of similar contribution in a pure reference fluid. The advantages of the HSE conformal solution theory are to avoid the use of empirical mixing rules involved in mixture calculations and to represent better composition dependence. However, the original HSE method cannot predict thermodynamic properties of mixtures well which contain highly nonspherical molecules since all the radial distribution functions of the mixture are assumed to be obtained by that of a pure reference in the MDA.

To overcome the drawback of the original HSE, this work substitutes the HCB equation of state for the HS equation of state in the repulsion term assuming that molecules in the mixture are described as the prolate spherocylinder model. Under the assumption that the departure of molecular shape from sphericity results in the deviation from the simple CSP, the relationship between the acentric factor and the value of length-width ratio was obtained.

Defining the equivalent volume of a convex body whose volume is the same as that of a hard sphere evaluated from the HSE method, this work produced better results of K-values in hydrocarbon mixtures than the original HSE method. This might be due to a better description of the repulsion contribution. For systems containing polar components, asymmetrical attraction terms such as electrostatic, induction, and dispersion contributions should be also taken into account and will be published later.

Table 1. Results on the K-value calculations for several binary hydrocarbon systems

System comp. 1-comp. 2	K-value ref.	Temp. (K)	No. of data	ξ_{ij}	K-value AAD HSE	K-value AAD This work
methane-ethane	A	158.2	5	0.993	3.5	3.4
		172.0	9	0.990	2.0	1.8
		189.7	8	0.991	2.8	2.5
		199.9	7	0.994	1.4	1.0
methane-propane	B	277.6	11	0.927	2.8	2.8
		294.3	13	0.937	2.3	2.1
		310.9	9	0.928	2.9	3.0
		344.3	8	0.917	1.5	1.8
methane-n-butane	C	233.2	9	0.871	8.3	7.7
		244.3	9	0.899	7.4	5.6
		255.4	8	0.881	6.8	4.5
		277.6	13	0.884	6.4	4.8
		310.9	17	0.875	4.2	3.5
methane-n-pentane	D, E	176.4	6	0.852	12.0	8.7
		191.1	9	0.865	9.8	7.3
		227.7	8	0.845	6.5	4.3
		273.2	10	0.869	7.5	4.2
		344.4	6	0.837	6.3	5.9
methane-n-hexane	F	210.8	13	0.802	18.1	12.5
		273.2	20	0.791	10.4	8.7
		323.2	10	0.786	11.5	9.5
		348.2	10	0.752	10.2	6.0
		423.2	10	0.772	9.3	4.3

References: (A) Wichterle and Kobayashi [1972], (B) Reamer et al. [1950], (C) Sage and Lacey [1955], (D) Chu et al. [1976], (E) Kahre [1975], (F) Shim and Kohn [1972].

NOMENCLATURE

A : Helmholtz free energy
a_o : proportional parameter
b_o : proportional parameter
d : hard sphere diameter
f : fugacity
g : radial distribution function

K : equilibrium ratio, y/x
k : Boltzmann constant
N : system of N molecules
n : number of moles
P : pressure
r : separation distance between molecular centers
T : temperature
U : total potential energy function
u : potential energy function
V : volume
X : dimensionless residual thermodynamic property
x : mole fraction; liquid phase mole fraction
y : vapor phase mole fraction
Z : compressibility factor

Greek Letters

α : dimensionless geometrical parameter in the HCB equation of state
γ : dimensionless geometrical parameter in the HCB equation of state
ε : energy parameter in a two-parameter pair potential energy function
η : packing fraction in the HS or HCB equation of state
θ_{ir} : energy shape factor of component i which is related to reference r
λ_{ij} : unlike pair interaction factor
ξ_{ij} : unlike pair interaction factor
σ : distance parameter in a two-parameter pair potential energy function; length-width ratio of a spherocylinder
ϕ_{ir} : volume shape factor of component i
ω : acentric factor

Superscripts

ES : equation of state
HS : hard sphere
HSM: hard sphere mixture
L : liquid phase
o : equivalent condition
ref : reference fluid property
V : vapor phase
* : property of an ideal gas state of a fluid
' : pseudo-critical property
– : pseudo-parameter condition; average property
+ : repulsion
- : attraction

Subscripts

C : critical property
i : component i
j : component j
N : component N; total property of a system of N molecules
o : universal function for pure fluids; condition at characteristic temperature
r : reference fluid

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