

# Density expansion (DEX) mixing rules: Thermodynamic modeling of supercritical extraction

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Conformal solution theory and the density expansion expression of the radial distribution function of fluids are used to derive a set of mixing rules. The new mixing rules are composition, density, and temperature dependent. To test the new mixing rules they are used for thermodynamic modeling of supercritical extraction. Comparison of the result of calculation by the mixing rules with the van der Waals mixing rules indicates a profound improvement over the latter in prediction of properties of mixtures consisting of species with large molecular size and shape differences.

## INTRODUCTION

The practical application of fluid phase equilibria for problems of interest in science and engineering necessitates the use of equations of state of fluid mixtures. Statistical mechanical equations of state of rather simple fluid mixtures are well developed,<sup>3,8,11,12</sup> but for mixtures containing polar species and/or species with large molecular size and shape differences theories of equations of state are in their infancy. Due to the difficulties which exist in the development of workable, analytic statistical mechanical mixture theories, the use of mixing rules for the development of mixture equations of state from pure fluid equations of state is a more practical alternative. The density expansion (DEX) mixing rules proposed here are based on statistical mechanics which can be used to extend existing pure fluid equations of state to mixtures. Predictions using the DEX mixing rules are demonstrated to be more accurate for mixtures consisting of species with large molecular size and shape differences than the van der Waals mixing rules.

## THEORY

According to statistical mechanics, macroscopic thermodynamic properties of a pure fluid are related to its microscopic molecular characteristics by the following equations<sup>5</sup>:

$$u = u_{ig} + 2\pi\rho \int_0^\infty \phi(r)g(r)r^2 dr, \quad (1)$$

$$P = \rho RT - (2/3)\pi\rho \int_0^\infty r\phi'(r)g(r)r^2 dr, \quad (2)$$

where  $u$  is the internal energy,  $P$  is the pressure,  $\phi(r)$  is the pair-intermolecular potential energy function, and  $g(r)$  is the radial (or pair) distribution function. Equations (1) and (2) are commonly called the energy and virial (or

pressure) equations, respectively. For a multicomponent mixture these equations assume the following forms:

$$u = u_{ig} + 2\pi\rho \sum_i \sum_j x_i x_j \int_0^\infty \phi_{ij}(r)g_{ij}(r)r^2 dr, \quad (3)$$

$$P = \rho RT - (2/3)\pi\rho \sum_i \sum_j x_i x_j \int_0^\infty r\phi'_{ij}(r)g_{ij}(r)r^2 dr. \quad (4)$$

In the above equations, summations are over all the (c) components of the mixture and  $x_i$  and  $x_j$  are the mole fractions. Equations (1)–(4) can be used in conjunction with conformal solution theory in the manner presented below to derive mixing rules based on different mixture theory approximations.

The basic problem in the development of one-fluid mixing rules through conformal solution theory of statistical mechanics is to introduce a pseudopure fluid which can represent the configurational properties of a mixture. Further, the pseudopure fluid and mixture molecular interactions must all be pairwise additive with the following expressions for their interaction potentials<sup>2,9,10,14</sup>:

$$\phi_{xx}(r) = f_{xx}\phi_{oo}(r/h_{xx}^{1/3}), \quad (5.1)$$

$$\phi_{ij}(r) = f_{ij}\phi_{oo}(r/h_{ij}^{1/3}), \quad (5.2)$$

where  $\phi_{xx}$  is potential energy function between molecules of the pseudopure fluid,  $\phi_{ij}$  is the potential energy function between molecules of kind  $i$  and  $j$  of the mixture,  $\phi_{oo}$  is a pure reference fluid intermolecular pair-interaction potential,  $f_{xx}$ ,  $h_{xx}$  are the conformal solution parameters of the pseudopure fluid, and  $f_{ij}$  and  $h_{ij}$  are the conformal interaction parameters of species  $i$  and  $j$  in the mixture. For example, when the molecules of a nonpolar pure fluid and mixture obey the Lennard-Jones (12-6) potential, functions  $f$  and  $h$  will be in the following forms:

$$f_{xx} = \epsilon_{xx}/\epsilon_{oo}, \quad h_{xx} = (\sigma_{xx}/\sigma_{oo})^3, \quad (6.1)$$

$$f_{ij} = \epsilon_{ij}/\epsilon_{oo}, \quad h_{ij} = (\sigma_{ij}/\sigma_{oo})^3, \quad (6.2)$$

where  $\epsilon_{xx}$  and  $\sigma_{xx}$  are the interaction parameters of the pseudopure fluid,  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the interaction parameters of species  $i$  and  $j$ , and  $\epsilon_{oo}$  and  $\sigma_{oo}$  are those of the reference pure fluid. By placing Eq. (5.1) in Eqs. (1) and (2), and Eq. (5.2) in Eqs. (3) and (4), and then equating configurational internal energy and pressure of the pseudopure fluid and the mixture we will obtain the following equations:

$$\begin{aligned} f_{xx}h_{xx} \int_0^\infty \phi_{oo}(y)g_{oo}(y)y^2 dy \\ = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \int_0^\infty \phi_{oo}(y)g_{ij}(y)y^2 dy, \end{aligned} \quad (7)$$

$$\begin{aligned} f_{xx}h_{xx} \int_0^\infty y\phi'_{oo}(y)g_{oo}(y)y^2 dy \\ = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \int_0^\infty y\phi'_{oo}(y)g_{ij}(y)y^2 dy, \end{aligned} \quad (8)$$

where  $y = r/\sigma$ . It should be pointed out that for the special case of the hard-sphere fluid, Eq. (7) vanishes and Eq. (8) will reduce to the following form:

$$h_{xx}g_{oo}(1) = \sum_i \sum_j x_i x_j h_{ij}g_{ij}(1), \quad (9)$$

where  $g(1)$  is the hard-sphere radial distribution function at the contact. Solution of Eqs. (7), (8) and/or (9) should produce the necessary expressions (mixing rules) relating  $f_{xx}$  and  $h_{xx}$  of the pseudopure fluid to  $f_{ij}$  and  $h_{ij}$  of components of the mixture. For this purpose we should use an approximation technique relating the radial distribution functions (RDF) in the mixture to the pure reference fluid RDF. In what follows different approximation techniques will be used for relating  $g_{ij}$  to  $g_{oo}$  in order to derive different sets of mixing rules.

#### CONFORMAL SOLUTION APPROXIMATION (CSA) FOR MIXTURE RDFs

According to this approximation technique the scaled RDFs in a mixture are assumed to be all identical, and they are equal to the pseudopure fluid RDF, i.e.,

$$g_{xx}(y) = g_{ij}(y) = g(y). \quad (10)$$

When we use this approximation, Eqs. (7) and (8) both reduce to the same mixing rule:

$$f_{xx}h_{xx} = \sum_i \sum_j x_i x_j f_{ij} h_{ij}. \quad (11)$$

Equation (11) is actually the second van der Waals mixing rule which is well known.<sup>9,15</sup> By using the hard-sphere potential [placing Eq. (10) in Eq. (9)] we derive the following mixing rule:

$$h_{xx} = \sum_i \sum_j x_i x_j h_{ij}. \quad (12)$$

This mixing rule is the first van der Waals mixing rule which, in conjunction with the second van der Waals mixing rule [Eq. (11)] is usually used for calculation of thermodynamic properties of mixtures.<sup>9,13,15</sup>

#### DENSITY EXPANSION (DEX) APPROXIMATION FOR MIXTURE RDFs

It is known that the RDF of a pure fluid can be expanded around the dilute gas RDF,  $\exp[-\phi(r)/kT]$ , in the form<sup>5</sup>

$$g_{xx}(y) = [1 + \rho^* g_{xx}^{(1)}(y) + O(\rho^{*2})] \exp[-\phi_{xx}(r)/kT],$$

where  $\rho^* = \rho\sigma_{oo}^3 h_{xx}$ . This expansion can be written in the following simple form:

$$g_{xx}(y) = [1 + F_{xx}(y)] \exp[-\phi_{xx}(r)/kT]. \quad (13)$$

Let us also assume that we could make a similar expansion for RDFs in a mixture around the dilute gas mixture RDFs as the following:

$$g_{ij}(y) = [1 + F_{ij}(y)] \exp[-\phi_{ij}(r)/kT]. \quad (14)$$

The justification behind this expansion lies in the assumption that  $F_{xx}(y)$  is the same for the mixture and pure components from the conformal solution point of view, i.e.,

$$g_{xx}(y) \exp[\phi_{xx}(r)/kT] = g_{ij}(y) \exp[\phi_{ij}(r)/kT]. \quad (15)$$

Now by placing Eqs. (13) and (14) in Eqs. (7) and (8) we will derive the following expressions:

$$\begin{aligned} \sum_i \sum_j x_i x_j f_{ij} h_{ij} \int_0^\infty \exp[-\phi_{ij}(r)/kT] \{ \phi_{oo}(y) [1 + F(y)] \} y^2 dy \\ = f_{xx} h_{xx} \int_0^\infty \exp[-\phi_{xx}(r)/kT] \\ \times \{ \phi_{oo}(y) [1 + F(y)] \} y^2 dy \end{aligned} \quad (16)$$

and

$$\begin{aligned} \sum_i \sum_j x_i x_j f_{ij} h_{ij} \int_0^\infty \exp[-\phi_{ij}(r)/kT] \{ \phi'_{oo}(y) [1 + F(y)] \} y^3 dy \\ = f_{xx} h_{xx} \int_0^\infty \exp[-\phi_{xx}(r)/kT] \\ \times \{ \phi'_{oo}(y) [1 + F(y)] \} y^3 dy. \end{aligned} \quad (17)$$

Let us now approximate

$$\begin{aligned} \exp[-\phi_{ij}(r)/kT] \\ = \exp[-(f_{ij} - f_{xx})\phi_{oo}(y)/kT] \exp[-f_{xx}\phi_{oo}(y)/kT] \\ \cong \{ 1 - (f_{ij} - f_{xx})\phi_{oo}(y)/kT \} \exp[-f_{xx}\phi_{oo}(y)/kT]. \end{aligned} \quad (18)$$

By placing this approximation in Eqs. (16) and (17) we will derive the following expressions, respectively,

$$\sum_i \sum_j x_i x_j f_{ij} h_{ij} \{ 1 - (f_{ij} - f_{xx})\langle \phi_{oo}(y)/kT \rangle_A \} = f_{xx} h_{xx} \quad (19)$$

TABLE I. Input data for calculation of solubility of solids in supercritical gases.

Property	Compound					Reference
	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	2,3-DMN	2,6-DMN	HMB	
<i>P<sub>c</sub></i> (atm)	72.8	49.7	28.7	28.7	23.53	16
<i>T<sub>c</sub></i> (K)	304.2	282.4	780.6	770.5	748.8	16
Solid Density (g/cm <sup>3</sup> )			1.003	1.142	1.0633	4
<i>P<sup>sat</sup></i> (PA)						
at 308 K			1.27	1.22	0.49	1, 7
318 K			3.49	3.45	1.41	
328 K			9.01	9.13	3.81	

and

$$\sum_i \sum_j x_i x_j f_{ij} h_{ij} \{1 - (f_{ij} - f_{xx}) \langle \phi_{oo}(y) / kT \rangle_B\} = f_{xx} h_{xx}. \quad (20)$$

In the above equations,

$$\langle \phi_{xx}(y) / kT \rangle_A = (1/kT) \int_0^\infty \phi_{xx}^2(y) g_{oo}(y) y^2 dy / \int_0^\infty \phi_{xx}(y) g_{oo}(y) y^2 dy \quad (21)$$

and

$$\langle \phi_{xx}(y) / kT \rangle_B = (1/kT) \int_0^\infty \phi'_{xx}(y) \phi_{xx}(y) g_{oo}(y) y^3 dy / \int_0^\infty \phi'_{oo}(y) g_{oo}(y) y^3 dy. \quad (22)$$

Fluctuation theory of statistical mechanics in the canonical ensemble will yield the following expression for  $\langle \phi_{xx}(r) /$

$kT \rangle_A$  with respect to the thermodynamic properties of the pseudopure fluid<sup>5</sup>:

$$\langle \phi_{xx}(y) / kT \rangle_A = (u_x - u_{ig}) / kT + T(C_{vx} - C_{vig}) / (u_x - u_{ig}). \quad (23)$$

For  $\langle \phi_{xx}(y) / kT \rangle_B$ , we will not be able to produce a simple expression relating it to thermodynamic properties of the pseudopure fluid but it can be shown that for repulsive potentials of the form  $\phi(r) = a/r^n$ , Eqs. (21) and (22) are identical. For potentials with repulsive and attractive parts these two expressions can be considered to be approximately the same. By placing Eq. (23) in Eq. (19) we will derive the following mixing rule which we will refer to as the density expansion (DEX) mixing rule:

$$f_{xx} h_{xx} = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \{1 - (f_{ij} - f_{xx}) [(u_x - u_{ig}) / kT + T(C_{vx} - C_{vig}) / (u_x - u_{ig})]\}. \quad (24)$$

TABLE II. The unlike-interaction parameter  $k_{12}$  for different solute and supercritical solvent interactions as calculated by the use of different mixing rules and at different temperatures.

Mixing rule	Solute Solvent Temp. (K)	2,3 DMN		2,6 DMN		HMB	
		CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>
VDW1	298						-0.4041
	303					-0.3074	
	308	-0.3587	-0.4903	-0.3550	-0.4845		
	318	-0.3359	-0.5176	-0.3524	-0.4980		-0.4663
	323					-0.3491	
	328	-0.3233	-0.6409	-0.3456	-0.5277		
	343					-0.3946	-0.5459
VDW2	298						-0.2569
	303					-0.1168	
	308	-0.1754	-0.3428	-0.1777	-0.3440		
	318	-0.1537	-0.3585	-0.1727	-0.3508		-0.3164
	323					-0.1611	
	328	-0.1398	-0.4408	-0.1635	-0.3679		
	343					-0.2092	-0.3913
DEX	298						-0.0626
	303					-0.0204	
	308	-0.0336	-0.0843	-0.0380	-0.0876		
	318	-0.0204	-0.0932	-0.0340	-0.0916		-0.0918
	323					-0.0458	
	328	-0.0103	-0.1559	-0.0265	-0.1024		
	343					-0.0725	-0.1294

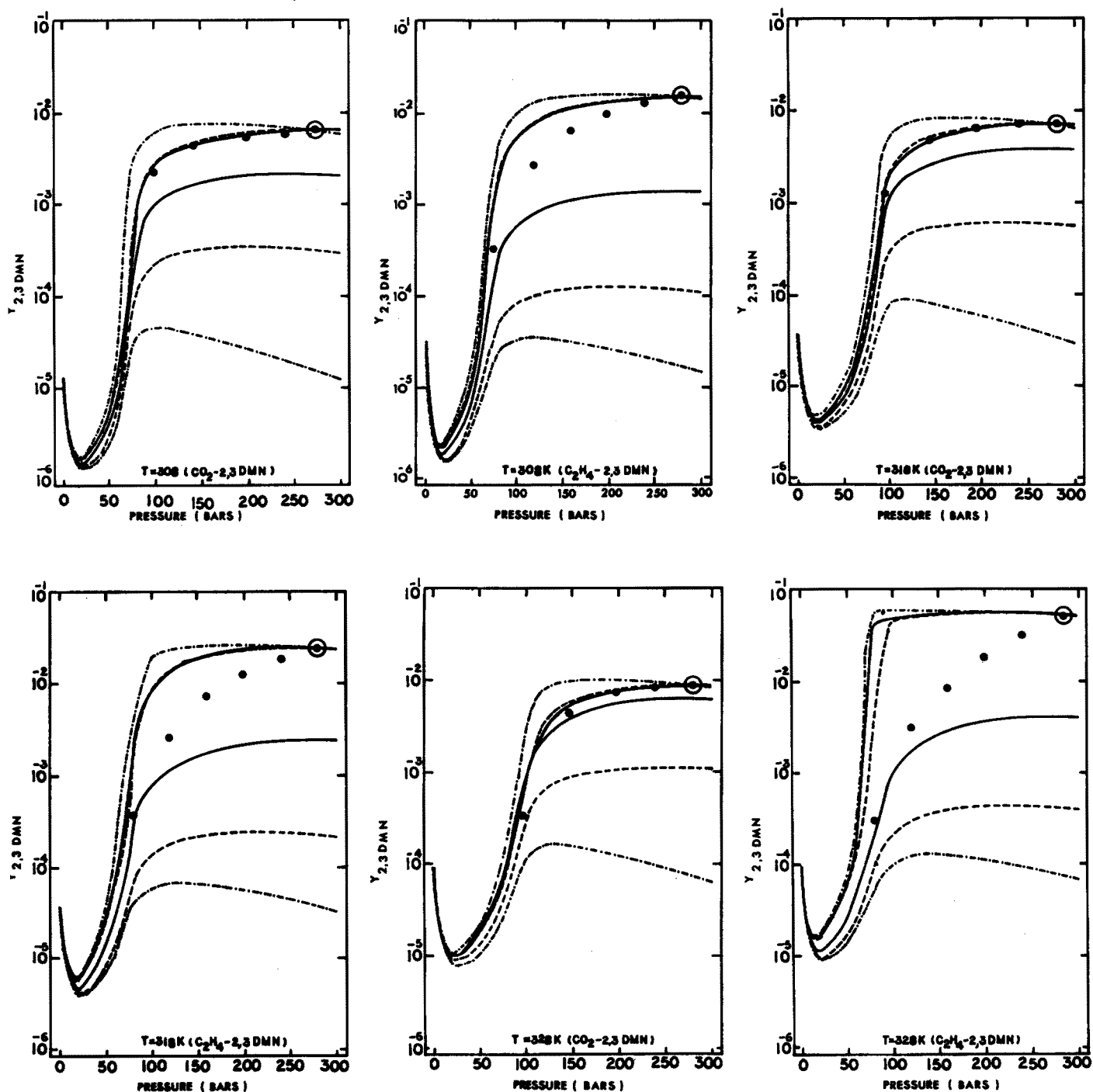


FIG. 1. Solubility of 2,3 dimethyl naphthalene (DMN) in supercritical  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  at different temperatures vs pressure. The solid dots are the experimental data (Ref. 7). The dotted-dashed lines are results of the vdW1 mixing rules, the dashed-dashed lines are results of the vdW2 mixing rules, and the solid lines are results of the DEX mixing rules. The circled solid dot is the experimental data point which is used to calculate  $k_{12}$  parameter. The lines that do not pass through the circled dot are for  $k_{12} = 0$ .

The latter mixing rule can be used, joined with the first van der Waals mixing rule, for calculation of mixture properties. It should be pointed out that since this mixing rule is a composition, temperature, and density dependent expression it must be used only for internal energy calculation where it originated. However, since it is also possible to derive it from the pressure (or virial) equation in an approximate fashion it can be used for pressure calculation as well.

## THERMODYNAMIC MODELING OF SUPERCRITICAL EXTRACTION

Application of mixture equations of state for prediction of solubility of heavy solids and liquids in supercritical gases is a good test of mixture theories (see Table I). Solubility of a condensed phase,  $v_2$  (mole fraction), in a vapor phase at super-critical conditions can be expressed as<sup>15</sup>

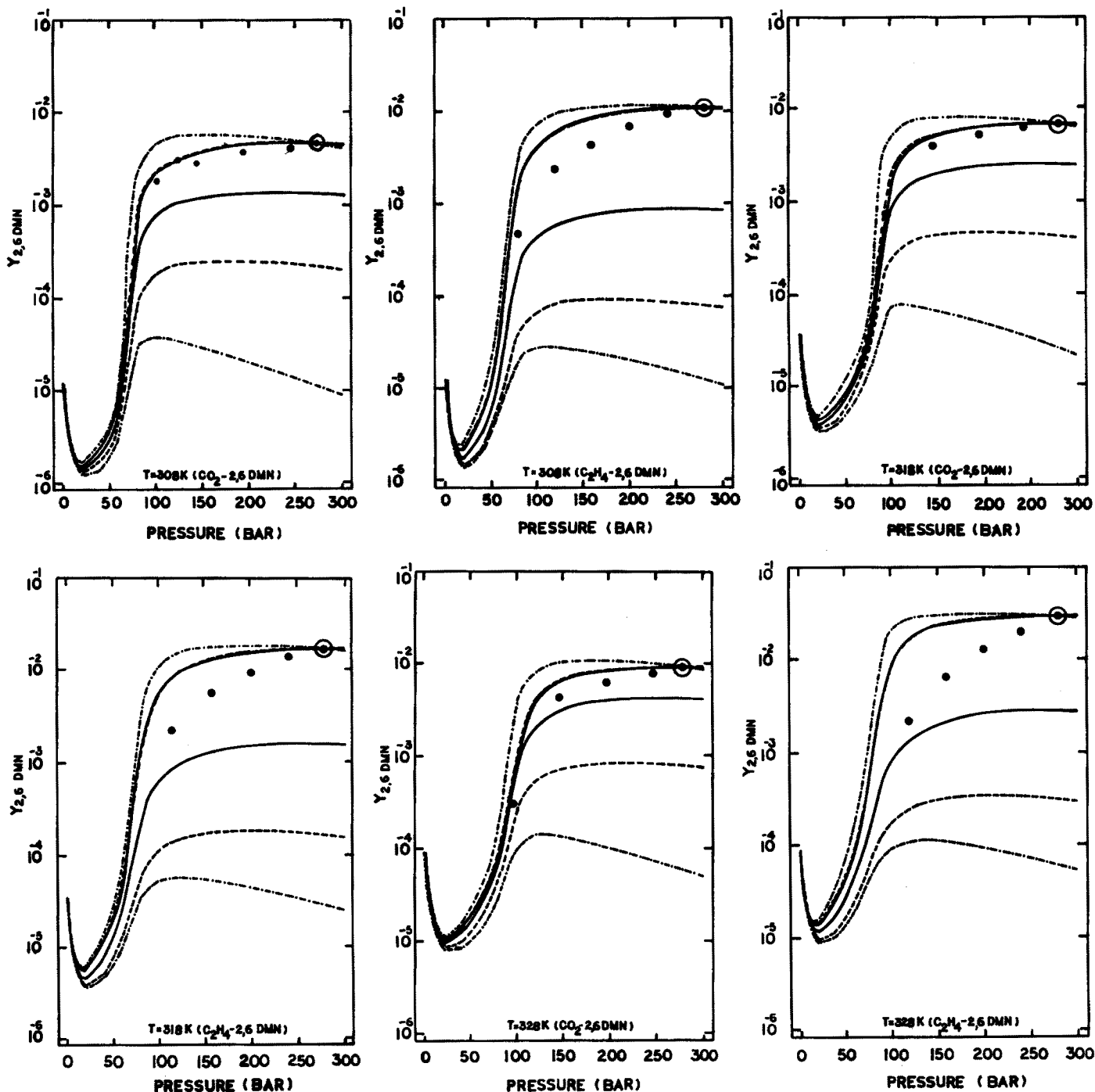


FIG. 2. Solubility of 2,6 dimethyl naphthalene (DMN) in supercritical  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  at different temperatures vs pressure. The solid dots are the experimental data (Ref. 7). The dotted-dashed lines are results of the vdW1 mixing rules, the dashed-dashed lines are results of the vdW2 mixing rules, and the solid lines are results of the DEX mixing rules. The circled solid dot is the experimental data point which is used to calculate  $k_{12}$  parameter. The lines that do not pass through the circled dot are for  $k_{12} = 0$ .

$$y_2 = (p_2^s/P)(1/\phi_2)\phi_2^s \exp \int_{p_2^s}^P (v_2^{\text{solid}}/RT)dP,$$

where  $\phi_2^s$  is the fugacity coefficient of the condensed phase at the saturation pressure  $p_2^s$ , and  $\phi_2$  is the vapor phase fugacity coefficient at pressure  $P$ . Provided we assume  $v_2^{\text{solid}}$  is independent of pressure and for small values of  $p_2^s$  the above expression will be converted to the following form:

$$y_2 = (p_2^s/P)(1/\phi_2)\exp[v_2^{\text{solid}}(P - p_2^s)/RT]. \quad (25)$$

In order to calculate the solubility from Eq. (25) we will need to choose an expression for the fugacity coefficient. Generally, for calculation of the fugacity coefficient an equation of state with an appropriate mixing rule is used. In the present analysis we use the van der Waals equation of state

$$(P + a/v^2)(v - b) = RT, \quad (26)$$

together with three different sets of mixing rules as will be described below. The choice of the van der Waals

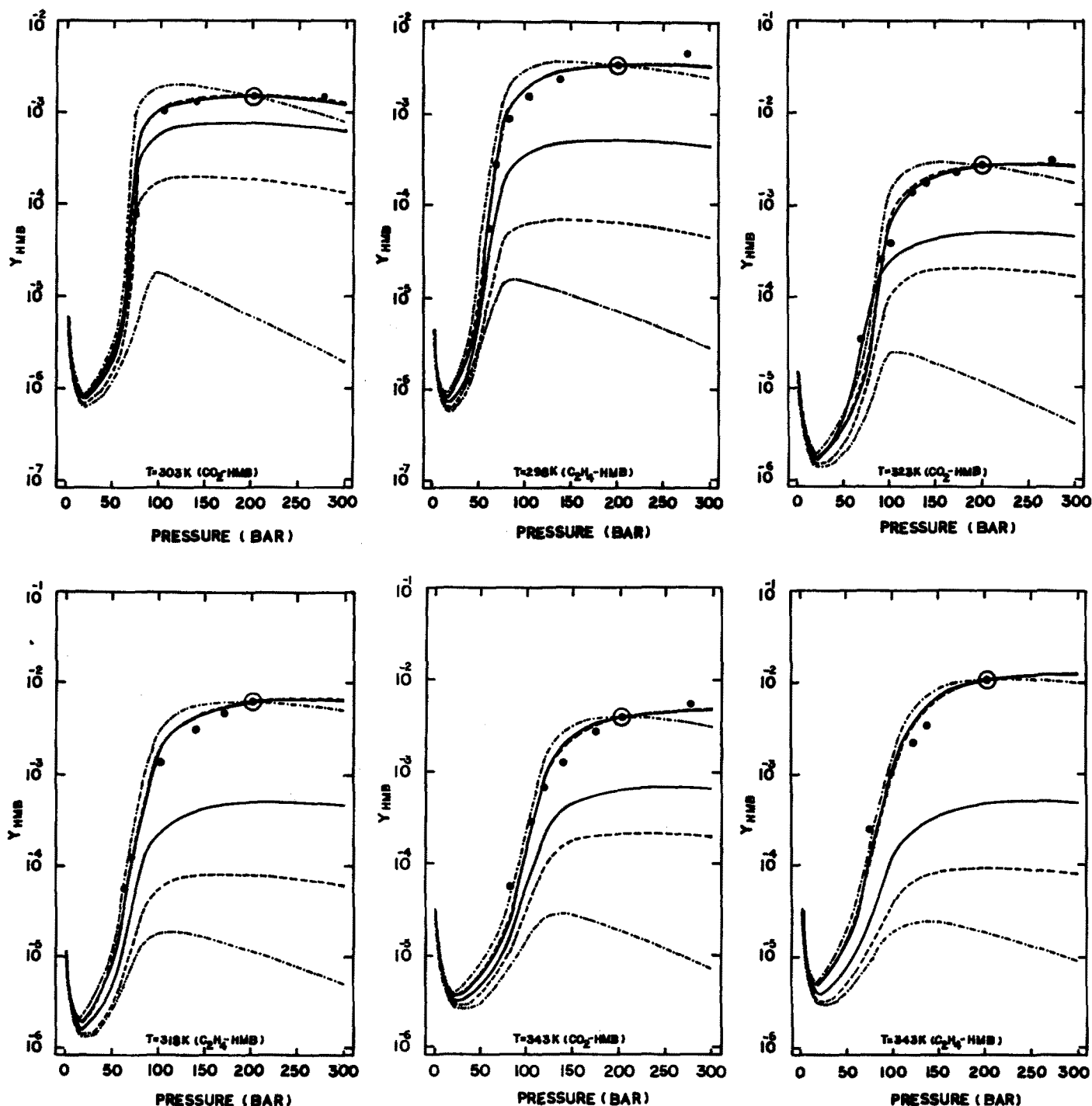


FIG. 3. Solubility of hexamethyl benzene (HMB) in supercritical  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  at different temperatures vs pressure. The solid dots are the experimental data (Ref. 6). The dotted-dashed lines are results of the vdW1 mixing rules, the dashed-dashed lines are results of the vdW2 mixing rules, and the solid lines are results of the DEX mixing rules. The circled solid dot is the experimental data point which is used to calculate  $k_{12}$  parameter. The lines that do not pass through the circled dot are for  $k_{12} = 0$ .

equation of state is because of its simplicity and it is not expected to affect the comparative study of mixing rules.

The first set of mixing rules that we will use and which we will refer to as the vdW1 mixing rules are the following:

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad (27)$$

$$b = \sum_i x_i b_i. \quad (28)$$

These mixing rules are commonly used in practical applications of equations of state.<sup>7,15,16</sup> Equation (27) is equivalent to Eq. (11) when  $f_{ij}h_{ij}$  is set equal to  $a_{ij}/a_{oo}$  and  $f_{xx}h_{xx}$  is set equal to  $a/a_{oo}$ .

Equation (28) is equivalent to Eq. (12), the first van der Waals mixing rule, when  $h_{ij}$  is set equal to  $b_{ij}/b_{oo}$  and  $h_{xx}$  is set equal to  $b/b_{oo}$  and with the assumption that  $b_{ij} = (b_{ii} + b_{jj})/2$ . For the unlike-interaction parameter  $a_{ij}$  ( $i \neq j$ ), we assume  $a_{ij} = (1 - k_{ij})(a_{ii} \cdot a_{jj})^{1/2}$ . With the

vdW1 mixing rules the following expression for the fugacity coefficient of a solute in a supercritical gas will be derived (Ref. 15, p. 45):

$$\phi_2 = [RT/v - b](1/P) \times \exp[b_2/(v - b) - 2 \sum_j x_j a_{2j}/vRT]. \quad (29)$$

The second set of mixing rules that we will use in the present analysis and which we will refer to as the vdW2 mixing rules, are the following:

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad (30)$$

$$b = \sum_i \sum_j x_i x_j b_{ij}. \quad (31)$$

The difference between these mixing rules and the vdW1 mixing rules is in the expression for  $b$ . For the unlike-interaction parameters of these mixing rules the following expressions will be used:

$$b_{ij} = [(b_i^3 + b_j^3)/2]^3, \quad (32)$$

$$a_{ij} = (1 - k_{ij})(a_{ii} \cdot a_{jj})^{1/2}. \quad (33)$$

With the vdW2 mixing rules the following expression for the fugacity coefficient of a solute in a supercritical gas will be derived:

$$\phi_2 = [RT/(v - b)](1/P) \exp \left[ \left( -b + 2 \sum_j x_j b_{2j} \right) / (v - b) - 2 \sum_j x_j a_{2j}/vRT \right]. \quad (34)$$

The third set of mixing rules that we will use in the present analysis is the DEX mixing rules which for the van der Waals equation of state assume the following forms:

$$a = (b/2) \{ (D - vRT)/C + [(D - vRT)^2/C^2 + 4vRT/b]^{1/2} \}, \quad (35)$$

$$b = \sum_i \sum_j x_i x_j b_{ij}, \quad (36)$$

where

$$C = \sum_i \sum_j x_i x_j a_{ij} \quad \text{and} \quad D = \sum_i \sum_j x_i x_j a_{ij}^2/b_{ij}.$$

The expression for  $b$  is equivalent to Eq. (12) which is the first vdW mixing rule and the expression for  $a$  is equivalent to Eq. (24) when the van der Waals equation of state is used for calculation of the internal energy and heat capacity expressions which appear in that equation and with replacing  $f_{ij}h_{ij} = a_{ij}/a_{00}$  and  $f_{xx}h_{xx} = a/a_{00}$ . With the DEX mixing rules the following expression for the fugacity coefficient of a solute in a supercritical gas will be derived

$$\phi_2 = [RT/(v - b)](1/P) \exp \left[ \left( -b + 2 \sum_j x_j b_{2j} \right) / (v - b) - \int_v^\infty (A_2/v^2 RT) dv \right], \quad (37)$$

where

$$A_2 = (1/n)[\partial(n^2 a)/\partial n_2]_{T,v,n_i}.$$

For the unlike-interaction parameters in these mixing rules the same expressions as Eqs. (32) and (33) are used.

The expression for the fugacity coefficient as derived by using the vdW1, vdW2, and DEX mixing rules are used here to predict solubility of 2,3 dimethyl naphthalene (2,3 DMN), 2,6 dimethyl naphthalene (2,6 DMN), and hexa methyl benzene (HMB) in supercritical carbon dioxide and ethylene. Prediction of solubility based on the three techniques requires numerical regression calculations. Computer time required for the DEX is slightly more than vdW1 and vdW2 mixing rules, but in principle, for all three techniques it is relatively small. The results of this calculation are reported by Figs. 1–3. There are two different values of solubilities reported in these figures for every set of mixing rules. One value is for prediction of solubilities by assuming  $k_{12} = 1$  and the other set of values is for the case when  $k_{12}$ s are calculated from an experimental data at each temperature. Numerical values of the  $k_{12}$  values in the latter case are reported in Table II for different solute–solvent combinations and at different temperatures for each of the three sets of mixing rules.

According to Figs. 1–3 when  $k_{12} = 1$  the predictions by the vdW2 mixing rules are closer to the experimental data than the predictions by the vdW1, while the results of the DEX mixing rules are superior to both of them. In the case when  $k_{12}$  is fitted to an experimental solubility data, for most of the cases studied predictions by the vdW2 and DEX mixing rules are almost identical, but superior to the predictions by the vdW1 mixing rules. However, the absolute values of  $k_{12}$  parameters calculated by the DEX mixing rules are smaller, by one order of magnitude, than the values calculated by the vdW2 mixing rules and they vary less with temperature. As a matter of fact the order of magnitude of  $k_{12}$  parameters calculated by the DEX mixing rules are closer to reality than the parameters calculated by either the vdW1 or vdW2 mixing rules and they also vary less with temperature. Since the vdW2 and DEX mixing rules give essentially the same accuracy, at least for the cases tested, a relevant criteria in preferring one over the other would be the values of  $k_{12}$  and its variation with temperature. Of course, an accurate theory of mixtures will produce interaction parameters which are independent of temperature. Overall, solubility predictions by the DEX mixing rules are superior to the vdW2 mixing rules and the predictions by the vdW2 mixing rules are superior to the vdW1 mixing rules.

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**Erratum: Density expansion (DEX) mixing rules: Thermodynamic modeling of supercritical extraction [J. Chem. Phys. 82, 406 (1985)]**

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In Eq. (20) the term  $(f_0 - f_{xx})$  must be replaced with  $(f_0/f_{xx} - 1)$  and  $\phi_{00}$  must be replaced with  $\phi_{xx}$ . In Eqs. (21 and 22), the term  $g_{00}$  must be replaced with  $g_{xx}$ . In Eq. (24)

the term  $(f_0 - f_{xx})$  must be replaced with  $(f_0/f_{xx} - 1)$ . Equation (35) must be replaced with the following equation:

$$a = b [C + bD/vRT] / [1 + C/vRT]. \quad (35)$$