VAN DER WAALS MIXING RULES FOR CUBIC EQUATIONS OF STATE. APPLICATIONS FOR SUPERCRITICAL FLUID EXTRACTION MODELLING

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Abstract—A new concept for the development of mixing rules for cubic equations of state consistent with statistical-mechanical theory of the van der Waals mixing rules is introduced. Utility of this concept is illustrated by its application to the Redlich–Kwong (RK) and the Peng–Robinson (PR) equations of state. The resulting mixing rules for the Redlich–Kwong and the Peng–Robinson equations of state are tested through prediction of solubility of heavy solids in supercritical fluids. It is shown that the new mixing rules can predict supercritical solubilities more accurately than the original mixing rules of the Redlich–Kwong and Peng–Robinson equations of state.

INTRODUCTION

There has been extensive progress made in recent years in research towards the development of analytic statistical-mechanical equations of state applicable for process design calculations (Alem and Mansoori, 1984). However, cubic equations of state are still widely used in chemical engineering practice for the calculation and prediction of properties of fluids and fluid mixtures (Renon, 1983). These equations of state are generally modifications of the van der Waals equation of state,

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{1}$$

which was proposed by van der Waals in 1873. According to van der Waals, the extension of this equation of state to mixtures requires replacement of a and b by the following composition-dependent expressions:

$$a = \sum_i^n \sum_j^n x_i x_j a_{ij} \tag{2}$$

$$b = \sum_i^n \sum_j^n x_i x_j b_{ij}. \tag{3}$$

Equations (2) and (3) are called the van der Waals mixing rules. In these equations, a_{ij} and b_{ij} ($i = j$) are parameters corresponding to pure component (i) while a_{ij} and b_{ij} ($i \neq j$) are called the unlike-interaction parameters. It is customary to relate the unlike-interaction parameters to the pure-component parameters by the following expression:

$$a_{ij} = (1 - k_{ij})(a_{ii}a_{jj})^{1/2} \tag{4}$$

$$b_{ij} = (b_{ii} + b_{jj})/2. \tag{5}$$

In eq. (4), k_{ij} is a fitting parameter which is known as the coupling parameter. With eq. (5) substituted in eq. (3), the expression for b will reduce to the following one-summation form:

$$b = \sum_i^n x_i b_{ii}. \tag{3.1}$$

Extensive research on equations of state have indicated that the van der Waals equation of state is not accurate enough for the prediction of properties of compressed gases and liquids (Rowlinson and Swinton, 1982). This deficiency of the van der Waals equation of state has initiated a great deal of research on the development of other equations of state, through the use of principles of statistical mechanics or by empirical or semi-empirical means. The majority of equations of state used in chemical engineering practice are of the second category and are mostly cubic in the volume, like the van der Waals equation of state itself, but contain other forms of the temperature and volume dependencies. One such equation of state which has a simple form is the Redlich–Kwong equation of state (Redlich and Kwong, 1949):

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v-b)}. \tag{6}$$

This equation of state has found widespread applications in chemical engineering calculations. We would also like to mention that there exist a large number of more sophisticated empirical versions of the van der Waals and Redlich–Kwong modifications. Of this category of equations of state, the Peng–Robinson equation of state (Peng and Robinson, 1976)

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \tag{7}$$

$$a(T) = a(T_c)\{1 + \kappa(1 - T_r^{1/2})\}^2 \tag{8}$$

$$a(T_c) = 0.45724 \, R_c^2 \, T_c^2/P_c \tag{8.1}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{9}$$

$$b = 0.0778 \, RT_c/P_c \tag{10}$$

is widely used for thermodynamic property calculations.

While there has been extensive activity in the development of new and more accurate empirical cubic equations of state, there has been little attention to the fact that the van der Waals mixing rules are used

erroneously in these equations, eqs (2) and (3). In other words, for the extension of applicability of a cubic equation of state it is not generally correct to use eqs (2) and (3.1) as the mixing rules without attention to the algebraic form of the equation of state. In the present paper we introduce a new concept for the development of mixing rules for cubic equations of state in the spirit of the van der Waals mixing rules. This concept is based on statistical-mechanical arguments and the fact that the van der Waals mixing rules are for constants of an equation of state and not for any thermodynamic state function which may appear in an equation of state. The resulting mixing rules for the Redlich–Kwong equation of state, which is a simple modification of the van der Waals equation of state, and for the Peng–Robinson equation of state, which is an advanced modification of the van der Waals equation of state, are tested through prediction of solubility of heavy solids in supercritical fluids.

THEORY OF THE VAN DER WAALS MIXING RULES

Leland and co-workers (1968a, b, 1969) were able to re-derive the van der Waals mixing rules with the use of statistical-mechanical theory of radial distribution functions. According to these investigators, for a fluid mixture with a pair intermolecular potential energy function between molecules of the mixture in the form

$$u_{ij}(r) = \varepsilon_{ij} f(r/\sigma_{ij}) \tag{11}$$

the following mixing rules will be derived:

$$\sigma^3 = \sum_i^n \sum_i^n x_i x_j \sigma_{ij}^3 \tag{12}$$

$$\varepsilon\sigma^3 = \sum_i^n \sum_i^n x_i x_j \varepsilon_{ij} \sigma_{ij}^3. \tag{13}$$

In these equations, ε_{ij} is the interaction energy parameter between molecules i and j and σ_{ij} is the intermolecular interaction distance between the two molecules. Coefficients a and b of the van der Waals equation of state are proportional to ε and σ according to the following expressions:

$$a = 1.1250 RT_c v_c \propto N_o \varepsilon\sigma^3 \tag{14}$$

$$b = 0.3333 v_c \propto N_o \sigma^3. \tag{15}$$

We can see that eqs (12) and (13) are identical with eqs [2] and [3], respectively. Statistical-mechanical arguments used in deriving eqs (12) and (13) dictate the following guidelines in using the van der Waals mixing rules:

(1) The van der Waals mixing rules are for constants of an equation of state.
(2) Equation (12) is a mixing rule for the molecular volume, and eq. (13) is a mixing rule for (molecular volume) × (molecular energy). It happens that b and a of the van der Waals equation of state are proportional to molecular volume and (molecular volume) × (molecular energy), respectively, and, as a result, these mixing rules are used in the form which was originally proposed by van der Waals.

(3) Knowing that σ_{ij} (for $i \neq j$), the unlike-interaction diameter, for spherical molecules, is equal to

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2. \tag{16}$$

This gives the following expression for b_{ij} of spherical molecules:

$$b_{ij} = [(b_{ii}^{1/3} + b_{jj}^{1/3})/2]^3. \tag{17}$$

Then for non-spherical molecules the expression for b_{ij} will be

$$b_{ij} = (1 - l_{ij})[(b_{ii}^{1/3} + b_{jj}^{1/3})]^3. \tag{18}$$

With the use of these guidelines, we now derive the van der Waals mixing rules for the two representative equations of state. A similar procedure can be used for deriving the van der Waals mixing rules for other equations of state.

Mixing rules for the Redlich–Kwong equation of state

The Redlich–Kwong equation of state, eq. (6), can be written in the following form:

$$Z = \frac{PV}{RT} = \frac{v}{v-b} - \frac{a}{RT^{1.5}(v+b)}. \tag{19}$$

In this equation of state, b has the dimension of a molar volume,

$$b = 0.26 v_c \propto N_o \sigma^3.$$

Then the mixing rule for b will be the same as that for the first van der Waals mixing rule, eq. (3). However, the mixing rule for a will be different from the second van der Waals mixing rule. Parameter a appearing in the Redlich–Kwong equation of state has the dimensions of $R^{-1/2}$ (molecular energy)$^{3/2}$ (molecular volume), that is,

$$a = 1.2828 RT_c^{1.5} v_c \propto N_o (\varepsilon/k)^{1.5} \sigma^3.$$

As a result, the second van der Waals mixing rule, eq. (13), cannot be used directly for the a parameter of the Redlich–Kwong equation of state. However, since $(R^{1/2}ab^{1/2})$ has the dimensions of (molecular energy) × (molecular volume), the second van der Waals mixing rule, eq. (13), can be written for this term. Finally, the van der Waals mixing rules for the Redlich–Kwong equation of state will be in the following form:

$$a = \left\{ \sum_i^n \sum_j^n x_i x_j a_{ij}^{2/3} b_{ij}^{1/3} \right\}^{1.5} \Big/ \left(\sum_i^n \sum_j^n x_i x_j b_{ij} \right)^{1/2} \tag{20}$$

$$b = \sum_i^n \sum_j^n x_i x_j b_{ij}. \tag{3}$$

These mixing rules, when combined with the Redlich–Kwong equation of state, will constitute the Redlich–Kwong equation of state for mixtures, consistent with the statistical-mechanical basis of the van der Waals mixing rules.

Mixing rules for the Peng–Robinson equation of state

In order to separate thermodynamic variables from

constants of the Peng–Robinson equation of state, we will insert eqs (8) and (9) into eq. (7) and we will write it in the following form:

$$Z = \frac{v}{v-b} - \frac{a/RT + d - 2\sqrt{(ad/RT)}}{(v+b) + (b/v)(v-b)} \quad (21)$$

where $a = a(T_c)(1+\kappa)^2$ and $d = a(T_c)\kappa^2/RT_c$.

This form of the Peng–Robinson equation of state suggests that there exist three independent constants in this equation of state: a, b and d. Now, following the prescribed guidelines for the van der Waals mixing rules, the mixing rules for a, b and d of the Peng–Robinson equation of state will be

$$a = \sum_i^n \sum_j^n x_i x_j a_{ij} \quad (22)$$

$$b = \sum_i^n \sum_j^n x_i x_j b_{ij} \quad (23)$$

$$d = \sum_i^n \sum_j^n x_i x_j d_{ij} \quad (24)$$

with the following interaction parameters:

$$a_{ij} = (1 - k_{ij})(a_{ii}a_{jj})^{1/2} \quad (25)$$

$$b_{ij} = (1 - l_{ij})\{(b_{ii}^{1/3} + b_{jj}^{1/3})/2\}^3 \quad (26)$$

$$d_{ij} = (1 - m_{ij})\{(d_{ii}^{1/3} + d_{jj}^{1/3})/2\}^3. \quad (27)$$

These mixing rules, when joined with the Peng–Robinson equation of state, eq. (7), will constitute the Peng–Robinson equation of state of a mixture, consistent with the statistical-mechanical basis of the van der Waals mixing rules.

APPLICATION FOR SUPERCRITICAL FLUID EXTRACTION MODELLING

A serious test of mixture equations of state is shown to be their application for the prediction of solubility of heavy solutes in supercritical fluids (Mansoori and Ely, 1985). In the present paper, we apply the van der Waals, the Redlich–Kwong and the Peng–Robinson equations of state for supercritical fluid extraction of solids and study the effect of choosing different mixing rules for predicting the solubility of solids in supercritical fluids.

The solubility of a condensed phase, y_2, in a vapour phase at supercritical conditions can be defined as:

$$y_2 = (P_2^{sat}/P)(1/\phi_2)\phi_2^{sat}\exp\left\{\int_{P_2^{sat}}^P (v_2^{solid}/RT)dP\right\} \quad (28)$$

where ϕ_2^{sat} is the fugacity coefficient of the condensed phase at the saturation pressure P_2^{sat}, and ϕ_2 is the vapour phase fugacity at pressure P. Provided we assume that v_2^{solid} is independent of pressure, the above expression is converted to the following form:

$$y_2 = (P_2^{sat}/P)(1/\phi_2)\exp\{v_2^{solid}(P - P_2^{sat})/RT\}. \quad (29)$$

In order to calculate solubility from eq. (29), we need to choose an expression for the fugacity coefficient. Generally, for calculation of a fugacity coefficient an equation of state with appropriate mixing rules is used in the following expression (Prausnitz, 1969):

$$RT \ln \phi_i = \int_V^\infty [(\partial P/\delta n_i)_{T,V,n_{j,i}} - (RT/V)]dV$$
$$- RT \ln Z \quad (30)$$

where $Z = Pv/RT$.

In the case of the van der Waals equation of state, eq. (1), with eqs (2) and (3) as the mixing rules, the following expression for the fugacity coefficient of a solute in a supercritical gas will be derived:

$$\phi_i = RT/(v-b)(1/P)\exp\{(-b + 2\Sigma x_j b_{ij})/(v-b)$$
$$- 2\Sigma x_j a_{ij}/vRT\}. \quad (31)$$

For the Redlich–Kwong equation of state, with eqs (2) and (3) as its mixing rules (as customary in the literature), the following expression for the fugacity coefficient is obtained:

$$\ln \phi_i = \ln(v/(v-b)) + (2\Sigma x_j b_{ij} - b)/(v-b) - \ln Z$$
$$+ a((2\Sigma x_j b_{ij} - b)/(b^2 RT^{1.5}))(\ln((v+b)/v)$$
$$- b/(v+b)) - ((2\Sigma x_j a_{ij})/(bRT^{1.5}))$$
$$\times \ln((v+b)/v). \quad (32)$$

Now with the use of the correct version of the van der Waals mixing rules, eqs (3) and (20), in the Redlich–Kwong equation of state, the fugacity coefficient will assume the following form:

$$\ln \phi_i = \ln(v/(v-b)) + (2\Sigma x_j b_{ij} - b)/(v-b) - \ln Z$$
$$+ (a(2\Sigma x_j b_{ij} - b)/(b^2 RT^{1.5}))(\ln((v+b)/v)$$
$$- b/(v+b)) - ((3\alpha^{1/2}(\Sigma x_j a_{ij}^{2/3} b_{ij}^{1/3})/b^{1/2}$$
$$- \alpha^{2/3}(\Sigma x_j b_{ij})/b^{3/2})/(bRT^{1.5}))$$
$$\times \ln((v+b)/v) \quad (33)$$

where

$$\alpha = \sum_i^n \sum_j^n x_i x_j a_{ij}^{2/3} b_{ij}^{1/3}.$$

The fugacity coefficient based on the Peng–Robinson equation of state with eqs (2) and (3) as the mixing rules (as usually derived) has the following form (Kurnik et al., 1981):

$$\ln \phi_i = ((2\Sigma x_j b_{ij} - b)/b)(Z-1) - \ln(Z - B)$$
$$- (A/2\sqrt{2}B)(2\Sigma x_j a_{ij}/a - (2\Sigma x_j b_{ij} - b)/b)$$
$$\times \{\ln((Z + 2\sqrt{2}B)/(Z - 2\sqrt{2}B))\} \quad (34)$$

where $A = aP/R^2T^2$ and $B = bP/RT$.

With the use of the correct version of the van der Waals mixing rules, eqs (22)–(24), in the Peng–Robinson equation of state, the following expression

for the fugacity coefficient is derived:

$$\ln \phi_i = ((2\Sigma x_j b_{ij} - b)/b)(Z - 1) - \ln(Z - B)$$
$$- (A/(2\sqrt{2}B))((2\Sigma x_j a_{ij} + 2RT\Sigma x_j d_{ij}$$
$$- 2\sqrt{(RT)}(a\Sigma x_j d_{ij}$$
$$+ d\Sigma x_i a_{ij})/\sqrt{(ad)})/a^* - (2\Sigma x_j b_{ij} - b)/b)$$
$$\times (\ln((Z + (1 + \sqrt{2})B)/(Z - (1 - \sqrt{2})B)))$$

(35)

where

$$a^* = a + RTd - 2\sqrt{(adRT)}$$
$$A = a^* P/(RT)$$
$$B = bRT/(RT).$$

We now utilize the above expressions for fugacities in order to predict the solubility of solids in supercritical gases at different temperatures and pressures, and compare the results with the experimental data.

RESULTS AND DISCUSSION

In Fig. 1, the solubility of 2, 3-dimethyl naphthalene (DMN) in supercritical carbon dioxide is plotted vs. pressure at 308 K along with predictions obtained from the van der Waals equation of state. According to

this figure, predictions by the van der Waals equation of state will improve when eq. (3), along with the combining rule, eq. (17), is used as the mixing rule for b instead of eq. (3.1) as customarily used. This comparison, and similar comparisons reported elsewhere (Mansoori and Ely, 1985) for other solute–solvent systems, establish the superiority of the double-summation mixing rule, eq. (3), for b over the single-summation expression, eq. (3.1).

In Fig. 2, the same experimental solubility data as in Fig. 1 are compared with predictions using the Redlich–Kwong equation of state. According to this figure, the corrected van der Waals mixing rules for the Redlich–Kwong equation of state, eqs (3) and (20), are clearly superior to the mixing rules which are customarily used, eqs (2) and (3.1), for this equation of state. Similar observations are made for the prediction of solubilities of other solids in supercritical fluids, which are not reported here.

The Peng–Robinson equation of state with its customary mixing rules, eqs (2) and (3), is widely used for predicting the solubility of heavy solutes in supercritical gases and for petroleum reservoir fluid-phase equilibrium calculations (Firoozabadi et al., 1978; Katz and Firoozabadi, 1978; Kurnik et al., 1981). In Fig. 3 the same experimental solubility data as in Figs 1 and 2 are compared with the predictions using the Peng–Robinson equation of state with its original mixing rules and with its corrected van der Waals mixing rules. According to this figure, the corrected
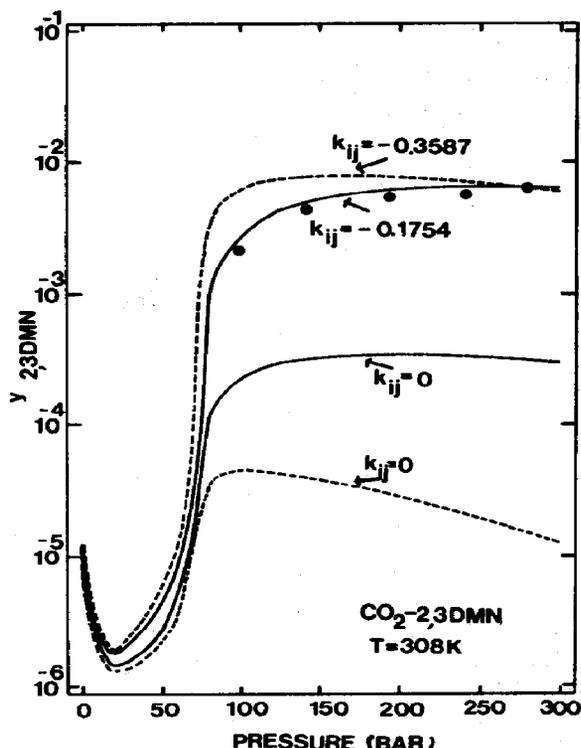

Fig. 1. Solubility of 2, 3-dimethyl naphthalene (DMN) in supercritical carbon dioxide at 308 K vs. pressure. The solid dots are the experimental data (Kurnik et al., 1981). The dashed lines are the results of the van der Waals equation of state with eqs (2) and (3.1) as the mixing rules. The solids lines are results of the van der Waals equation of state with eqs (2) and (3) as the mixing rules and eqs (4) and (17) as the combining rules.
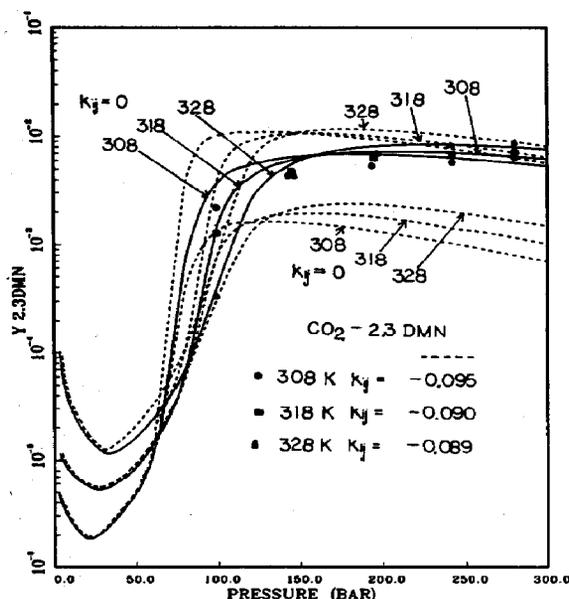
Fig. 2. Solubility of 2, 3-dimethyl naphthalene (DMN) in supercritical carbon dioxide at 308, 318 and 328 K vs. pressure. The solid dots are the experimental data (Kurnik et al., 1981). The dashed lines are the results of the Redlich–Kwong equation of state with eqs (2) and (3.1) as the mixing rules. The solid lines are the results of the Redlich–Kwong equation of state with eqs (3) and (20) as the mixing rules and eqs (4) and (17) as the combining rules.

van der Waals mixing rules of the Peng–Robinson equation of state apparently do not improve solubility predictions over the original mixing rules. However, variation of solubility vs. pressure for the new mixing rules is more consistent with the experimental data than the old mixing rules. Also considering the fact that the new mixing rules for the Peng–Robinson equation of state contain three adjustable parameters (k_{ij}, l_{ij} and m_{ij}) whereas the old mixing rules contain only two adjustable parameters (k_{ij} and l_{ij}) makes the new mixing rules more attractive. A demonstration of the superiority of the new mixing rules for the Peng–Robinson equation of state is shown here in Figs 4–9. According to these figures, when the unlike-interaction adjustable parameters of the mixing rules are fitted to the experimental data, the Peng–Robinson equation of state with the corrected van der Waals mixing rules can predict solubility of heavy solids in supercritical fluid more accurately than with the original mixing rules over different ranges of temperature and pressure and for different solutes and supercritical solvents.

Fig. 4. Solubility of 2, 3-dimethyl naphthalene (DMN) in supercritical carbon dioxide as calculated by the Peng–Robinson equation of state using eqs (2) and (3) as the mixing rules and compared with the experimental data.
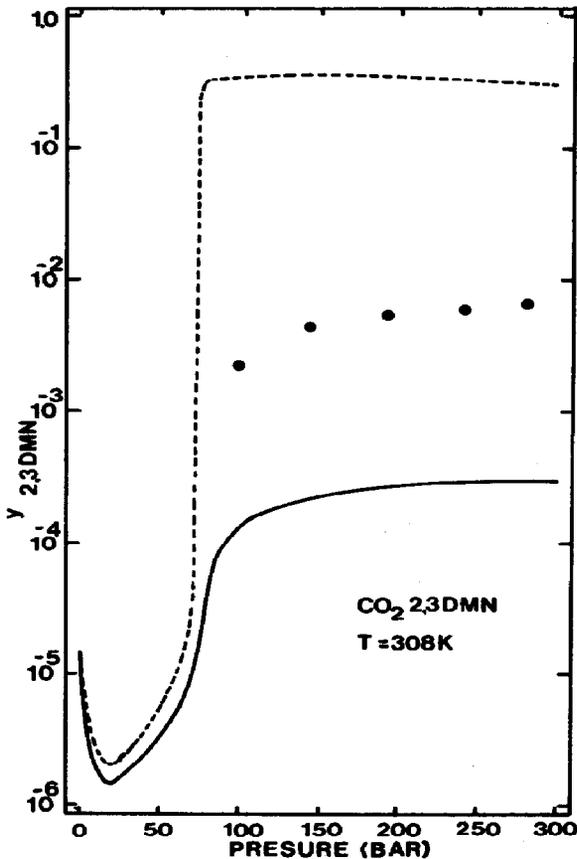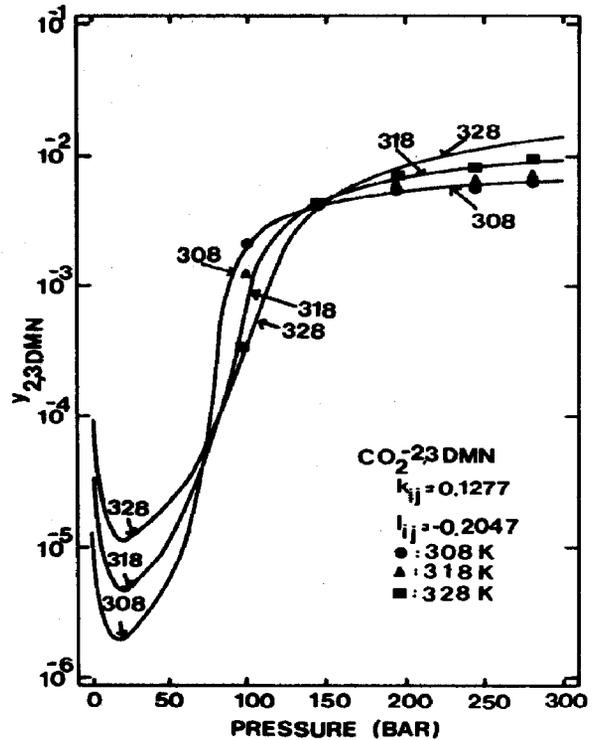

Fig. 3. Solubility of 2, 3-dimethyl naphthalene (DMN) in supercritical carbon dioxide at 308 K vs. pressure. The dashed lines are the results of the Peng–Robinson equation of state with eqs (2) and (3) as the mixing rules. The solid lines are the results of the Peng–Robinson equation of state with eqs (3) and (20) as the mixing rules. Both sets of lines are for $k_{ij} = 0$.
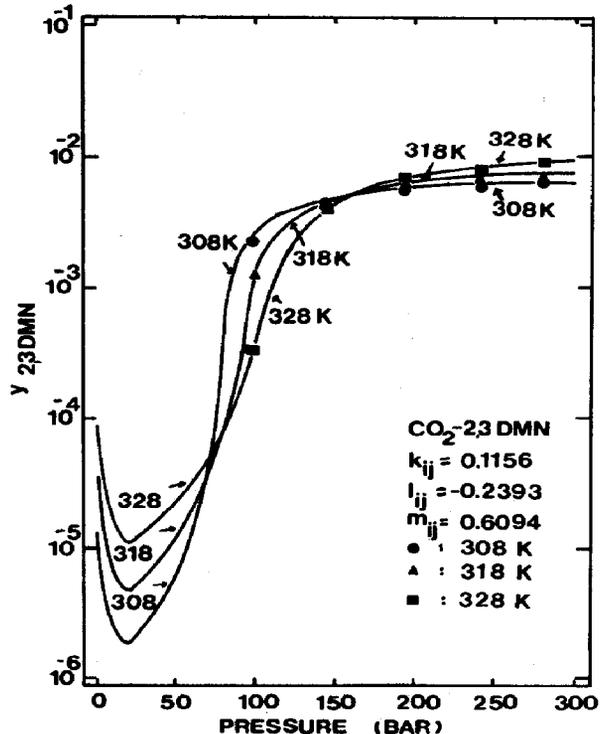

Fig. 5. Solubility of 2, 3-dimethyl naphthalene (DMN) in carbon dioxide as calculated by the Peng–Robinson equation of state with eqs (22)–(24) as the mixing rules and compared with the experimental data.
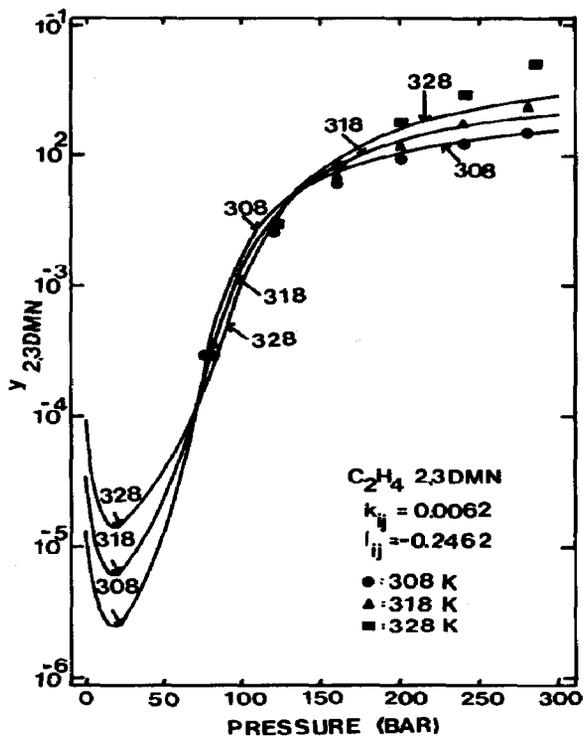
Fig. 6. Solubility of 2, 3-dimethyl naphthalene (DMN) in supercritical ethylene as calculated by the Peng–Robinson equation of state with eqs (2) and (3) as the mixing rules and compared with the experimental data.
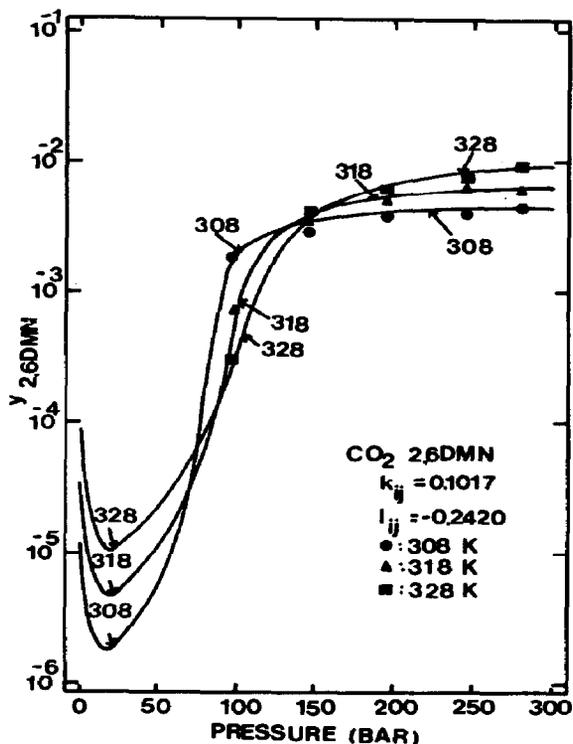

Fig. 8. Solubility of 2, 6-dimethyl naphthalene (DMN) in carbon dioxide as calculated by the Peng–Robinson equation of state with eqs (2) and (3) as the mixing rules and compared with the experimental data.
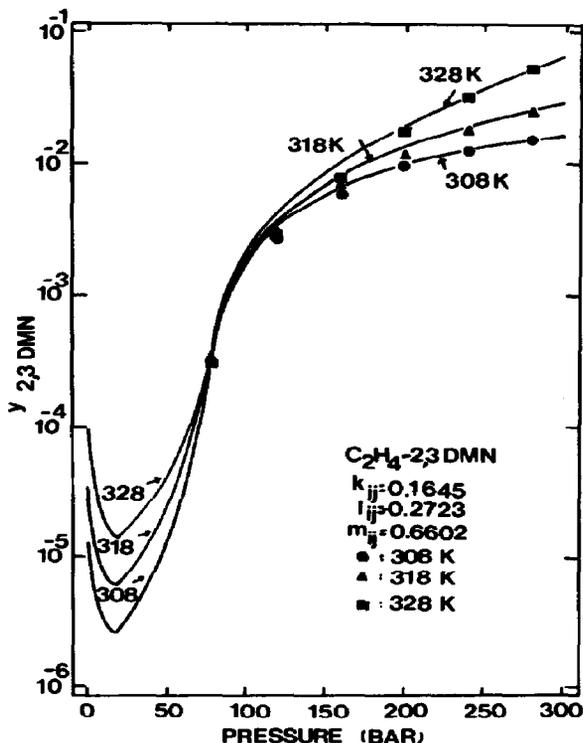

Fig. 7. Solubility of 2, 3-dimethyl naphthalene in supercritical ethylene as calculated by the Peng–Robinson equation of state with eqs (22)–(24) as the mixing rules and compared with the experimental data.
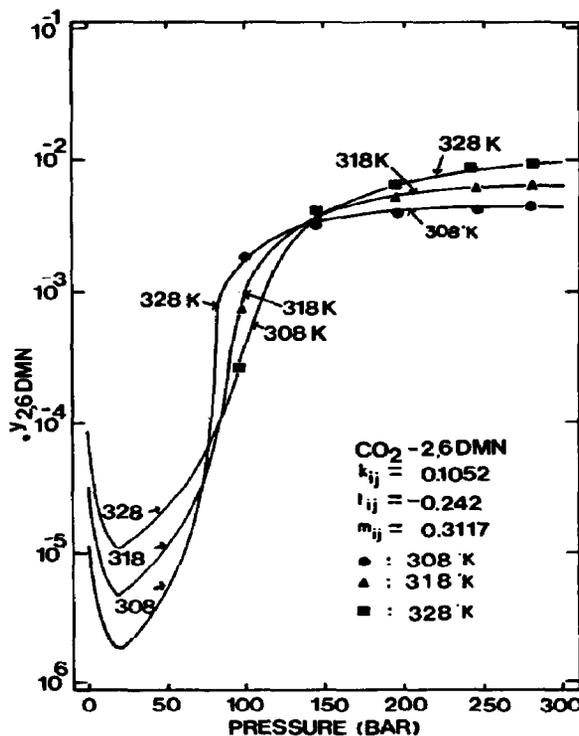

Fig. 9. Solubility of 2, 6-dimethyl naphthalene (DMN) in supercritical carbon dioxide as calculated by the Peng–Robinson equation of state with eqs (22)–(24) as the mixing rules and compared with the experimental data.

NOTATION

A, B	Variable in the Peng–Robinson equation of state
a, b	parameter in the equation of state
d	parameter in the Peng–Robinson equation of state
k_{ij}	binary interaction parameter
l_{ij}	binary interaction parameters in the Peng–Robinson equation of state
m_{ij}	binary interaction parameters in the Peng–Robinson equation of state
N_o	Avogadro's number
P	pressure, Bar
R	universal gas constant
T	temperature, K
u	intermolecular potential energy function
v	molar volume, cm^3/mol
y	gas phase mole fraction
Z	compressibility factor

Greek letters

ε	interaction energy parameter
ω	acentric factor
ϕ	fugacity coefficient
σ	intermolecular length parameter

Subscripts

i, j	component identifiers
2	solute
c	critical property

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