Evaluation of attraction terms in equations of state on the prediction of solubility of some biomolecules in supercritical carbon dioxide

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Abstract

In the present work, effect of the attraction terms of four recently modified Peng–Robinson equations of state on the prediction of solubility of caffeine, cholesterol, uracil and erythromycin was studied. The attraction terms of two of these equations are linear relative to the acentric factor and for the other two are exponential. It is found that the later show less deviation. Also interaction parameters for the studied systems are obtained and the percentage of average absolute relative deviation (%AARD) in each calculation is displayed.

Keywords: Equation of state; Solubility; Supercritical carbon dioxide; Biomolecules

Supercritical extraction is an increasingly important technology because it allows the substitution of non-toxic, environmentally safe solvents such as carbon dioxide for traditional liquid solvents such as methylene chloride and hexane [1].

Over the last few decades, the solubilities of different solutes in supercritical fluids have been measured extensively [2–5]. However, solubility data of solids and their mixtures in supercritical fluid are limited and the accurate measurement of the solid solubility in supercritical fluid is also difficult and time consuming thus there is considerable interest in mathematical models that can accurately predict the phase behavior of such systems; equations of state in combination with mixing rules are currently the most widely models used for the calculation of solubility of component in supercritical fluid [6]. Some of the works done in this area are: Escobedo-Alvarado et al. [1], Higashi et al. [3] and Housaindokht and Bozorgmehr [7].

In the present work, effect of the attraction terms of four recently modified Peng–Robinson equations of state on the prediction of solubility of caffeine, cholesterol, uracil and erythromycin were studied. They are modified Peng–Robinson equation of state by Danesh et al. (MPR1) [8] and Gasem et al. (MPR2, MPR3 and MPR4) [9]. The attraction terms of MPR1 and MPR2 is linear relative to the acentric factor and for the MPR3 and MPR4 are exponential. It is

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Abbreviation: MPR, modified Peng–Robinson.

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Nomenclature

T absolute temperature

Greek symbols
α equation of state parameter
ω acentric factor

Subscript
r   reduced state variable

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found that the later show less deviation. Also interaction parameters for the studied systems are obtained and the percentage of average absolute relative deviation (%AARD) in each calculation is displayed.

1. Theory and calculation

The solubility of solids in SCF is given by:

$$y = \frac{P^{\text{sub}}\exp[V_S(P - P^{\text{sub}}/RT)]}{\phi^{\text{SCF}}P} \tag{1}$$

In Eq. (1), ϕ^{SCF} is the fugacity coefficient of solute in supercritical phase and can be calculated using an Equation of state by the thermodynamic relationship [6]. The attraction terms of the equations of state used in this study are given in Appendix A.

In the mixing rules, interaction parameters are adjusted to maximize the agreement between the equation of state calculations and experimental data. Optimum interaction parameters were obtained by minimizing the following fitness function:

$$\%\text{AARD} = \frac{100}{N}\sum_{i}^{N}\frac{\left|y_{\text{exp}} - y_{\text{calc}}\right|}{y_{\text{exp}}} \tag{2}$$

where N is the number of experimental data. Values of required physical properties of all compounds used are displayed in Table 1.

2. Results and discussion

In this study it is intended to show the comparison among MPR1 till MPR4 equations of state in predicting the solubility of caffeine, cholesterol, uracil and erythromycin in supercritical carbon dioxide (Fig. 1). The experimental data adopted from Huang et al. [10] and Burgos-Solórzano et al. [11].

To study the behavior of the equation of state over a wide range of temperature and pressure the Joule–Thomson (JT) inversion curves are among the best criteria [12]. Recently Haghighi et al. stated that exponential form of attraction term of the equation of state gave better prediction of the high temperature branch of the JT inversion curve

Table 1
Required physical properties of all compound used (refs. [10] and [11]).

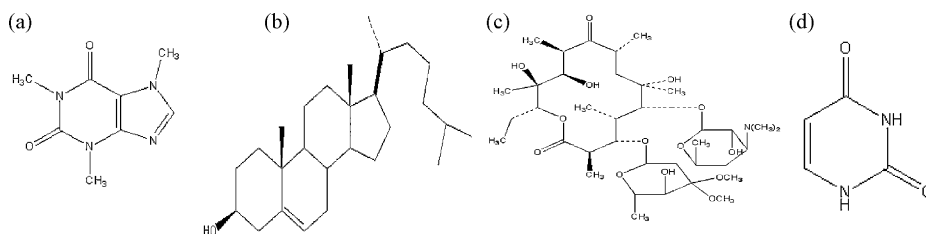| Compound	T_C (K)	P_C (bar)	ω	V_S (cm^3/mol)	P^{sub} (bar, $T = 313.15$ K)
Carbon dioxide	304.2	73.76	0.225	–	–
Caffeine	855.6	41.5	0.555	145.7	3.7×10^{-9}
Cholesterol	1168.23	41.55	0.950	371.56	3.1×10^{-7}
Erythromycin	1577.3	65	−0.510	608	2.9×10^{-22}
Uracil	991.3	68.5	0.596	688	1.3×10^{-11}

Fig. 1. Solutes studied: (a) caffeine, (b) cholesterol, (c) erythromycin, and (d) uracil.

Table 2
Regressed interaction parameters between CO_2 and solute ($T = 313.15$ K).

EOS compound	MPR1		MPR2		MPR3		MPR4	
	k_{12}	%AARD	k_{12}	%AARD	k_{12}	%AARD	k_{12}	%AARD
Caffeine	−0.3895	28.80	−0.4341	26.20	−0.4340	25.80	−0.4355	25.80
Cholesterol	0.5346	7.20	0.4921	8.01	0.4972	6.98	0.4929	8.12
Erythromycin	0.0743	59.30	−0.0337	62.80	−0.0339	63.40	−0.0490	63.30
Uracil	−0.1024	38.30	−0.1752	36.90	−0.1643	36.60	−0.1679	36.70

[13,14]. However, the Peng–Robinson is commonly used for modeling the solubility of polar and non-polar solutes in supercritical fluids [15]. Thus among many equations of state that are nowadays available we have selected the two modified Peng–Robinson equations of state with exponential attraction terms and for comparison we have selected two modified Peng–Robinson equations of state with linear attraction term relative to the acentric factor.

Optimum values of k_{12} (interaction parameter) for different CO_2–solutes systems are shown in Table 2. An examination of Table 2 indicates that the %AARD varies from 6.98 to 63.40. It has been found from the table that overall %AARD for MPR3 is less than other equations. The calculated solubility of each solute from equations of state with optimum interaction parameters as a function of pressure in supercritical CO_2 is shown in Figs. 2–5.

The solubility of caffeine, cholesterol and uracil in supercritical carbon dioxide, predicted by MPR1 till MPR4 equations, and compared with the experimental data are shown in Figs. 2–4, respectively. According to this figure, all equations of state are in good agreement with experimental data.

The solubility of erythromycin in supercritical carbon dioxide, predicted by MPR1 till MPR4 equations, and compared with the experimental data is shown in Fig. 5. According to this figure, the equations of state model fail in this case. The poor prediction is realized through two factors: first, inaccuracy of physical properties of pure components such as critical properties and molar volume, for example, at 40 MPa and 310 K, an 11% error in the solid
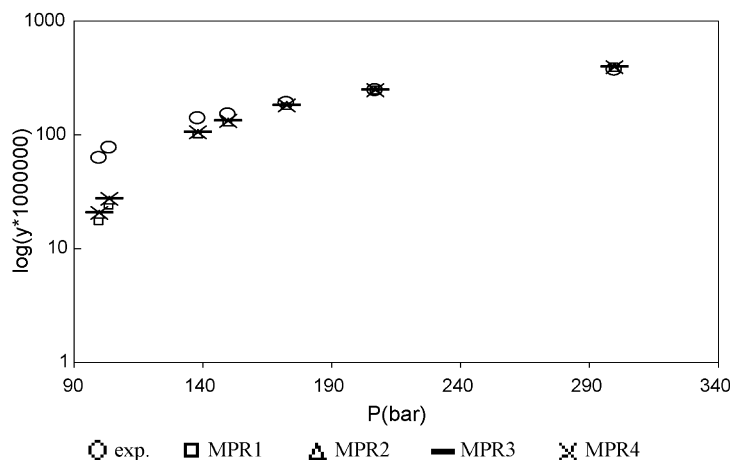
Fig. 2. Solubility of caffeine in supercritical CO_2 as a function of pressure CO_2 as a function of pressure.
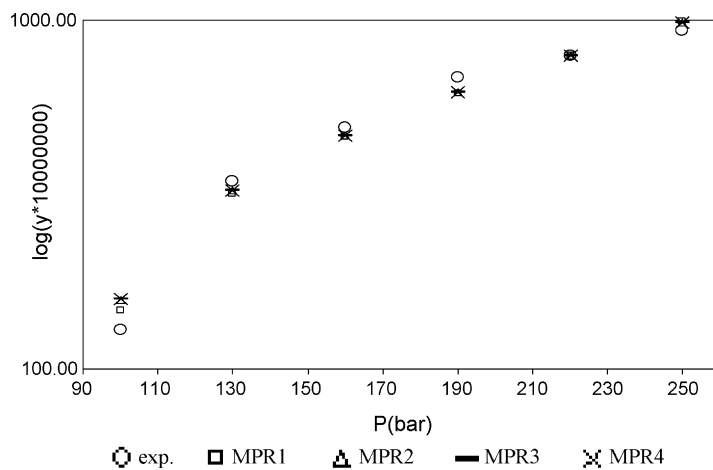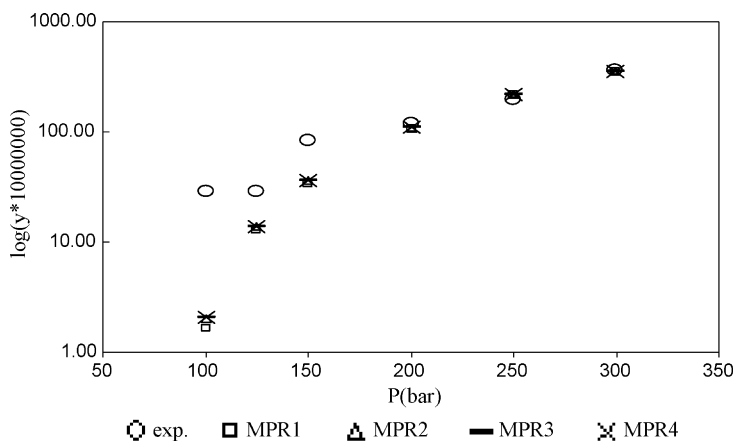
Fig. 3. Same as Fig. 1 for cholesterol.

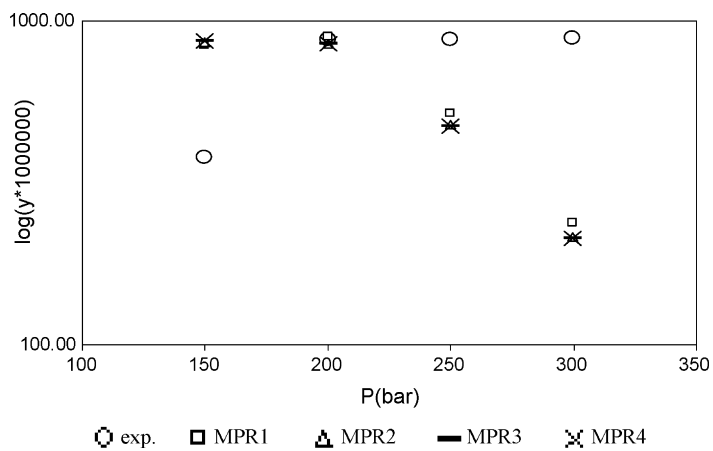Fig. 4. Same as Fig. 1 for uracil.

Fig. 5. Same as Fig. 1 for erythromycin.

molar volume of naphthalene would correspond to a 21% error in extraction percentage (14); and second, highly asymmetric in size of Erythromycin and carbon dioxide.

The results depicted in Figs. 2–5 show that deviation usually occurs at the vicinity of critical region because thermodynamic states of fluid and fluid mixtures near critical points are characterized by the presence of long-range fluctuations in the concentration, for example, calculation of the specific heat capacity from an equation of state may produce large error [16].

3. Conclusion

In the present study, we have provided a comparison among four modified Peng–Robinson equations of state. A conclusion central to our study is seems that the equations of state with exponential form of attraction term have less deviation in predicting solubility of components used in this study in supercritical carbon dioxide than those equations of state have linear form of attraction term.

Appendix A

The alpha functions for MPR1–MPR4 EOS are:

$$\alpha(T_r) = [1 + 1.21(0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3)(1 - \sqrt{T_r})^2 \tag{3}$$

$$\alpha(T_r) = (1 + (0.37464 + 1.54230\omega - 0.26992\omega^2)(1 - T_r^{0.5}))^2 \tag{4}$$

$$\alpha(T_r) = T_r^{-0.792615}\exp(0.401219(1 - T_r^{-0.99262})) + \omega\left(\begin{array}{c} T_r^{-1.98471}\exp(0.02496(1 - T_r^{-9.98471})) \\ -T_r^{-0.792615}\exp(0.401219(1 - T_r^{-0.99262})) \end{array}\right) \tag{5}$$

$$\alpha(T_r) = \exp((2.00 + 0.836T_r)(1 - T_r^{0.134+0.508\omega-0.0467\omega^2})) \tag{6}$$

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