Solubility Prediction of Some Disperse Azo Dyes in Supercritical Carbon Dioxide using Equation of States (EOSs)

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Abstract

The solubility of three disperse azo dyes, 4-(N,N-dimethylamino)-4'-itroazobenzene (D_1), 4-(N,N-diethylamino)-4'-nitroazobenzene (D_2) and Parared (D_3) in supercritical carbon dioxide have been correlated with two equations of state. All critical properties have been estimated with a group contribution method (GCM). As far we know, solubility data for these dyes have never been correlated using an equation of state (EOS). Therefore, it is worthwhile to model the solubility of these disperse Azo dyes. In this work, the aim is correlating reported data with a new (M-factor) EOS and comparing obtained results with the results of Peng-Robinson EOS (PR-EOS) together with two adjustable parameter van der Waals mixing and combining rules. The calculated results showed that M-factor EOS is more accurate than PR-EOS. It can be employed to speed up the process of supercritical fluid (SCF) applications in industry.

Keywords: Solubility; disperse azo dyes; supercritical carbon dioxide; correlation; equation of state (EOS).

1. Introduction

In the past decades, there has been an increasing interest in the use of supercritical fluids as an alternative to the use of organic solvents in many industrial applications, such as in chemical and biochemical reactions, extraction and purification processes, particle production, textile industry, etc. (Teja et al, 2000, Jafari Nejad et al, 2010a, 2010b, 2010c, Jung et al, 2001, Cooper et al, 2003, Kazarian et al, 2000, Kikic et al, 2003).

Supercritical carbon dioxide is the most commonly used supercritical fluid. The critical temperature and pressure of carbon dioxide is relatively low (304 K and 73.7 bar, respectively) (Jafari Nejad et al, 2009) and one of the most environmentally acceptable solvents in use today, and textile processes using this solvent have many advantages when compared to conventional aqueous processes (Fasihi et al, 2004). Supercritical carbon dioxide gives an option avoiding water discharge, it is low in cost, nontoxic, and nonflammable, and the carbon dioxide can be recycled. Also, when dying from an aqueous medium, reduction clearing is carried out to stabilize the color intensity, producing further water waste. Reduction clearing is not carried out following supercritical dyeing. Supercritical carbon dioxide also has other advantages. The application of the dye to the fabric can be controlled and a better quality of application achieved (Saus et al, 1995, Clifford et al, 1996). The dyes used in supercritical dyeing are the nonionic, so-called disperse dyes.

To develop and design the supercritical fluid dyeing (SFD) process a lot of basic dye solubility data and modeling of these solubility data are necessary. Disperse Dyes for dyeing polyester textile is divided into two groups: Azo and anthraquinone derivatives (Bae et al, 1996, Haarhaus et al, 1995, Joung et al, 1998).

In the mathematical modeling of solubility data in supercritical fluids, one should keep in mind that the solubility systems can be categorized in three groups, a single solute in a supercritical fluid, mixed solutes in a supercritical fluid and a single solute in mixed supercritical fluids or supercritical fluid plus an organic solvent. Different equations have been presented for mathematical modeling of solubility data in SC CO_2. One can categorize these models into two groups, theoretical or semi-empirical equations (similar to models based on equations of state) and empirical equations (such as density based equations). Models derived from equations of state need complicated computational procedures that are not provided in commonly used commercial software. Also, these models employ the solute properties, such as critical properties, acentric factor, molar volumes and vapor pressure, which often cannot be easily determined experimentally. The numerical values of the solute properties can affect solubility predictions using models derived from equations of state [2]. To avoid some of these difficulties as well as more complicated computational routines, most authors opt to use empirical correlations such as density-based correlations (Chrastil, Bartle, M´endez-Santiago–Teja, Jafari Nejad et al. and etc. models), or the Ziger–Eckert semi-empirical correlation. These models are based on simple error minimization using least-squares methods, and for the majority of them, there is no need to estimate and use critical and thermophysical properties of the involved solutes (Jafari Nejad et al, 2009, 2010).

In this study, solubilites of three disperse Azo dyes, 4-(N,N-dimethylamino)-4'-nitroazobenzene (D_1), 4-(N,N-diethylamino)-4'-nitroazobenzene (D_2) and Parared (D_3) (Fasihi et al, 2004) in supercritical carbon dioxide have been correlated with two equation of state; Peng-Robinson EOS (PR-EOS) together with two adjustable parameter van der Waals mixing and combining rules and new (M-factor) EOS (Jafari Nejad et al, 2009). As far we know, solubility data for these dyes never has been correlated using an

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equation of state (EOS). Therefore, it is worthwhile to model the solubility of these disperse Azo dyes.

2. Theory

The use of different models to correlate the solubility data was investigated using models based on a cubic EOS (Peng–Robinson (PR-EOS); together with two adjustable parameter van der Waals (vdW) mixing and combining rules and a new equation of state (EOS).

2.1. Peng–Robinson equation of state (PR-EOS)

The solubility of a solute (y_2) at equilibrium with a fluid, at high pressures, can be calculated using the following expression:

$$y_2 = \frac{P_2^{sat}}{P}\frac{1}{\phi_2^{SCF}}\exp\left[\frac{\upsilon_2(P - P_2^{sat})}{RT}\right] \tag{1}$$

Here, P_2^{sat} is the saturation pressure of the solute, υ_2 the molar volume of the solute and φ_2^{SCF} is the fugacity coefficient of the solute in the fluid phase, which expresses the non-ideality of the fluid phase. The fugacity coefficient can be calculated with an equation of state. In this work, the Peng–Robinson EOS (Eqs. (2) – (5)), here defined for pure substances, were used:

$$P = \frac{RT}{\upsilon - b} - \frac{a}{\upsilon(\upsilon + b) + b(\upsilon - b)} \tag{2}$$

$$a = 0.45724\left(\frac{R^2 T_c^2}{P_c}\right)\left\{1 + n\left[1 - \left(\frac{T}{T_c}\right)^{0.5}\right]\right\}^2 \tag{3}$$

$$n = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{4}$$

$$b = 0.07780\frac{RT_c}{P_c} \tag{5}$$

To use the above EOS for a binary mixture, we employed the classical van der Waals (vdW) mixing and combining rules, with two adjustable parameters, k_{ij} and l_{ij} (vdW2):

$$a = \sum_i\sum_j y_i y_j (a_i a_j)^{0.5}(1 - k_{ij}) \tag{6}$$

$$b = \sum_i\sum_j y_i y_j \left(\frac{b_i + b_j}{2}\right)(1 - l_{ij}) \tag{7}$$

The binary interaction parameters, k_{ij} and l_{ij}, are obtained by fitting experimental data, through the minimization of an objective function (Robinson et al, 1976, Coimbra et al, 2005).

Using the conventional mixing rules for a mixture, the fugacity coefficient for component h in a mixture is given by (Prausnitz et al, 1999):

$$Ln\phi_h = \frac{b_k}{b}\left(\frac{P\upsilon}{RT} - 1\right) - Ln\frac{P(\upsilon - b)}{RT}$$
$$- \frac{a}{2\sqrt{2}bRT}\left[\frac{2\sum_i y_i a_{ih}}{a} - \frac{b_h}{b}\right]Ln\frac{\upsilon + (1 + \sqrt{2})b}{\upsilon + (1 - \sqrt{2})b} \tag{8}$$

Where, y_i is the mole fraction of component i.

The individual absolute relative deviations (IARD) of calculated solubilities from observed values are used as an accuracy criterion to compare the calculated solubilities with experimental values. IARD was calculated by:

$$IARD(\%) = 100\left(\frac{|y_2^{cal} - y_2^{exp}|}{y_2^{exp}}\right) \tag{9}$$

The average-absolute-relative-deviation (AARD) defines as:

$$AARD(\%) = \frac{100}{N}\sum\frac{|y_2^{cal} - y_2^{exp}|}{y_2^{exp}} \tag{10}$$

In this equation, N is the number of experimental data points, y_2^{cal} and y_2^{exp} are calculated solubilities and experimental solubility, respectively.

2.2. Theory of new (M-factor) equation of state

The virial EOS was originally introduced by Kammerligh-Onnes as of ascending power of density to represent the compressibility factor. Later on, Ursell and Mayer (1957) developed the statistical mechanic for virial equation, which is formally presented as a series expansion of either the radial distribution function or the grand canonical partition function for low-density gases. The virial coefficients are related to the intermolecular potential energy so that B is linked through rigorous relations to the so-called pair potential energy function, which is responsible for many thermodynamic and transport properties of fluid (Vetere, 1999), C is related to the energy of interaction between triples of molecules, and so forth. The Leiden virial equation of state gives the compressibility factor as a power series in the reciprocal molar volume:

$$Z = \frac{P\upsilon}{RT} = 1 + \frac{B}{\upsilon} + \frac{C}{\upsilon^2} + \frac{D}{\upsilon^3} + \dots \tag{11}$$

The mathematically analogous power series in the pressure can be derived from Eq.11 and is known as the Berlin virial EOS:

$$Z = \frac{P\upsilon}{RT} = 1 + B'P + C'P^2 + D'P^3 + \dots \tag{12}$$

The molar volume in Eq.12 was explicitly obtained and then substituted into Eq.11. Hence two set of coefficients in Eq.11 and Eq.12 are related as below:

$$B' \approx \frac{B}{RT} \quad C' \approx \frac{C - B^2}{(RT)^2} \quad D' \approx \frac{D - 3BC + 2B^3}{(RT)^3}$$
$$E' \approx (RT)^4\left(\frac{E - 5B^4 - 2C^2 - 4BD}{(RT)^4} + 10B^2 C\right) \tag{13}$$

Because the C, D, E and higher virial coefficients are responsible for molecular interactions, thus these are generically dependent on binary interactions. From Eq.13,

it is intelligible that whatever the molecular interaction effects become more intense, the second virial coefficient takes higher order of magnitude. For example, C' and D' are proportional to second and third power of B. Mathematically, there are the same terms of B/RT in all of the above relations. Also, much less have been known the third and fourth virial coefficients than the second virial coefficient though data of third coefficient for certain gases can be found in literature (Johnston et al, 1934, Nicola et al, 2005). Besides, it is feasible that effects of all terms in Eq.13, except B-included, be reconsidered by means of several temperature dependent coefficients. For these reasons, in Eq.13, when the third, fourth and higher order virial coefficients be nonce ignored, Eq.13 diminishes to

$$B^{'} = \frac{B}{RT}, \quad C^{'} = \alpha(T)\left(\frac{B}{RT}\right)^2,$$
$$D^{'} = \beta(T)(\frac{B}{RT})^3, \quad E^{'} = \gamma(T)\left(\frac{B}{RT}\right)^4 \quad (14)$$

Since the third, fourth and higher order virial coefficients depend only on temperature; several coefficients were inserted behind the relations of Eq.14 to estimate considerable effects of eliminated virial coefficients. These coefficients only have temperature dependency and would make up effects of C, D… which had been removed at previous step. Substituting $B^{'}, C^{'}, D^{'}, E^{'}, \ldots$ from Eq.14 into Eq.12 gives

$$Z = 1 + \frac{BP}{RT} + \alpha(T)\left(\frac{BP}{RT}\right)^2 + \beta(T)\left(\frac{BP}{RT}\right)^3 + \gamma(T)\left(\frac{BP}{RT}\right)^4 + .. \quad (15)$$

Eq.15 may be written as

$$Z = 1 + [\frac{BP_c}{RT_c}]\frac{P_r}{T_r} + \alpha(T)[\frac{BP_c}{RT_c}]^2(\frac{P_r}{T_r})^2 + \beta(T)[\frac{BP_c}{RT_c}]^3(\frac{P_r}{T_r})^3$$
$$+ \gamma(T)[\frac{BP_c}{RT_c}]^4(\frac{P_r}{T_r})^4 + \ldots \quad (16)$$

Pitzer and Curl (1957) proposed a correlation, which expresses the quantity $\frac{BP_c}{RT_c}$ as

$$\frac{BP_c}{RT_c} = f^{(0)}[T_r] + \omega f^{(1)}[T_r] \quad (17)$$

The function $f^{(0)}$ gives the reduced second virial coefficients for simple fluids ($\omega = 0$) while $f^{(1)}$ is a correction function which, when multiplied by ω gives the effect of eccentricity on the second virail coefficient. The two functions $f^{(0)}$ and $f^{(1)}$ were determined from experimental data and modified by Tsonapaulos (1975). Meng et al. (2004) presented a modified corresponding correlation that compares well with experimental data for the second virial coefficient for most non-polar pure compounds, since the predictions have been corrected for most physics effects such as adsorption. Detailed comparisons with the well-known Tsonopoulos correlation

showed that the model is somewhat better than Tsonopoulos correlation for non-polar substances. The correlation for non-polar fluids is:

$$f^{(0)}[T_r] = 0.13356 - \frac{0.30252}{T_r} - \frac{0.15668}{T_r^2} - \frac{0.00724}{T_r^3}$$
$$- \frac{0.00022}{T_r^8} \quad (18)$$

$$f^{(1)}[T_r] = 0.17404 - \frac{0.15581}{T_r} + \frac{0.38183}{T_r^2} - \frac{0.44044}{T_r^3}$$
$$- \frac{0.00541}{T_r^8} \quad (19)$$

For slightly polar substances it is better to utilize Tsonopoulos correlation. Also for polar substances, the second virial coefficient may be calculated from Janecek et al. (2003) correlation or Pires et al. (2001) correlation. For mixtures, the mixing second virial coefficient can be usually predicted with the help of mixing rules. The binary second virial coefficient, for example, is given by:

$$B_m = \sum_i \sum_j y_i y_j (1 - S_{ij}) B_{ij} \quad (20)$$

Where S_{ij} is interaction parameter, is obtained by fitting experimental data, through the minimization of an objective function. For the first time Mohebbi and Mohammadikhah (2007) have represented a new EOS based on the virial equation including M-factor, reduced temperature and reduced pressure. The dimensionless form of M-factor is:

$$M = \left[\frac{BP_c}{RT_c}\right]\left(\frac{P_r}{T_r}\right) = \frac{BP}{RT} \quad (21)$$

With substituting Eq.21 into Eq.15 we get

$$Z = 1 + M + \alpha(T)M^2 + \beta(T)M^3 + \gamma(T)M^4 + \ldots \quad (22)$$

As a consequence, this equation explains that the compressibility factor of each substance just depends on M-factor and temperature. Though M-factor is a compound parameter but can be assumed as a novel parameter with different properties than its composer parameters such as T_r or P_r. Thus the compressibility factor can be written as:

$$Z = Z(M, T_r) \quad (23)$$

From Eq. 22, the modified form can be rewritten as:

$$Z = f^1(T_r) + f^2(T_r)M + f^3(T_r)M^2 + f^4(T_r)M^3 \quad (24)$$

The reason of election third order polynomial versus M is the fitting of this equation all the experimental data with $R^2 > 0.99$ (Mohebbi et al, 2007, Jafari Nejad et al 2009). Mohammadikhah, Abolghasemi and Jafari Nejad (2009) have developed this EOS for prediction of solute solubility in supercritical carbon dioxide. The coefficients of Eq. 24 are (for $T_r < 1.1$, in this work):

$$f^1(T_r) = 1 \quad (25)$$

$$f^2(T_r) = 1 \tag{26}$$

$$f^3(T_r) = 75.36T_r^2 - 157.7T_r + 82.86 \tag{27}$$

$$f^4(T_r) = \left| \frac{0.05038T_r + 0.0001896}{T_r^3 - 2.508T_r^2 + 2.098T_r - 0.5845} \right| \tag{28}$$

Where these coefficients are for $M \geq -0.39312T_r^3 + 0.0252T_r^2 - 0.001235$, and for $M < -0.39312T_r^3 + 0.0232T_r^2 - 0.001235$, these coefficients become:

$$f^1(T_r) = \frac{0.6592T_r^2 - 0.7257T_r + 0.208}{T_r^2 - 2.4T_r + 2.607} \times 0.95 \tag{29}$$

$$f^2(T_r) = \frac{729.5T_r^2 - 2499T_r + 821.8}{T_r^2 - 1836T_r + 4545} \times 0.95 \tag{30}$$

$$f^3(T_r) = 0 \tag{31}$$

$$f^4(T_r) = 0 \tag{32}$$

The fugacity coefficient of component i in the fluid mixture is:

$$Ln\hat{\phi}_i = \int_0^P \frac{(\overline{Z_i} - 1)}{P} dP \tag{33}$$

$$P = \frac{MRT}{B} \Rightarrow dP = \frac{RT}{B} dM \tag{34}$$

$$Ln\hat{\phi}_i = \int_0^M \frac{(\overline{Z_i} - 1)}{M} dM \tag{35}$$

The Eq.25 is a multi-domain equation, thus:

$$Ln\hat{\phi}_i = \int_0^{M_1} \frac{(\overline{Z_i} - 1)}{M} dM + \int_{M_1}^M \frac{(\overline{Z_i} - 1)}{M} dM$$
$$= (Ln\hat{\phi}_i)_1 + (Ln\hat{\phi}_i)_2 \tag{36}$$

$$M_1 = -0.39312T_r'^3 + 0.0252T_r'^2 - 0.001235 \tag{37}$$

$$T_r' = T_r(1 - S_{ij}) \tag{38}$$

The expression for φ_2 is (Jafari Nejad et al, 2009):

$$Ln\hat{\phi}_2 = (Ln\hat{\phi}_2)_1 + (Ln\hat{\phi}_2)_2 = (f^1 - 1)Ln(\frac{M}{M_1})$$
$$+ \frac{f^2}{B}(M - M_1)\frac{\partial nB}{\partial n_2} + \frac{1}{B}\frac{\partial nB}{\partial n_2}M_1 + \frac{f^3}{2B^2}\frac{\partial nB}{\partial n_2}M_1^2 \tag{39}$$
$$+ \frac{f^4}{3B^3}\frac{\partial nB^3}{\partial n_2}M_1^3$$

Thus the solubility of a liquid solute at equilibrium with a fluid, at high pressures, can be calculated using the Eq.1.

3. Material and Methods

The structures of the selected disperse azo dyes and their physicochemical properties are given in Table 1. Fasihi et al. (2004) carry out the solubility measurements of these disperse azo dyes at temperatures 308, 318, 328, 338, 348 and 358 K over a pressure range from 122 to 355 bar. The experimental results are listed in Table 2 in terms of equilibrium mole fraction, y. In order to compare the accuracy of the new correlation with the PR-EOS, it is assumed that all the experimental data are correct. The solubility of D_2 is greater than that of D_1 and D_3 by a factor of about 7 and 20, respectively. The addition of one CH_2-group to D_2 molecule, results in a significant solubility enhancement of D_2 in comparison with D_1 (Fasihi et al, 2004). Similar results have been reported in the literature (Draper et al, 2000).

It should be noted that in this study the program of calculations were written in MATLAB Software by the authors.

Table 1. Structure of dyes and their physicochemical properties (Fasihi et al, 2004)

Dyes	Structure	Melting point (K)	M_w (g/mole)
D_1		488-489	270.12
D_2		418-419	298.14
D_3		529-530	293.13
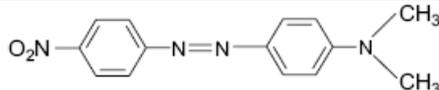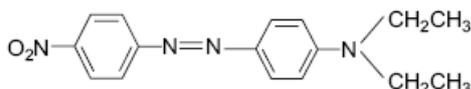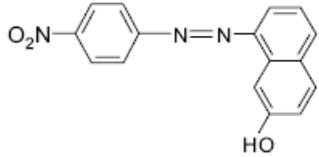
Table 2. Correlation and experimental (Fasihi et al, 2004) results of solubilities of three disperse azo dyes, D_1, D_2 and D_3 in SC-CO$_2$ at various temperatures and pressures.

Conditions		D_1		D_2		Conditions		D_3	
T (K)	P (bar)	$10^6 y$	$10^6 y^{Cal}$	$10^5 y$	$10^5 y^{Cal}$	T (K)	P (bar)	$10^6 y$	$10^6 y^{Cal}$
308	122	2.93	2.9307	0.98	0.97830	328	122	0.32	0.3197
	152	2.74	2.7407	1.12	1.1178		152	0.48	0.4802
	182	2.61	2.6070	1.51	1.5121		182	0.78	0.7800
	213	2.93	2.9267	1.76	1.7566		213	1.16	1.1585
	243	3.61	3.6102	2.11	2.1145		243	1.45	1.4525
	274	3.83	3.8355	2.36	2.3602		274	1.73	1.7237
	304	3.81	3.8077	2.6	2.5929		304	2.06	2.0676
	334	4.62	4.6215	2.91	2.9205		334	2.46	2.4681
	355	4.84	4.8328	3.16	3.1703		355	2.75	2.7542
318	122	1.46	1.4613	0.8	0.8012	338	122	0.44	0.4401
	152	2.12	2.1224	1.25	1.2478		152	0.5	0.5011
	182	2.83	2.8299	1.66	1.6570		182	0.75	0.7491
	213	3.5	3.5034	1.97	1.9705		213	1.43	1.4321
	243	4.21	4.2041	2.73	2.7291		243	1.77	1.7735
	274	4.2	4.2001	2.88	2.8796		274	2.43	2.4371
	304	4.74	4.7470	2.93	2.9303		304	3.08	3.0791
	334	5.07	5.0600	4.09	4.0863		334	3.51	3.5152
	355	6.23	6.2183	4.36	4.3528		355	3.95	3.9551
328	122	2	2.0015	0.51	0.5104	348	122	-	-
	152	2.05	2.0484	0.85	0.8501		152	0.41	0.4092
	182	2.89	2.8923	1.41	1.4091		182	1.06	1.0623
	213	4.23	4.2346	2.22	2.2231		213	1.25	1.2506
	243	4.61	4.6104	2.93	2.9293		243	1.95	1.9537
	274	5.37	5.3625	3.26	3.2532		274	2.9	2.8964
	304	7.06	7.0543	4.33	4.3199		304	3.5	3.4965
	334	8.27	8.2566	5.12	5.1292		334	4.35	4.3374
	355	9.85	9.8661	5.6	5.6115		355	5.16	5.1753
338	122	1.65	1.6490	0.28	0.2797	358	122	0.22	0.2201
	152	2.08	2.0807	0.79	0.7904		152	0.47	0.4698
	182	3.37	3.3697	1.48	1.4817		182	1.27	1.2696
	213	4.94	4.9429	2.36	2.3610		213	2.22	2.2249
	243	6.57	6.5664	3.9	3.8957		243	2.85	2.8429
	274	8.05	8.0484	4.77	4.7655		274	3.8	3.7971
	304	10.3	10.3021	6.23	6.2419		304	4.76	4.7709
	334	11.99	11.9983	7.46	7.4527		334	5.91	5.9237
	355	13.77	13.7641	8.55	8.5453		355	6.46	6.4405
348	122	1.59	1.5910	0.24	0.2400				
	152	2.03	2.0302	0.76	0.7593				
	182	3.71	3.7078	1.52	1.5190				
	213	6.22	6.2236	2.88	2.8847				
	243	8.01	8.0052	5.75	5.7411				
	274	9.78	9.7735	7.07	7.0802				
	304	12.62	12.6362	8.28	8.2726				
	334	15.22	15.2350	9.92	9.9255				
	355	18.37	18.3735	11.1	11.0985				

4. Result and discussion

For the application of the EOSs based models, it is necessary to have knowledge of the molar volume and saturation pressure of dyes, critical temperature, critical pressure and Pitzer's acentric factor of the solute and of solvent.

Saturation pressure of solute can be calculated with Reidel-Plank-Miller Method, critical properties estimated with group contribution method (GCM), Pitzer's acentric factor estimated using Lee-Kesler's Method (Joback et al, 1987, Reid et al, 1987). All estimated critical properties for D_1, D_2 and D_3 are listed in Table 3.

Results of calculated solubility corresponding to each experimental data are summarized in Table 2. The optimal fitted binary parameters and the respective AARD combined with the van der Waals mixing and combining rules, with two adjustable parameters (vdW2) and new EOS for D_1, D_2 and D_3 are presented in Table 4, Table 5 and Table 6, respectively. Good correlation results were obtained between the calculated and experimental solubility, to all fitted models. All fitted models were shown to be able to successfully correlate experimental solubility data. The AARD of new EOS is significantly lower than that obtained from PR-EOS. The mean

Table 3. Estimated critical and other thermo physical properties of D_2

Property	Value for D_1	Value for D_3	Value for D_3
T_c (K)	1148.49 [a]	1184.61 [a]	1322.78 [a]
P_c (bar)	21.0034 [a]	16.8241 [a]	25.5592 [a]
ω	0.92634 [b]	0.95803 [b]	1.18618 [b]
V_c (cm^3/mole)	703.5 [a]	815.5 [a]	685.5 [a]

[a] Estimated by Joback's Method (Joback et al, 1987, Reid et al, 1987)
[b] Estimated by Lee-Kesler's Method (Joback et al, 1987, Reid et al, 1987)

Table 4. Correlation results obtained with the PR-EOS and M-factor EOS for D_1: The binary interaction parameters, k_{ij} and l_{ij}, B_{ij} is virial coefficients, S_{ij} is interaction parameter, where 1 is CO_2 and 2 is D_1, The average-absolute-relative-deviation (AARD %).

T(K)	Peng-Robinson EOS			New EOS				
	k_{12}	l_{12}	AARD (%)	s_{12}	B_{11}	B_{22}	B_{12}	AARD (%)
308	0.368	0.183	27.30	-0.1352	-114.2769	-980646.544	-1959.457	0.074
318	0.327	0.146	18.74	-0.0968	-105.8903	-771714.101	-1771.305	0.109
328	0.293	0.120	23.00	-0.0584	-98.2619	-613250.216	-1613.052	0.099
338	0.277	0.105	31.20	-0.0202	-91.2953	-491918.569	-1478.365	0.040
348	0.199	0.097	17.93	0.0172	-84.9096	-398174.865	-1362.487	0.062

Table 5. Correlation results obtained with the PR-EOS and M-factor EOS for D_2: The binary interaction parameters, k_{ij} and l_{ij}, B_{ij} is virial coefficients, S_{ij} is interaction parameter, where 1 is CO_2 and 2 is D_2, The average-absolute-relative-deviation (AARD %).

T(K)	Peng-Robinson EOS			New EOS				
	k_{12}	l_{12}	AARD (%)	s_{12}	B_{11}	B_{22}	B_{12}	AARD (%)
308	0.427	0.201	37.00	-0.1326	-114.2769	-1647877.9	-2456.104	0.210
318	0.401	0.197	25.72	-0.0958	-105.8903	-1293977.5	-2212.230	0.093
328	0.389	0.183	17.93	-0.0584	-98.2619	-1025817.9	-2007.930	0.127
338	0.377	0.176	23.33	-0.0211	-91.2953	-820712.79	-1834.732	0.092
348	0.356	0.154	31.02	0.0156	-84.9096	-662430.36	-1686.281	0.084

Table 6. Correlation results obtained with the PR-EOS and M-factor EOS for D_3: The binary interaction parameters, k_{ij} and l_{ij}, B_{ij} is virial coefficients, S_{ij} is interaction parameter, where 1 is CO_2 and 2 is D_3, The average-absolute-relative-deviation (AARD %).

T(K)	Peng-Robinson EOS			New EOS				
	k_{12}	l_{12}	AARD (%)	s_{12}	B_{11}	B_{22}	B_{12}	AARD (%)
328	0.399	0.187	28.01	-0.0569	-98.2619	-2134017.6	-2092.757	0.184
338	0.387	0.174	31.29	-0.0234	-91.2953	-1695316.1	-1893.365	0.146
348	0.323	0.161	23.07	-0.0127	-84.9096	-1357802.4	-1724.621	0.181
358	0.301	0.143	15.86	0.0442	-79.0363	-1096007.8	-1580.315	0.160

differences between global AARD (= (AARD)/ (total number of data sets)) for the new EOS and PR-EOS are statistically significant. The global AARD values for these data sets are shown in Figure 1. The mean AARD for the new EOS is 0.12 %, which is significantly lower than that obtained from PR-EOS (25.10 %). The new EOS presented more accurate correlation for solubility data in supercritical CO_2. It can be employed to speed up the process of SCF applications in industry.

5. Conclusion

Solubility data of dyes in supercritical fluids (SCF) are crucial for designing supercritical fluid dying processes. In this study, solubilites of three disperse Azo dyes, 4-(N,N-dimethylamino)-4'-nitroazobenzene (D_1), 4-(N,N-diethylamino)-4'-nitroazobenzene (D_2) and Parared (D_3) in supercritical carbon dioxide have been correlated with two equation of state; PR-EOS together with two adjustable parameter van der Waals mixing and combining rules and M-factor EOS. The mean AARD for the M-factor EOS is

0.12 %, which is significantly lower than that obtained from PR-EOS (25.10 %). The M-factor EOS presented more accurate correlation for solubility data in supercritical CO_2. It can be employed to speed up the process of SCF applications in industry.
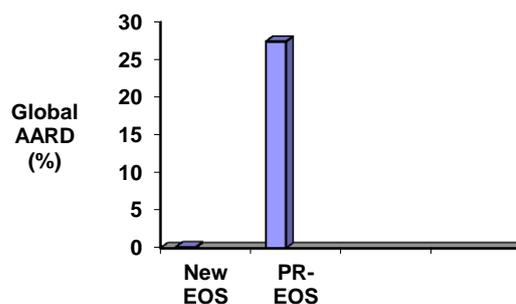
Figure.1. Mean (Global) AARD values for M-factor EOS and PR-EOS.

Nomenclature

List of symbols

α	energy parameter of the cubic equation of state ($N\ m^4\ mol^{-2}$)
AARD	average absolute relative deviation (%)
B	volume parameter in the PR EOS and in the SRK EOS ($m^3\ mol^{-1}$)
A,B,C,D,..	virial coefficients
$A^{'}, B^{'}, C^{'}$,	virial coefficients
EOS	equation of state
GCM	group contribution method
IARD	individual absolute relative deviations
k_{ij}	binary interaction parameter
l_{ij}	binary interaction parameter
M	M factor (BP/RT)
P	pressure (Pa)
PR	Peng–Robinson
R	ideal gas constant ($J\ mol^{-1}\ K^{-1}$)
S	Interaction parameter
SCF	supercritical fluids
T	temperature (K)
V	Volume
v	molar volume ($m^3\ mol^{-1}$)
vdW2	van der Waals mixing and combining rules with two adjustable parameters
y	mole fraction
Z	compressibility factor

Greek symbols

$\alpha(T), \beta(T), \gamma(T)$	Coefficients of Eq. (22)
ϕ	Fugacity coefficient
ρ	density of pure CO_2 (kgm^{-3})
ω	Pitzer's acentric factor

Subscripts

1	solvent
2	solute
c	critical property
i, j, h, p, k	components
m	mixture
r	reduced

Superscripts

cal	calculated
exp	experimental
SCF	supercritical phase
sat	saturation

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