

# APPLICATION OF THE KIRKWOOD-BUFF SOLUTION FORMALISM AND THE HARD SPHERE EXPANSION METHOD WITH THE MODIFIED MEAN DENSITY APPROXIMATION TO PREDICT SOLUBILITY OF SOLUTES IN SUPERCRITICAL FLUIDS

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**Abstract** – The Kirkwood-Buff solution theory to give the relations between macroscopic thermodynamic properties and the fluctuation integrals ( $G_{ij}$ ) was utilized to predict solubility of solutes in supercritical fluids. The solvent-solute fluctuation integral ( $G_{21}$ ) in the derivation for solubility of solute is expressed in terms of the solvent-solvent fluctuation integral ( $G_{11}$ ) using the hard sphere expansion (HSE) conformal solution method with the modified mean density approximation (MMDA) where the scaling factor ( $R_{12}$ ) represents the ratio of the first peak heights of the radial distribution functions for the mixture and the reference fluid having the mean density determined from the mean density approximation (MDA). The values of  $R_{12}$  were evaluated by considering it as an adjustable parameter and solving the Ornstein-Zernike equation with the hypernetted chain (HNC) closure, and were compared. It is shown that solubility can be evaluated with an equation of state for pure supercritical fluid, three molecular parameters, and the scaling factor ( $R_{12}$ ) without knowledge of critical properties of solutes, which can not be measured precisely for some organic solids. This model based on the molecular theory leads to better results in solubility calculations than both the Peng-Robinson equation of state with the classical mixing rule and the previous method with the original MDA instead of the MMDA. It might be due to the superiority of the MMDA over the original MDA.

**Key words:** Modified Mean Density Approximation (MMDA), Solubility, Supercritical Fluid, Kirkwood-Buff Fluctuation Integral

## INTRODUCTION

Supercritical Fluid Extraction (SFE) has been of substantial interest to both the academic and industrial fields because supercritical fluids with gas-like and liquid-like characteristics provide a convenient means to achieve solvating properties by increasing pressure without changing chemical structure and to have several advantages over the conventional solvent extraction method. Therefore, SFE becomes increasingly important in the food, pharmaceutical, petroleum industries, and so on.

Since thermodynamic property data of supercritical fluids are expensive and time-consuming to obtain, it would be desirable to predict phase equilibria from modelling with minimal experimental data. The most widely used method of analyzing supercritical fluid equilibrium data is one with cubic equations of state. To calculate solubility of solutes in supercritical fluids by using an equation of state with appropriate mixing rule, information on critical properties and acentric factor of solutes is needed. It is, however, known to be very difficult to measure critical properties in some organic solutes because decomposition occurs before the critical point is reached. For those components, estimation methods may be used but those were not known to be accurate [Schmitt et al., 1986]. Also, the use of the classical mixing rule in the derivative of volumetric properties can diminish the accuracy of the solubility prediction.

There are several approaches to make use of statistical ther-

modynamics to provide a better description of solubility of solutes in supercritical fluids. One of the approaches is based on the Kirkwood-Buff solution theory that has established a bridge between the molecular interactions on a microscopic level and the thermodynamic properties using the concentration fluctuations from the grand canonical ensemble [Kirkwood et al., 1951].

Pfund et al. [1988] developed the excluded-volume (EV) and local-composition (LC) models based on the Kirkwood-Buff fluctuation integrals to model solubility, and Kwon and Mansoori [1993] also incorporated the HSE method with the MDA in the fluctuation integral. In all the fluctuation integral approaches, the solvent-solute fluctuation integral was replaced by the solvent-solvent fluctuation integral at infinite dilution where an equation of state for only pure supercritical fluid is required.

The MDA provides a simple way to predict the radial distribution functions (RDFs) from pure fluid information. The MMDA which was proposed to get better prediction of the important structural integrals arising in the asymmetrical attraction contribution of the perturbation theory is used during the derivation of the HSE instead of the original MDA to express the solute-solvent fluctuation integral in terms of the solvent-solvent fluctuation integral.

## THEORY

The Kirkwood-Buff solution theory provides a connection between the microscopic structure of molecules and the thermodynamic properties of the fluid through the use of the integrals of

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the radial distribution function  $g_{ij}(r)$  and the direct correlation function  $c_{ij}(r)$  defined as:

$$G_{ij} = \int_0^\infty [g_{ij}(r) - 1] 4\pi r^2 dr \quad (1)$$

$$C_{ij} = \int_0^\infty c_{ij}(r) 4\pi r^2 dr \quad (2)$$

where  $G_{ij}$  and  $C_{ij}$  are called the Kirkwood-Buff fluctuation integral and the direct correlation function integral, respectively, and  $\rho_i$  is the number density of component  $i$ , and  $\rho_i G_{ij}$  gives the number of  $i$  molecules in excess of the bulk average that surround the central  $j$  molecule. Then, the bulk thermodynamic properties such as isothermal compressibility ( $\chi_T$ ), partial molar volume ( $\bar{V}_i$ ), and the derivative of chemical potential ( $\mu_i$ ) with respect to the number of particles are related to  $G_{ij}$  or  $C_{ij}$  through the Kirkwood-Buff solution formalism as follows [O'Connell, 1971, 1981]

$$\frac{1}{\rho RT \chi_T} = \frac{1}{RT} \left( \frac{\partial P}{\partial \rho} \right)_T = \frac{\sum_{k=1}^c \sum_{l=1}^c x_k x_l |B|^{kl}}{|B|} = \sum_{k=1}^c \sum_{l=1}^c x_k x_l (1 - C_{kl}) \quad (3)$$

$$\rho \bar{V}_i = \frac{\sum_{k=1}^c x_k (1 - C_{ik})}{\sum_{k=1}^c \sum_{l=1}^c x_k x_l (1 - C_{kl})} \quad (4)$$

$$kT \left( \frac{\partial \rho_i}{\partial \mu_i} \right)_{\mu_{m \neq i}} = \rho_i \rho_j G_{ij} + \delta_{ij} \rho_i = \frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{V} \quad (5)$$

where  $|B|^{kl}$  denotes the cofactor of the element  $B_{kl}$  in the  $c \times c$  matrix  $B$ , and  $x_k$  is the mole fraction of component  $k$ . The elements  $B_{kl}$  of the matrix  $B$  are defined as

$$B = [B_{kl}] = \rho x_k [\delta_{kl} + x_l G_{kl}] \quad (6)$$

where  $\delta_{kl}$  is the Kronecker delta.

In order to make use of the Kirkwood-Buff solution formalism for solubility modeling of solutes in supercritical fluids, the number density, at first, is expressed as a function of three degrees of freedom present in binary supercritical mixture, that is, temperature, chemical potentials of solvent and solute. With the expression of the solute(2)-solvent(1) fluctuation integral  $G_{21}$  in binary supercritical mixture and under the assumption of the low solute concentration in the supercritical fluid state, the solubility of solid solute ( $y_2$ ) in a supercritical fluid can be expressed as [Cochran et al., 1987; Pfund et al., 1988].

$$\ln y_2 = \ln(P_2^{sat}/P) + V^{sat}(P - P_2^{sat}) + \ln Z^o + \frac{1}{RT} \int_{P_2^{sat}}^P G_{21}^o dP \quad (7)$$

In Eq. (7), the superscript 'o' denotes the infinitely dilute condition. The integral term based on molecular theory in Eq. (7) may improve the accuracy of solubility modeling compared with the corresponding term in the equation-of-state result having the derivative of volumetric properties as follows

$$\ln y_2 = \ln(P_2^{sat}/P) + V^{sat}(P - P_2^{sat}) + \ln Z + \frac{1}{RT} \int_{\infty}^V \left[ \frac{\partial}{\partial n_2} (PV)_{T, V, n_1} - RT \right] \frac{dV}{V} \quad (8)$$

where  $n$  is the number of moles. The accuracy of Eq. (8) may be diminished by the inadequacy of the classical mixing rule.

Pfund et al. [1988] developed the excluded volume (EV) and local-composition (LC) models to express the infinite dilution fluctuation integral  $G_{21}^o$  in terms of the pure solvent fluctuation integral  $G_{11}^o$ , and the results were better than those with an equation of state and classical mixing rule used.

Cochran et al. [1991], and later Kwon and Mansoori [1993] proposed the hard sphere expansion (HSE) model to estimate  $G_{21}^o$  where the MDA is embedded. The MDA, which plays an important role in derivation of conformal solution methods such as the HSE [Mansoori and Leland, 1972], and the hard convex body expansion (HCB) [Kwon and Leland, 1989], can be expressed as

$$g_{ij}(r) = g_o(r/\sigma_{ij}, \rho' \sigma_{ij}^3, kT/\epsilon_{ij}) \quad (9)$$

where  $g_o$  is the RDF of the reference fluid,  $k$  the Boltzmann constant. In Eq. (9),  $\rho'$  is the mean density given by the relation  $\rho' = \rho_m (\sigma_x/\sigma_{ij})^3$  where  $\rho_m$  is the mixture density and  $\sigma_x$  is the effective diameter defined as in Eq. (10) [Chen et al., 1987].

$$\sigma_x = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \quad (10)$$

As shown in Eq. (9), the RDF of a pair in a mixture is related to that of a hypothetical pure fluid.

Hoheisel and Lucas [1984] pointed out that the MDA gives poor predictions of the RDF as the size ratio of components in the mixture increases. Ely [1986] also showed that the MDA consistently underestimates the height of the first peak for 1-1 pair at a larger size ratio. There were some efforts to modify the MDA for improving the predictions of the RDF in mixture and structural integrals. Hoheisel and Lucas [1984] applied their computer simulation data in the Lennard-Jones mixture to correlate a scaling function to modify structural integrals estimated by the original MDA. Ely [1986] proposed an MMDA by introducing a parameter indicating the ratio of the contact values of the RDFs of hard sphere mixture and pure hard sphere fluid to scale the RDF of pure hard sphere fluid approximated by the MDA.

In this work, a modified MDA (MMDA) is proposed by introducing the scaling factor  $R_{ij}$  which means the ratio of the heights of the first peaks of the radial distribution functions in the mixture and hypothetical reference fluid having the mean density determined from the MDA.

$$g_{ij}(r) = R_{ij} g_o(r/\sigma_{ij}, \rho' \sigma_{ij}^3, kT/\epsilon_{ij}) \quad (11)$$

The MMDA in Eq. (11) has the same form as that proposed by Ely [1986]. While Ely defined  $R_{ij}$  as the ratio of the contact values of the RDFs as explained before,  $R_{ij}$  will be treated as an adjustable parameter and will be tested its propriety by solving the integral equation for  $g_{ij}$  and  $g_o$  in Eq. (11). It may be a drawback of this approximation that  $g_{ij}(r)$  in Eq. (11) does not approach unity as  $r \rightarrow \infty$  unless  $R_{ij}$  is unity, but it is not a problem in practice because of the smaller contribution of  $g(r)$  to fluctuation integral when  $r$  becomes large as Ely [1986] pointed out. It can be shown in Eq. (11) that the MMDA is equal to the MDA when the value of  $R_{ij}$  is 1.

Expanding  $g_{ij}$  of mixture with respect to the RDF of hard

sphere in powers of  $\epsilon_{ij}/kT$  yields

$$g_o(r/\sigma_{ij}, \rho' \sigma_{ij}^3, kT/\epsilon_{ij}) = R_{ij} \left[ g^{hs}(y_{ij}, \rho_m d_x^3) + \frac{\epsilon_{ij}}{kT} \Gamma_1(y_{ij}, \rho_m d_x^3) + \left( \frac{\epsilon_{ij}}{kT} \right)^2 \Gamma_2(y_{ij}, \rho_m d_x^3) + \dots \right] \quad (12)$$

where  $d_x$  is the effective pure-fluid diameter,  $y$  is the dimensionless distance ( $= r/\sigma$ ), and  $\Gamma_i$ 's are the dimensionless universal functions.

Substituting Eq. (12) into Eq. (1) gives the following Eq. (13) relating  $G_{21}^o$  at a low concentration of solute to  $G_{11}^o$  and  $G^{hs,o}$  at infinite dilution using the molecular parameters  $\sigma_{11}$ ,  $\sigma_{12}$ , and  $\alpha_{12}$ , and the scaling parameter  $R_{12}$ .

$$G_{21}^o = G_{12}^o = R_{12} \alpha_{12} G_{11}^o + R_{12} \frac{\sigma_{12}^3}{\sigma_{11}^3} \left( 1 - \frac{\epsilon_{12}}{\epsilon_{11}} \right) G^{hs,o} \quad (13)$$

where

$$\alpha_{12} = \frac{\sigma_{12}^3 \epsilon_{12}}{\sigma_{11}^3 \epsilon_{11}} \quad (14)$$

$$G^{hs,o} = \sigma_{11}^3 \int_0^\infty [g^{hs}(y) - 1] 4\pi y^2 dy \quad (15)$$

The solvent-solvent fluctuation integral  $G_{11}^o$  in the first term of the right hand side in Eq. (13) can be evaluated through the isothermal compressibility relation in Eq. (3) when an equation of state is chosen. For pure components, Eq. (3) can lead to

$$G_{11}^o = \frac{1}{\rho_o} (\rho^o RT \kappa_T^o - 1) = \frac{1}{\rho^o} \left[ \left[ Z^o + \rho^o \left( \frac{\partial Z^o}{\partial \rho^o} \right) \right]^{-1} - 1 \right] \quad (16)$$

In the same way, it is possible to determine  $G^{hs,o}$  in Eq. (15) with a hard sphere equation of state given. Even though the Carnahan-Starling equation of state [1969] is known to be the most accurate, it makes it impossible to integrate the last term in Eq. (7) analytically [Cochran et al., 1991]. The following type of the hard sphere equation of state proposed by several researchers [Kim et al., 1986; Moshen-Nia et al., 1993] is used because of its simplicity and thus applicability of analytical integration as done in the previous work [Kwon and Mansoori, 1993].

$$Z^{hs} = \frac{1 + c_2 \eta}{1 - c_1 \eta} \quad (17)$$

where  $\eta (= \pi \rho \sigma^3/6)$  is the packing fraction,  $c_1$  and  $c_2$  are constants whose values for the equation proposed by Moshen-Nia et al. [1993] are 1.88 and 2.48, respectively. Eq. (17) is also known to be accurate in the range of  $0 \leq \eta \leq 0.35$  [Moshen-Nia et al., 1993]. From Eqs. (15) and (17),  $G^{hs,o}$  is described as follows

$$G^{hs,o} = \frac{2 - c_1 \eta}{1 + 2c_2 \eta - c_1 c_2 \eta^2} \quad (18)$$

It can be seen from Eqs. (13), (15), and (16) that there are four parameters (two molecular size parameters  $\sigma_{11}$ ,  $\sigma_{12}$ , and one dimensionless parameter  $\alpha_{12}$ , and the scaling factor  $R_{12}$ ) needed

to determine solubility of solute instead of the knowledge of critical properties of solute, which can not be measured accurately for some organic solids.

While Pfund et al. [1988] used an equation of state with over 50 constants to calculate the properties of pure supercritical fluid [Huang et al., 1985] and executed the numerical integration, the Peng-Robinson equation of state [1976], which is still widely used in predicting thermodynamic properties of fluids and their mixture, is chosen in this work. The Peng-Robinson equation of state is given by

$$Z = \frac{1}{1 - b\rho} - \left( \frac{a}{RT} \right) \frac{\rho}{1 + 2b\rho - (b\rho)^2} \quad (19)$$

The results obtained by this MMDA model will be compared with those by Eqs. (8) and (19) for supercritical fluid mixtures along with the following classical mixing rule.

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad (20)$$

$$b = \sum_i x_i b_i \quad (21)$$

where  $k_{ij}$  is an adjustable parameter determined to fit experimental solubility data.

The scaling factor  $R_{12}$  used in the MMDA will be determined by regarding it as an adjustable parameter. On the other hand,  $R_{12}$  can be evaluated through computer simulation such as the molecular dynamics (MD) and Monte Carlo (MC) method or by solving the integral equation in order to check the propriety of the value evaluated by optimization. Supercritical solutions considered in this work are extremely dilute with solute mole fractions typically of the order  $10^{-3}$ - $10^{-4}$ . In many cases, however, the use of single solute molecule is not sufficient to calculate the property of interest accurately by computer simulation method [Li et al., 1995].

Assuming that solvent and solute molecules are described by the Lennard-Jones potential and the intermolecular interaction is pairwise-additive, the value of  $R_{12}$  can be evaluated by solving the Ornstein-Zernike equation in combination with a closure for the RDFs of mixture and pure reference fluid defined from the MDA and comparing the first peaks of the RDFs. The Ornstein-Zernike integral equation is given by

$$h(r) = c(r) + \rho \int c(r-r') h(r') dr' \quad (22)$$

where  $h(r)$  is the total correlation function and  $c(r)$  is the direct correlation function [Hansen and McDonald, 1986].

The hypernetted chain (HNC) approximation is adopted here as a closure with the Ornstein-Zernike integral equation since the HNC closure is accurate enough to describe the thermodynamic and structural properties treated in this work even though it does not give a correct critical point [Tanaka and Nakanishi, 1994]. The HNC closure is

$$h(r) = \exp[-\beta u(r) + t(r)] - 1 \quad (23)$$

where  $\beta$  is  $1/kT$ ,  $u(r)$  is the intermolecular potential, and  $t(r)$  is the indirect interaction part defined as follows

$$t(r) = h(r) - c(r) \quad (24)$$

Therefore, it is possible to solve Eqs. (22) and (23) for  $g_{12}(r)$  and  $g_o$  in Eq. (11) for mixture and reference fluid having the mean density determined from the definition of the MDA. In order to get the RDFs the integral equation is solved iteratively until the difference in the indirect interaction part  $t(r)$  between two successive iterations becomes less than the threshold value,  $10^{-5}$ , for all distance ranges treated here.

To apply the Ornstein-Zernike equation to solve for the RDFs of the mixture and the reference fluid with the MDA, the like and unlike molecular parameters should be known and thus the following Bertholet mixing rule is used.

$$\sigma_{12} = \frac{\sigma_{11} + \sigma_{22}}{2} \quad (25)$$

$$\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{22}} \quad (26)$$

## RESULTS AND DISCUSSION

To apply the Kirkwood-Buff fluctuation integrals and the HSE along with the MMDA to calculate solubility of solid solutes in supercritical fluids and to compare the solubility data with those by the Peng-Robinson equation of state with the classical mix-

ing rule, several aromatic compounds in supercritical carbon dioxide and ethylene were tested. Tables 1 and 2 listed the sources from which the data needed to calculate solubility were taken.

As in the previous work [Kwon and Mansoori, 1993] where the original MDA is embedded, the Peng-Robinson equation of state and the hard-sphere equation of state proposed by Moshennia et al. [1993] are used to evaluate  $G_{11}^o$  for pure supercritical fluid and  $G^{hs,o}$  for hard sphere fluid, respectively.

The same values for all molecular parameters ( $\sigma_{11}$ ,  $\sigma_{12}$ , and  $\alpha_{12}$ ) are used to check if the results in this work are better than those in the previous work with the original MDA, and only the scaling factor  $R_{12}$  is considered an additional parameter to be optimized to fit the experimental data. The following two cases are considered: (i) all molecular parameters are temperature-independent (ii) one parameter of the parameters related to energy parameter as shown in Eq. (14) is temperature-dependent. The scaling parameter  $R_{12}$  is, however, regarded as temperature-dependent in both cases.

For both cases, the values of molecular size parameters  $\sigma_{11}$  and  $\sigma_{12}$  were found to be not so sensitive to solubility as  $\alpha_{12}$ . Fig. 1 shows the results on solubility of naphthalene in carbon dioxide at 308 K by the original MDA and the MMDA when

**Table 1. Temperature and pressure ranges tested in this work and data sources of carbon dioxide systems**

Carbon dioxide system	Temperature range (K)	Pressure range (bar)	Solubility ref.	Sublimation pressure	Critical properties	Acentric factor	Solid molar volume
Acridine	308.1-343	101.6-364.1	A	A	B	B	C
Aenzoic acid	308-343.1	101.1-364.1	A, G	A	F	F	C
Biphenyl	308.8-330.5	104.6-484	I	A	F	F	C
2,3-Dimethylnaphthalene	308-328	99-280	G	G	B	B	C
2,6-Dimethylnaphthalene	308-328	96-280	G	G	B	B	H
Fluorene	303-343	69.9-483.5	E	E	B	B	C
Hexamethylbenzene	303-343	69.9-438.5	E	E	B	B	C
Naphthalene	308-328	60.8-334.3	G, J	E	F	F	C
1,4-Naphthoquinone	318-343	100.9-364	A	A	B	B	A
Phenanthrene	303-343	80.9-414.5	E, G	E	H	H	C
Phenol	309-333	78.3-246.2	E	K	F	F	C
Pyrene	308-343	83.6-483.4	E	C	B	B	C
Triphenylmethane	303-323	69.9-414.5	E	C	B	B	C

**Table 2. Temperature and pressure ranges tested in this work and data sources of ethylene systems**

Ethylene system	Temperature range (K)	Pressure range (bar)	Solubility ref.	Sublimation pressure	Critical properties	Acentric factor	Solid molar volume
Anthracene	323-358	104.4-483.6	D	E	F	F	C
Benzoic acid	308-343.1	101.1-364.1	G	A	F	F	C
2,3-Dimethylnaphthalene	308-328	77-280	G	G	B	B	C
2,6-Dimethylnaphthalene	308-328	78-280	G	G	B	B	H
Fluorene	298-343	69.9-483.5	E	E	B	B	C
Hexamethylbenzene	298-343	63-483.5	E	E	B	B	C
Naphthalene	285-323	50.7-303.9	D, J	E	F	F	C
Phenanthrene	298-343	56.1-280	D, G	E	H	H	C
Pyrene	318-348	104.3-483.6	E	C	B	B	C

## REFERENCE

- (A) Schmitt and Reid [1986]  
 (B) Haselow et al. [1986]  
 (C) Weast, R. C. [1984]  
 (D) Johnston and Eckert [1981]  
 (E) Johnston et al. [1982]  
 (F) Reid et al. [1987]  
 (G) Kurnik et al. [1981]  
 (H) Bartle et al. [1992]  
 (I) McHugh and Paulaitis [1980]  
 (J) Tsekhanskaya et al. [1964]  
 (K) Van Leer and Paulaitis [1980]

the same values in the previous work were assigned to  $\sigma_{11}$  and  $\sigma_{12}$ . The MMDA gave better prediction of solubility than the

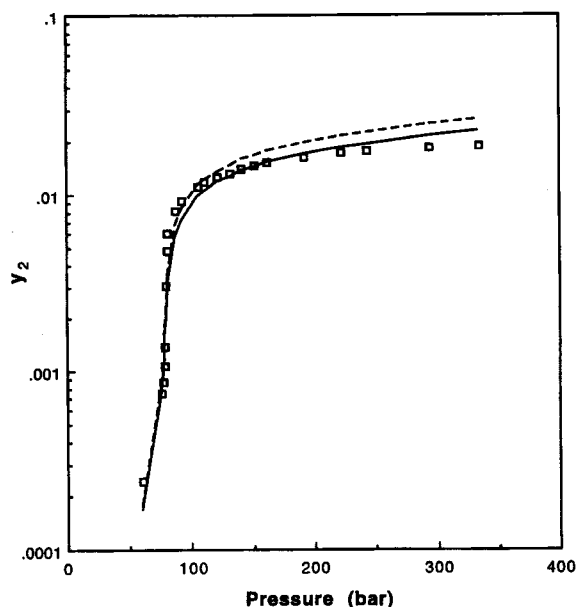


Fig. 1. Comparison of the solubility predictions of naphthalene- $\text{CO}_2$  system at 308 K by the MDA and MMDA when  $\alpha_{12}$  is considered as temperature-independent. (---: MDA, —: MMDA,  $\square$ : exp.)

original MDA. The results in case of temperature-independent parameters are listed in Table 3 for carbon dioxide systems and in Table 4 for ethylene systems. Both results were compared with those from the MDA as well as the Peng-Robinson equation of state with the classical mixing rule. As shown in Tables 3 and 4, the MMDA produced better results on solubility prediction than both cases.

When one of the parameters,  $\alpha_{12}$ , related to energy parameters was considered temperature-dependent as in the binary interaction parameter  $k_{12}$  in Eq. (20), the values of  $\alpha_{12}$  and  $R_{12}$  were optimized and regressed as a function of temperature while the same values of  $\sigma_{11}$  and  $\sigma_{12}$  were used. The results in the carbon dioxide-naphthalene system are shown in Fig. 2 and all results considered in this case are listed in Tables 5 and 6, which show this MMDA model also provides improvement over the MDA and the Peng-Robinson equation of state with the classical mixing rule.

Most of values of scaling factor,  $R_{12}$ , were found not to be far from unity. From the fact that better results were obtained with small deviation of  $R_{12}$  from unity, it can be concluded that the radial distribution function plays an important role in evaluating fluctuation integrals as expected, and that the better results in both temperature-independent and temperature-dependent systems might be due to the superiority of the MMDA over the original MDA.

Up to now, we calculated solubilities using the scaling factor

Table 3. Solubility results on carbon dioxide systems with the HSE model when all parameters are independent of temperature ( $\sigma_{11}=4.6 \text{ \AA}$ )

Carbon dioxide system	Number of points	PR EOS		HSE (MDA) model			HSE (MMDA) model	
		$k_{12}$	AAD	$\sigma_{12}$	$\alpha_{12}$	AAD	$R_{12}$	AAD
Acridine	28	0.1001	13.01	7.96	5.948	15.91	0.979-1.017	8.83
Benzoic acid	55	0.0102	26.75	7.338	5.209	19.05	0.998-1.009	17.22
Biphenyl	42	0.1510	55.12	7.82	5.179	25.14	1.013-1.147	17.15
2,3-Dimethylnaphthalene	15	0.0913	10.58	7.875	5.287	9.66	0.998-1.010	7.97
2,6-Dimethylnaphthalene	15	0.1061	5.65	7.538	4.95	12.25	0.996-1.007	9.60
Fluorene	30	0.0865	9.92	7.9	5.541	16.37	0.994-1.036	8.97
Hexamethylbenzene	27	0.1009	17.17	7.8	5.224	24.14	0.976-1.024	17.97
Naphthalene	64	0.0965	23.97	7.25	4.395	21.83	0.985-1.053	14.47
1,4-Naphthoquinone	18	0.0502	30.55	7.797	5.701	10.52	0.999-1.006	7.97
Phenanthrene	36	0.1032	22.38	8.08	5.92	23.81	0.987-1.032	14.53
Phenol	41	0.1261	23.78	6.95	3.73	21.7	0.998-1.099	8.29
Pyrene	22	0.9637	28.49	8.183	6.352	29.28	0.992-1.016	18.22
Triphenylmethane	22	0.0877	19.32	8.824	7.206	21.75	0.985-1.010	16.94
AAD	415		24.26			20.43		13.59

Table 4. Solubility results on ethylene systems with the HSE model when all parameters are independent of temperature ( $\sigma_{11}=4.7 \text{ \AA}$ )

Ethylene system	Number of points	PR EOS		HSE (MDA) model			HSE (MMDA) model	
		$k_{12}$	AAD	$\sigma_{12}$	$\alpha_{12}$	AAD	$R_{12}$	AAD
Anthracene	29	0.0501	13.74	7.53	5.478	10.18	0.993-1.004	8.38
Benzoic acid	15	-0.0653	18.31	7.127	5.194	13.89	1.000-1.012	10.62
2,3-Dimethylnaphthalene	18	0.0101	15.56	6.52	4.765	15.82	0.993-1.002	13.99
2,6-Dimethylnaphthalene	18	0.036	9.07	6.92	4.961	18.12	0.990-1.009	15.10
Fluorene	24	0.0083	17.95	7.67	5.822	23.07	0.997-1.023	18.28
Hexamethylbenzene	24	0.0218	19.1	7.945	5.952	12.1	0.978-1.003	7.32
Naphthalene	84	0.0151	36.84	7.22	4.766	15.46	0.998-1.015	14.60
Phenanthrene	45	0.0245	32.88	7.95	6.44	10.7	0.991-1.001	9.66
Pyrene	15	0.0089	14.73	8.185	6.952	21.15	0.996-1.010	11.32
AAD	272		25.00			14.91		12.39

as an additional parameter. On the other hand, the value of  $R_{12}$  can be determined by solving the Ornstein-Zernike equation along

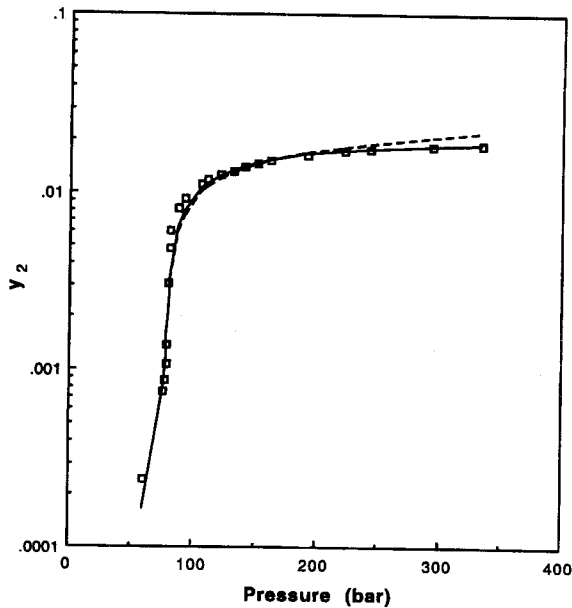


Fig. 2. Comparison of the solubility predictions of naphthalene- $\text{CO}_2$  system at 308 K by the MDA and MMDA when  $\alpha_{12}$  is considered as temperature-dependent. (---: MDA, —: MMDA,  $\square$ : exp.)

with the HNC closure for the RDFs of the mixture and reference fluid. The values of the parameters  $\sigma_{22}$ ,  $\epsilon_{12}$ , and  $\epsilon_{22}$ , which are needed to solve the Ornstein-Zernike integral equation using the Lennard-Jones potential, can be determined from the relation of the Bertholet mixing rule in Eqs. (25) and (26) and the known values of  $\sigma_{11}$ ,  $\sigma_{12}$  and  $\alpha_{12}$ .

In the carbon dioxide-naphthalene system at 328 K and 125 bar as an example, the value of  $\sigma_{22}$  calculated from  $\sigma_{11}$  ( $=4.60 \text{ \AA}$ ) and  $\sigma_{12}$  ( $=7.25 \text{ \AA}$ ) is  $9.90 \text{ \AA}$ , and those of  $\epsilon_{11}$ ,  $\epsilon_{12}$ , and  $\epsilon_{22}$  are also determined from  $\alpha_{12}$  ( $=4.395$ ). The Ornstein-Zernike integral equation with the HNC closure was solved to find out the locations of the first peaks of the RDFs in the mixture and the reference fluid where the MDA was used. Fig. 3 shows the results on the RDFs in mixture and pure reference fluid with the MDA when  $y_2$  is 0.001. The heights of the first peaks of mixture ( $g_{12}$ ) and reference fluid ( $g_o$ ) were found to be 1.973 and 1.930, respectively. Therefore, the value of  $R_{12}$  becomes 1.022 from the definition of  $R_{12}$  in Eq. (11), which is very close to 1.020 determined by optimization. Though the MDA does not reproduce  $g_{12}$  of the mixture as shown in Fig. 3 when the size parameters of the constituents of the mixture are quite different, the MDA has been successfully utilized to derive conformal solution methods due to an error cancellation in evaluating integrals containing RDF such as  $G_{ij}$  in Eq. (1) [Tan, 1987].

Applicability of the hard sphere equation of state used in this work needed should also be mentioned. As explained before, the

Table 5. Solubility results on carbon dioxide systems with the HSE model when  $\alpha_{12}$  is considered as temperature-dependent ( $\sigma_{11}=4.6 \text{ \AA}$ )

Carbon dioxide system	Number of points	PR EOS		HSE (MDA) model		HSE (MMDA) Model		
		$k_{12}$	AAD	$\alpha_{12}$	AAD	$\alpha_{12}$	$R_{12}$	AAD
Acridine	28	0.0964-0.1064	9.67	5.86-5.997	9.06	5.684-5.867	0.998-1.092	6.80
Benzoic acid	55	-0.0015-0.0246	14.16	5.2-5.238	17.18	4.857-7.254	0.606-1.111	12.87
Biphenyl	42	0.1242-0.1553	37.06	5.215-5.475	14.3	5.149-6.197	0.775-1.038	7.16
2,3-Dimethylnaphthalene	15	0.0861-0.0955	6.77	5.282-5.312	8.22	5.031-5.396	0.961-1.100	5.18
2,6-Dimethylnaphthalene	15	0.1047-0.1073	4.93	4.911-4.966	9.68	4.586-5.605	1.073-1.129	3.93
Fluorene	30	0.0826-0.0909	8.78	5.512-5.631	8.37	5.382-5.612	1.009-1.052	5.87
Hexamethylbenzene	27	0.0989-0.1033	17.04	5.149-5.276	18.54	4.924-5.051	1.079-1.109	11.09
Naphthalene	64	0.0938-0.9819	23.79	4.348-4.541	13.23	4.177-4.757	0.928-1.104	11.95
1,4-Naphthoquinone	18	0.0471-0.0548	29.88	5.7-5.719	7.85	5.666-5.847	0.958-1.012	6.68
Phenanthrene	36	0.0914-0.1082	15.53	5.875-6.019	14.34	5.793-6.106	0.926-1.070	12.21
Phenol	41	0.0951-0.1304	19.95	3.706-3.915	7.51	3.681-5.082	0.669-1.019	6.09
Pyrene	22	0.0904-0.1043	26.36	6.332-6.396	15.17	6.202-6.290	1.031-1.048	15.15
Triphenylmethane	22	0.086-0.0934	15.99	7.2-7.28	15.79	7.030-7.049	1.029-1.057	14.60
AAD	415		18.93		12.80			9.73

Table 6. Solubility results on ethylene systems with the HSE model when  $\alpha_{12}$  is considered as temperature-dependent ( $\sigma_{11}=4.7 \text{ \AA}$ )

Ethylene system	Number of points	PR EOS		HSE (MDA) model		HSE (MMDA) model		
		$k_{12}$	AAD	$\alpha_{12}$	AAD	$\alpha_{12}$	$R_{12}$	AAD
Anthracene	29	0.938-0.0526	8.28	5.455-5.486	7.64	5.362-5.690	0.920-1.048	7.47
Benzoic acid	15	-0.0571-0.0743	15.13	5.18-5.225	10.12	4.903-5.740	0.854-1.107	9.51
2,3-Dimethylnaphthalene	18	0.0001-0.0141	13.73	4.759-4.813	13.92	4.332-6.264	0.695-1.148	9.83
2,6-Dimethylnaphthalene	18	0.0308-0.0379	8.05	4.934-4.99	15.52	4.597-6.807	0.631-1.128	10.56
Fluorene	24	0.0037-0.0155	15.62	5.816-5.852	19.43	5.521-6.234	0.873-1.114	11.08
Hexamethylbenzene	24	0.0587-0.0284	18.99	5.877-5.952	7.76	5.928-6.397	0.864-1.010	5.40
Naphthalene	84	0.0109-0.0181	35.43	4.757-4.8181	14.33	4.650-5.864	0.745-1.033	11.83
Phenanthrene	45	0.0094-0.0377	22.48	6.405-6.642	9.76	6.187-8.037	0.698-1.067	6.16
Pyrene	15	0.0046-0.0136	12.31	6.94-6.984	11.24	6.900-6.995	0.985-1.026	10.87
AAD	272		21.55		12.38			9.40

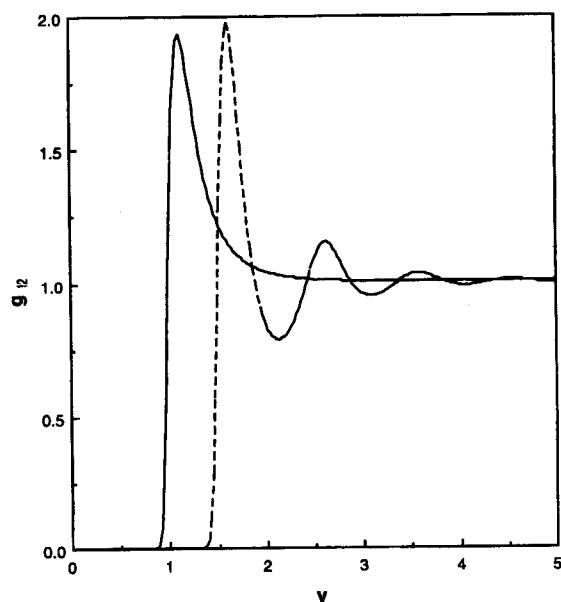


Fig. 3.  $g_{12}(r)$  and  $g_0(r)$  at 328 K and 125 bar from the Ornstein-Zernike integral equation with the HNC closure when  $y_2=0.001$ .

[—:  $g_0(r)$ , ---:  $g_{12}(r)$ ]

packing fraction  $\eta$  in Eq. (17) should be less than 0.35, which was satisfied in the whole range tested in this work. When another hard sphere equation of state proposed by Kim et al. [1986] was used, the results were found to be almost same. The simple type of equation like Eq. (17) was substituted for the Carnahan-Starling equation for the analytical integration of Eq. (15) as mentioned before.

## CONCLUSION

Using the formalism on the Kirkwood-Buff fluctuation integral for solubility prediction by Cochran et al. [1987], the MMDA instead of the original MDA for the HSE conformal solution method was used to evaluate solubility of solids in supercritical fluids.

In this work, the scaling factor  $R_{12}$  representing the ratio of the first peak heights of the radial distribution functions in the mixture and reference fluid with the MDA was needed. When  $R_{12}$  was considered as an additional parameter, better results on solubility prediction were obtained than those of the previous work with the original MDA as well as by the Peng-Robinson equation of state with the classical mixing rule. The values of  $R_{12}$  by optimizing to fit experimental data were found not to be far from those by solving the Ornstein-Zernike integral equation with the HNC closure.

Better results for both temperature-independent and temperature-dependent systems might be due to the superiority of the MMDA over the original MDA.

## NOMENCLATURE

a, b : parameters in the Peng-Robinson equation of state  
 $B_{kl}$  : element of the matrix defined in Eq. (6)

$c(r)$  : direct correlation function  
 $C$  : direct correlation function integral defined in Eq. (2)  
 $g_{11}$  : pair distribution function for solvent-solvent pairs  
 $g_{12}$  : pair distribution function for solvent-solute pairs  
 $G_{11}$  : solvent-solvent Kirkwood-Buff fluctuation integral  
 $G_{11}^o$  : solvent-solvent Kirkwood-Buff fluctuation integral at infinite dilution of solute  
 $G_{12}$  : solvent-solute Kirkwood-Buff fluctuation integral  
 $h(r)$  : pair correlation function  
 $k$  : Boltzmann's constant  
 $N$  : number of particles  
 $P$  : pressure  
 $R$  : gas constant  
 $R_{12}$  : scaling factor in the MMDA  
 $t(r)$  : indirect part of potential of mean force  
 $T$  : temperature  
 $u(r)$  : intermolecular potential  
 $V$  : molar volume  
 $x$  : mole fraction  
 $y$  : dimensionless distance  
 $y_2$  : solubility  
 $Z$  : compressibility factor

## Greek Letters

$\alpha_{12}$  : parameter defined in Eq. (14)  
 $\epsilon_{ij}$  : energy parameter for the Lennard-Jones potential  
 $\eta$  : packing fraction  
 $\kappa_T$  : isothermal compressibility  
 $\sigma_{ij}$  : size parameter for the Lennard-Jones potential  
 $\rho$  : number density

## Superscripts

HS : hard sphere  
 $o$  : at infinite dilution of the solute  
 sat : saturation condition

## Subscript

$o$  : pure reference fluid

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