

Modeling of Solubility of Disperse Blue Dyes in Supercritical carbon Dioxide Using Equation of States (EOSs)

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Abstract—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. The solubility of six blue dispersed dyes, C.I. Disperse Blue 134, C.I. Disperse Blue 79, C.I. Disperse Blue 79:1, C.I. Disperse Blue 3, C.I. Disperse Blue 60 and C.I. Disperse Blue 14 in supercritical carbon dioxide have been correlated with two equation of state. All critical properties have been estimated with a group contribution method (GCM). Solubility data for these dyes has never been correlated using an equation of state (EOS). Therefore, it is worthwhile to model the solubility of these dyes with EOSs. In this work, the aim is correlating reported data with a new 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 new EOS is more accurate than PR-EOS. It can be employed to speed up the process of SCF applications in industry.

Index Terms—Dispersed Blue Dye, Solubility, Supercritical Fluid, Equation of State (EOS), Modeling.

I. 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[1-12].

Since the dyeing industry uses water as a dyeing medium and a lot of dispersing agents and surfactants to overcome the inherent hydrophobicity of the textile and the dye, it discharges a lot of hard-to-destroy (very little biodegradable) wastewater. To reduce the environmental pollution problem, supercritical carbon dioxide is considered as a potential alternative dyeing medium to water as it is inherently nontoxic and does not require any dispersing agents and surfactants in the dyeing process. Furthermore, a lot of energy (roughly 50%) can be saved in the supercritical fluid dyeing (SFD) process, as it requires neither the washing step nor the drying step, whereas the conventional wet-dyeing process requires both steps [13-19].

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) [20] and one of the most environmentally acceptable solvents in use today, and textile processes using this solvent have many advantage when compared to conventional aqueous processes [21]. 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 dyeing 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 [22, 23]. 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 [24-26].

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 CO₂. 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 [27]. 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

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properties of the involved solutes [20, 27].

In this study, solubility of six disperse dyes: blue 134, blue 79, blue 79:1, blue 3, blue 60 and blue 14 [19, 28-32] in supercritical carbon dioxide have been correlated with two equation of states. All critical properties have been estimated with a group contribution method (GCM). Solubility data for these dyes has been correlated using an equation of state (EOS), namely Peng-Robinson EOS. Therefore, it is worthwhile to model the solubility of these diamines with a new accurate EOS. In this work, the aim is correlating reported data with a new 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.

II. THEORY

A. Peng-Robinson Equation of State (PR-EOS)

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

$$y_2 = \frac{P_2^{\text{sat}}}{P} \frac{1}{\phi_2^{\text{SCF}}} \exp \left[\frac{v_2(P - P_2^{\text{sat}})}{RT} \right] \quad (1)$$

Here, P_2^{sat} is the saturation pressure of the solute, v_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:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (2)$$

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

$$n = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (4)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (5)$$

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):

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

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

The binary interaction parameters, k_{ij} and l_{ij} , are obtained by fitting experimental data, through the minimization of an objective function [33, 34].

Using the conventional mixing rules for a mixture, the fugacity coefficient for component h in a mixture is given by [35]:

$$\begin{aligned} \ln \phi_h = & \frac{b_k}{b} \left(\frac{Pv}{RT} - 1 \right) - \ln \frac{P(v-b)}{RT} \\ & - \frac{a}{2\sqrt{2}bRT} \left[\frac{2 \sum_i y_i a_{ih}}{a} - \frac{b_h}{b} \right] \ln \frac{v + (1 + \sqrt{2})b}{v + (1 - \sqrt{2})b} \end{aligned} \quad (8)$$

where, y_i is the mole 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:

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

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

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

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

B. Theory of New (M-factor) Equation of state

The virial EOS was originally introduced by Kammerlign-Onnes as of ascending power of density to represent the compressibility factor. Later on, Ursell and Mayer [36] 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 [37], 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:

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots \quad (11)$$

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

$$Z = \frac{Pv}{RT} = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (12)$$

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:

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

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 [38, 39]. 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

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

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' , ... from Eq.14 into Eq.12 gives

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

Eq.15 may be written as

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

Pitzer and Curl [38] proposed a correlation, which expresses the quantity $\frac{BP_c}{RT_c}$ as

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

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 virial coefficient. The two functions $f^{(0)}$ and $f^{(1)}$ were determined from experimental data and modified by Tsonopoulos [40]. Meng et al. [41] 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:

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

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

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. [42] correlation or Pires et al. [43] 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 [44] 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

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

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 $R^2 > 0.99$ [20, 44]. Jafari Nejad, Abolghasemi and Mohammadikhah have developed this EOS for prediction of solute solubility in supercritical carbon dioxide [20]. The coefficients of Eq. 24 are (for $T_r < 1.1$, in this work):

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

$$f^2(T_r) = 1 \quad (26)$$

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

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

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:

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

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

$$f^3(T_r) = 0 \quad (31)$$

$$f^4(T_r) = 0 \quad (32)$$

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

$$\ln \hat{\phi}_i = \int_0^P \frac{(\bar{Z}_i - 1)}{P} dP \quad (33)$$

$$P = \frac{MRT}{B} \Rightarrow dP = \frac{RT}{B} dM \quad (34)$$

$$\ln \hat{\phi}_i = \int_0^M \frac{(\bar{Z}_i - 1)}{M} dM \quad (35)$$

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

$$\ln \hat{\phi}_i = \int_0^{M_1} \frac{(\bar{Z}_i - 1)}{M} dM + \int_{M_1}^M \frac{(\bar{Z}_i - 1)}{M} dM \quad (36)$$

$$= (\ln \hat{\phi}_i)_1 + (\ln \hat{\phi}_i)_2$$

$$M_1 = -0.39312 T_r^3 + 0.0252 T_r^2 - 0.001235 \quad (37)$$

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

The expression for ϕ_2 is [20]:

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

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

III. MATERIALS AND METHODS

The physicochemical and critical properties of the six disperse blue dyes are given in Table 1. The experimental results are from references [19, 28-32]. In order to compare the accuracy of the new correlation with the PR-EOS, it is assumed that all the experimental data are correct.

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

IV. RESULTS 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 [45, 46]. All estimated critical properties for six disperse dyes are listed in Table 1.

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 M-factor EOS for six blue dyes are presented in Table 2. S_{12} is interaction parameter, is obtained by fitting experimental data, through the minimization of an objective function. In this study, reported S_{12} in table 2 at defined temperature is average of calculated S_{12} in all pressures at this defined temperature. 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 M-factor EOS is significantly lower than that obtained from PR-EOS. The mean differences between global AARD (= (AARD)/(total number of data sets)) for the M-factor EOS and PR-EOS are statistically significant. The M-factor EOS presented more accurate correlation for solubility data in supercritical CO₂. It can be employed to speed up the process of SCF applications in industry.

TABLE 1. ESTIMATED CRITICAL AND OTHER THERMOPHYSICAL PROPERTIES OF BLUE DYES.

Property	Blue 3	Blue 14	Blue 60	Blue 79	Blue 79:1	Blue 134
T_c (K) ^a	1237.29	1143.8	1159.75	1982.6	2064.8	1221.24
P_c (bar) ^a	29.2184	27.1833	20.4931	10.6309	12.0395	19.1358
ω ^b	1.4985	1.1876	1.1775	0.7966	0.8574	1.2316
Mw (gr/mole)	296	266.30	321.369	639.42	625.39	322.4
V_c (cm ³ /mole) ^a	787.5	753.5	912.5	1500.5	1426.5	977.5

^a Estimated by Joback's Method [45, 46]

^b Estimated by Lee-Kesler's Method [45, 46]

TABLE 2. CORRELATION RESULTS OBTAINED WITH THE PR-EOS AND M-FACTOR EOS FOR DYES: THE BINARY INTERACTION PARAMETERS, K₁₂ AND L₁₂, B₁₂ IS VIRIAL COEFFICIENTS, S₁₂ IS INTERACTION PARAMETER, WHERE 1 IS CO₂ AND 2 IS DYE, THE AVERAGE-ABSOLUTE-RELATIVE-DEVIATION (AARD %).

Dye	T(K)	Peng-Robinson EOS			M-factor EOS				AARD (%)
		k ₁₂	l ₁₂	AARD (%)	s ₁₂	B ₁₁	B ₂₂	B ₁₂	
blue 14	313.15	0.324	0.236	17.09	-0.0096	-109.856	-818052.31	-1731.863	0.0948
	353.15	0.318	0.217	12.71	0.1265	-81.824	-337986.21	-1208.139	0.0422
	393.15	0.301	0.198	13.10	0.2498	-61.682	-159985.68	-908.745	0.0260
blue 60	313.15	0.347	0.262	5.81	-0.1381	-109.397	-1195257.9	-2143.296	0.1370
	333.15	0.337	0.249	19.09	-0.0373	-94.215	-753625.04	-1765.241	0.0961
	363.15	0.319	0.236	12.03	0.0329	-76.192	-407780.56	-1384.609	0.0706
	393.15	0.301	0.211	11.78	0.1403	-61.682	-234486.03	-1121.867	0.0403
	423.15	0.289	0.202	15.91	0.2535	-49.966	-143997.64	-932.436	0.0387
blue 3	323.7	0.401	0.303	7.99	-0.0256	-101.455	-1451525.0	-1956.190	0.1059
	353.7	0.376	0.299	13.76	0.0583	-81.503	-745272.00	-1471.909	0.0644
	383.7	0.361	0.274	21.01	0.1744	-65.909	-411003.59	-1160.699	0.0455
	413.7	0.352	0.238	19.81	0.2564	-53.405	-241699.83	-945.062	0.0489
blue 79:1	353.2	0.387	0.300	14.45	0.1047	-81.795	-95589025.4	-5971.140	0.2288
	373.2	0.359	0.283	10.93	0.1310	-70.962	-61735816.6	-4806.044	0.2876
	393.2	0.343	0.271	6.73	0.1701	-61.661	-40832690.8	-3979.277	0.2379
blue 79	353.2	0.412	0.341	17.74	0.0907	-81.795	-70173539.2	-5682.729	0.2075
	373.2	0.396	0.311	11.98	0.1237	-70.962	-45357383.3	-4614.215	0.2787
	393.2	0.378	0.283	13.13	0.1668	-61.661	-30029259.8	-3850.124	0.3042
blue 134	323.15	0.366	0.301	19.23	0.0487	-101.873	-1661379.77	-2314.173	0.1440
	353.15	0.348	0.293	10.99	0.1441	-81.824	-854916.79	-1756.567	0.0674
	383.15	0.337	0.278	16.92	0.2344	-66.164	-473127.422	-1396.048	0.0503

V. CONCLUSIONS

Solubility data of dyes in supercritical fluids (SCF) are crucial for designing supercritical fluid dyeing processes. In this study, solubilities of six disperse blue dyes, C.I. Disperse Blue 134, C.I. Disperse Blue 79, C.I. Disperse Blue 79:1, C.I. Disperse Blue 3, C.I. Disperse Blue 60 and C.I. Disperse Blue 14 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 which is significantly lower than that obtained from PR-EOS. The M-factor EOS presented more accurate correlation for solubility data in supercritical CO₂. It can be employed to speed up the process of SCF applications in industry.

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