

Calculation of solubility of three anthraquinone dyes in supercritical carbon dioxide: equations of state and density functional theory approaches

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ABSTRACT

Solubility of three Anthraquinone dyes in supercritical fluid has been calculated. For this purpose, the Peng-Robinson equations of state, the Modified Peng-Robinson equation of state by Gasem et al. and Dashtizadeh et al. equation of state have been applied. Error values of each equation of state in different conditions of temperature, mixing rule and estimating methods have been reported. The quantum mechanics density functional theory method along with 6-31G basis set was used and interaction energy between each of structures and supercritical carbon dioxide were calculated. Obtained interpretations from quantum calculations are consistent with the results from equations of state.

Keyword: Anthraquinone dye, density functional theory, solubility, group contribution method

INTRODUCTION

Supercritical carbon dioxide is utilized in extraction of dyes according to the following reasons: *I.* being tunable extraction with supercritical fluid, which means the amount of extraction is specified by temperature and pressure controls. On the other hand, solvent removal occurs by reducing the pressure. *II.* Up level of water consumption and its contamination are important problems in industries related to dye of different yarn. For example in 1987, 282.4 million cubic meters of water have been consumed including these industries in Germany [1-7], the use of supercritical fluid reduces the amount of water consumption and prevents from its pollution. *III.* Supercritical carbon dioxide is an appropriate eco friendly fluid. Creating supercritical state for carbon dioxide is more easily than the other supercritical solvents due to its low temperature and critical pressure. *IV.* Carbon dioxide will not damage solute material with respect to the relative low temperature and critical pressure [8-10].

Because of high cost of extraction with supercritical fluid, the optimum conditions for the extraction are typically measured with respect to temperature and pressure [11-15]. Activity coefficient model and equation of state model are usually used for calculations of the extraction process. It is characterized that in high temperature and pressure conditions the use of equations of state model is more appropriate [13]. Therefore, this model has been used in many cases in calculating the solubility in supercritical fluid. Another advantage of the equation of state model involves its being easier to use in mathematics that makes it more usable.

Equations of state are divided into three categories of theoretical, empirical and semi-empirical equations of state [16]. Theoretical equations of state are obtained from statistical thermodynamics and the radial distribution function. The main advantage of these equations is as follows. *I.* The equation parameters have physical meaning. *II.* They are usable for a wide range of materials, because they are obtained based on intermolecular potential. Nevertheless, their usages are usually with high errors. Empirical equations of state result from fitting of experimental data related to materials. The main advantage of these equations is high accuracy. However, their usage is less common by the following reasons. *I.* The parameters of these equations have no physical meaning *II.* The numbers of parameters in these equations are usually high, so its use is not easy. *III.* Usually, these equations are usable for a small range of materials. For the reasons discussed above, often the semi-empirical equations of state are used in thermodynamic modeling [17].

Semi-empirical equations of state are mainly in form of the generalized van der Waals equation. There are two phrases as repulsion and attraction in van der Waals equation. The basis for modification in semi-empirical equations of state is to associate repulsion and attraction terms with the physical parameters that usually their temperature dependence is considered [17]. However, in use of these equations of state, physical parameters of materials such as critical temperature, critical pressure and acentric factor are required for calculating the solubility of various compounds in supercritical fluid. Attraction and repulsion terms depend on mole fractions in applying these equations for mixtures [18, 19]. Dependency mode of these terms to mole fraction are called mixing rule.

The aim of this project is evaluating of effects of different factors in creating errors for calculating the solubility of several dyes in supercritical carbon dioxide. For this purpose, the effect of physical parameters, the effect of selected equation of state and effect of selected mixing rule on rate of calculations errors have been investigated. Also, the error rate resulted from experimental data uncertainty of compounds solubility has been assessed in supercritical fluid. Results of this study in selection of appropriate state equation can be used for calculating the solubility of other compounds in supercritical fluids. Ab initio quantum mechanic approach has been applied to explain obtained results.

MATERIALS AND METHODS

Putting to be equal the solute Fugacity in solid phase and its Fugacity in supercritical fluid is the basis of calculations for the compounds solubility in supercritical fluid [20, 21].

$$f_i^s = f_i^{SCF} \tag{1}$$

By considering an assumption that supercritical fluid can not be solved in solid, solute mole fraction in supercritical fluid is obtained as follows:

$$y = \frac{p^{sub} \exp \left[\frac{V_S (P - P^{sub})}{RT} \right]}{\phi^{SCF} P} \tag{2}$$

In this equation, P^{sub} , V_S and ϕ^{SCF} are sublimation vapor pressure, molar volume and Fugacity coefficient of solute in supercritical fluid, respectively. Fugacity coefficient is obtained from equation of state.

2.1 Solute selection

Anthraquinones are aromatic compounds that mainly counted as constructive materials of many dyes. Also, these ingredients are used as additives in paper industries. Selection of these materials has been done based on the availability of experimental values of their solubility in supercritical carbon dioxide at different temperatures and pressures [22-24]. Three anthraquinone compounds used in this study are: 1-hydroxy-9,10-anthraquinone (denoted as AQ1), 1-hydroxy-2-methyl-9,10-anthraquinone (denoted as AQ2) and 1-hydroxy-2-(methoxymethyl)-9,10-anthraquinone (denoted as AQ3).

2.2 Equation of state selection

A semi-empirical equation of state can be indicated as follows:

$$P = P^{repulsion} - P^{attraction} \tag{3}$$

In which repulsion and attraction terms are dependent on the size of molecules and intermolecular forces, respectively. The Peng-Robinson equation is a semi-empirical equation has been applied successfully in thermodynamic modeling. In this report, the Peng-Robinson equation of state (denoted as PR) with two modified equations of state, the modified Peng-Robinson by Gasem et al. (denoted as MPR) [25] and Dashtizadeh et al. equation of state [26] (denoted as PAZ) are taken into account to study the effects of equation of state on solubility calculations error in supercritical fluids. Attraction term of equation of state has been corrected in the Gasem et al. equation of state, while repulsion term in Dashtizadeh et al. equation of state has also been corrected. Modified effectiveness of attraction or repulsion terms can be determined by comparing the results obtained from these equations in calculating the solubility of compounds in supercritical fluid.

2.3 Choosing of the mixing rule

Dependence of attraction term and repulsion term on mole fraction of materials has also been included in creating mixing rules like equations of state. Accordingly, various mixing rules have been presented. Here, mixing rule of

first van der Waals type (denoted as Mix1) and second van der Waals type (Mix2) have been selected. These mixing rules in each of attraction and repulsion terms are considered as only one adjustable parameter, while in other mixing rules more than one adjustable parameter have been applied. Adjustable parameters are obtained from fitting of equation of state results with experimental values. Mixing rules selection of first and second van der Waals type was done to determine effectiveness of modified attraction term or modified repulsion term in calculating the solubility of compounds in supercritical fluid and to forbear from the improved contribution of results caused by fitting with the experimental data.

2.4 Solute physical parameters

Critical temperature, critical pressure, and acentric factor are needed for using equation of state. The values of these parameters for most compounds are not usually available experimentally. The Groups Contribution method should be used to estimate them. In this method, each contribution of constituent groups of molecular structure is applied in predicting physical properties. In this project, Joback estimating methods, Lydersen and Klincewicz methods have been used to calculate physical parameters of studied compounds.

2.4.1 Lydersen Method

This method belongs to the group Contribution methods, which is used in predicting of properties such as critical temperature, critical pressure and critical volume. In Lydersen method, the following equations are used for estimating these properties:

$$T_C = \frac{T_b}{0.567 + \sum G_i - (\sum G_i)^2} \quad (4)$$

$$P_C = \frac{M}{(0.34 + \sum G_i)^2} \quad (5)$$

In which, T_b is the normal boiling point, M represents as the molecular mass and G_i is the groups contribution in calculated property in the molecule. Lydersen advantage is its easy usage.

2.4.2 Klincewicz method

The group contribution and structural properties correlation of material are applied in this method to estimate physical parameters of substance. Following equations are used in Klincewicz method for estimating these properties:

$$T_C = 45.40 - 0.77 \times M + 1.55 \times T_b + \sum n_j \nabla_j \quad (6)$$

$$\left(\frac{M}{P_C}\right)^{1/2} = 0.335 + 0.010 \times M + \sum n_j \nabla_j \quad (7)$$

Where T_b is the boiling point, M represents as the molecular mass and A is the number of atoms. In Klincewicz method, less information is used to calculate the physical properties, which is the advantage of this method.

2.4.3 Joback method

This method is considered as the modified Lydersen method. Following equations are used in Joback method for estimating these properties:

$$T_b = 198 + \sum G_i \quad (8)$$

$$T_C = T_b [0.584 + 0.965 \sum G_i - (\sum G_i)^2]^{-1} \quad (9)$$

$$P_C = (0.113 + 0.0032 \times N_A - \sum G_i)^{-2} \quad (10)$$

Where T_b is the boiling point, M represents as the molecular mass and A is the number of atoms. More of the physical properties of material (such as enthalpy of formation, heat capacity and free energy of formation) can be calculated using Joback method which is the advantage of this method.

Acentric factor is also required in addition to critical temperature and pressure for using equations of state to calculate the solubility of compounds in the supercritical fluid. Acentric factor is considered as deviation of

molecule structure from spherical situation. Here, Lee-Kesler equation has been used to estimate this factor. In Lee-Kesler equation, critical temperature and pressure values are required to estimate acentric factor [27].

Values of critical temperature, critical pressure and acentric factor of studied compounds were calculated using PE software [28] according to the methods described above. The results have been reported in Table 1.

Table 1. The physical properties values estimated for studied compounds

Compound	Method								
	Lydersen			Klinswicez			Joback		
	$T_c(K)$	$P_c(bar)$	ω	$T_c(K)$	$P_c(bar)$	ω	$T_c(K)$	$P_c(bar)$	ω
AQ1	1121.5	27.1	0.745	1181.3	28.0	0.446	1134.1	36.3	0.819
AQ2	1126.0	24.7	0.879	1212.4	26.3	0.429	1153.5	30.9	0.815
AQ3	1176.8	17.0	0.747	1277.4	23.8	0.407	1197.5	28.1	0.913

The applied objective function to calculate the error is as follows:

$$\%AARD = \frac{100}{N} \sum_i \frac{|y^{CALC} - y^{EXP}|}{y^{EXP}} \tag{11}$$

3. Results and Discussion

Error percentage for each of used equations of state along with Mix1 mixing rule has been reported in calculating dyes solubility of AQ1, AQ2 and AQ3 at different temperatures as described in Figure 1. The Lydersen method has been used in generating figure to estimate the required physical parameters. According to the figure, error values of equations of state increases by increasing the temperature.

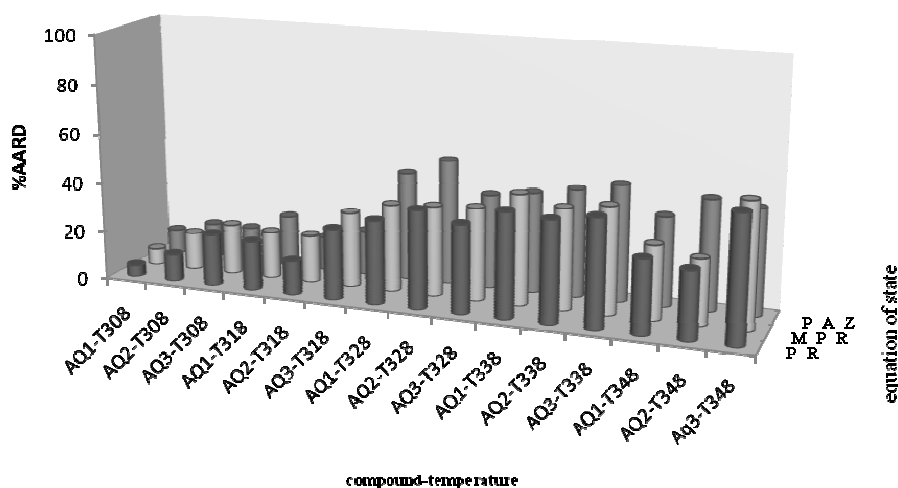


Fig. 1 the %AARD values for studied equation of state along with Mix1 mixing rule, the Lydersen estimation method and 308 K, 318K, 328K, 338K, 348K

Error percentage for each of used equations of state along with Mix2 mixing rule has been reported in calculating dyes solubility of AQ1, AQ2 and AQ3 at different temperatures as referenced in Figure 2. The Lydersen method has been used in generating figure to estimate the required physical parameters. According to the figure, error values of equations of state of MPR and PAZ have been decreased considerably that indicate these equations depend on the mixing rule significantly.

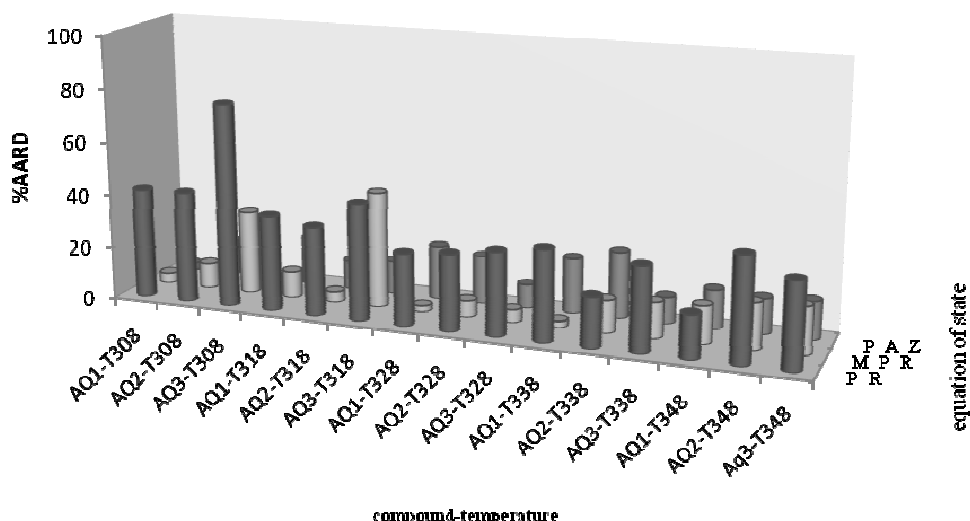


Fig. 2 the %AARD values for studied equation of state along with Mix2 mixing rule, the Lydersen estimation method and 308 K, 318K, 328K, 338K, 348K

Error percentage for each of used equations of state along with Mix1 mixing rule has been reported in calculating dyes solubility of AQ1, AQ2 and AQ3 at different temperatures as described in Figure 3. The Klincewicz method has been used in generating figure to estimate the required physical parameters. According to the figure, error values have been increased by increasing the temperature. On the other hand, error values of this figure are lower than of those in figure 2 and show that estimating method has an effective role in creating the error.

Error percentage for each of used equations of state along with Mix2 mixing rule has been reported in calculating dyes solubility of AQ1, AQ2 and AQ3 at different temperatures as referenced in Figure 4. The Klincewicz method has been used in generating figure to estimate the required physical parameters. According to the figure, error values of MPR and PAZ equations have been decreased compared to reported errors in figure 3 that indicate these equations have more dependency on mixing rule than PR state equation.

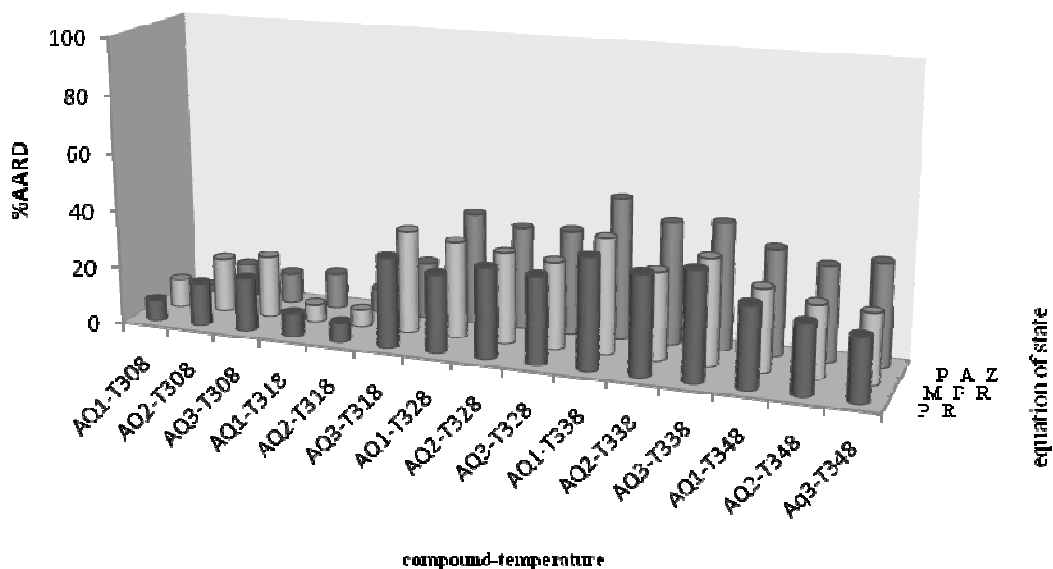


Fig. 3 the %AARD values for studied equation of state along with Mix1 mixing rule, the Klincewicz estimation method and 308 K, 318K, 328K, 338K, 348K

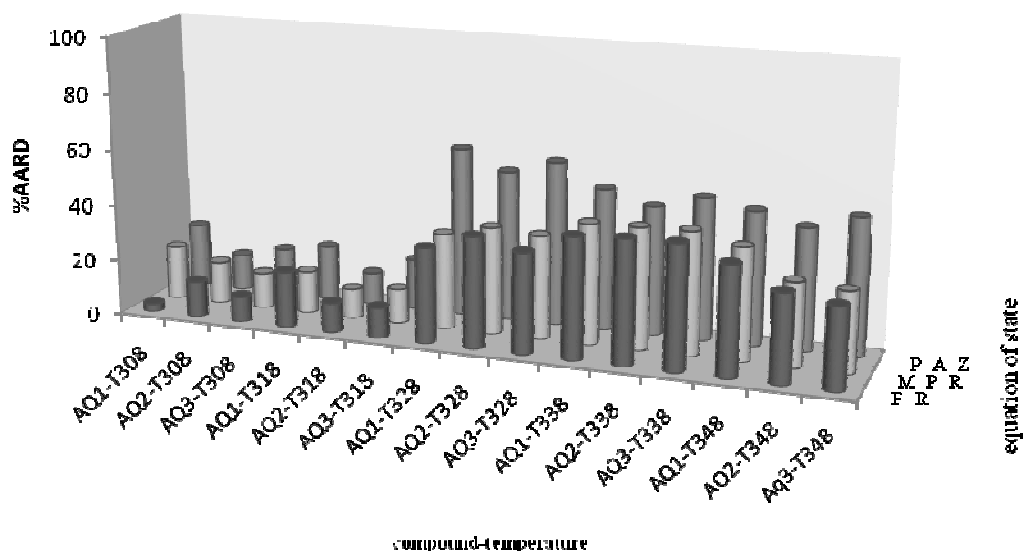


Fig. 4 the %AARD values for studied equation of state along with Mix2 mixing rule, the Klinewisez estimation method and 308 K, 318K, 328K, 338K, 348K

Error percentage for each of used equations of state along with Mix1 mixing rule has been reported in calculating dyes solubility of AQ1, AQ2 and AQ3 at different temperatures as described in Figure 5. The Joback method has been used in generating the figure to estimate the required physical parameters.

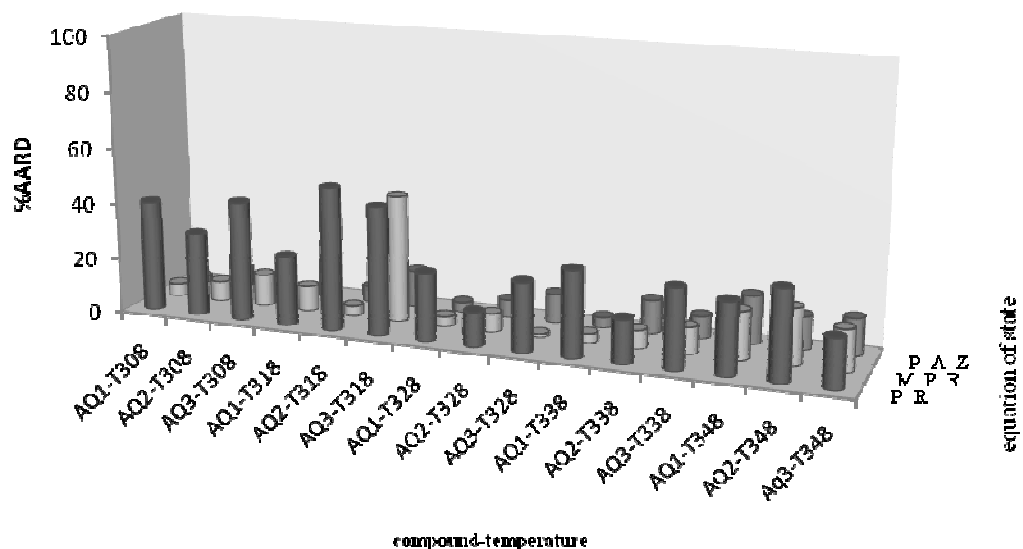


Fig. 5. The %AARD values for studied equation of state along with Mix1 mixing rule, the Joback estimation method and 308 K, 318K, 328K, 338K, 348K

Error percentage for each of used equations of state along with Mix2 mixing rule has been reported in calculating dyes solubility of AQ1, AQ2 and AQ3 at different temperatures as referenced in Figure 6. The Joback method has been used in generating figure to estimate the required physical parameters. According to the figure, error values of MPR and PAZ equations have been decreased compared to reported errors in figure 5 that indicate these equations have more dependency on mixing rule than PR state equation.

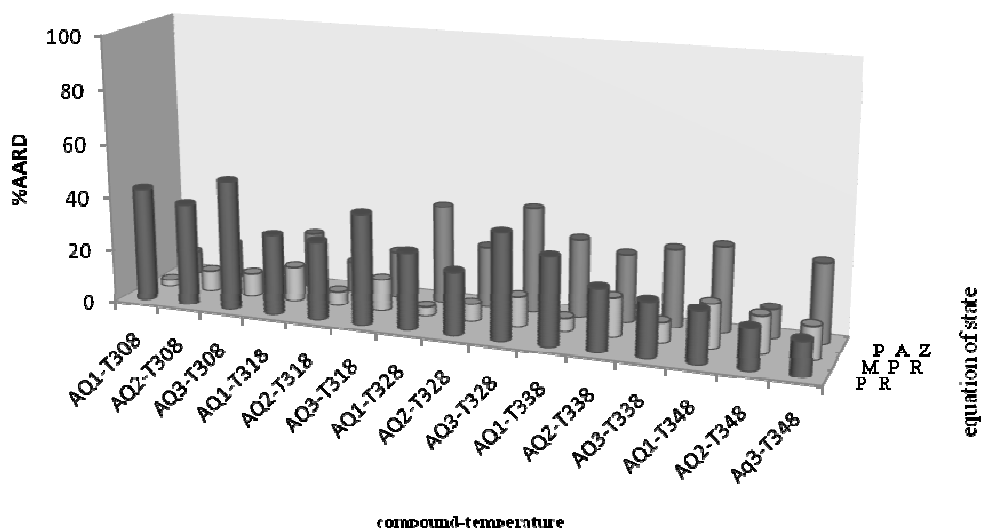


Fig. 6. The %AARD values for studied equation of state along with Mix2 mixing rule, the Joback estimation method and 308 K, 318K, 328K, 338K, 348K

Here, Table 2 has been presented for better comparison between equations of state in whole range of studied conditions. In this table, each of equation of state conditions has been reported with lowest error. This table characterizes that MPR equation is the most appropriate equation of state in calculating the solubility of studied dyes. Also, PAZ equation of state is a better equation at temperature of 308 (K) which is close to critical temperature of carbon dioxide. Most appropriate equation of state is MPR equation by considering Joback estimating method and Mix2 mixing rule.

Table 2. The equation of state with minimum error value in each studied condition

Method rule	Mixing Temperature														
	308			318			328			338			348		
	AQ1	AQ2	AQ3	AQ1	AQ2	AQ3	AQ1	AQ2	AQ3	AQ1	AQ2	AQ3	AQ1	AQ2	AQ3
Mix1 Lyderson	PR	PR	PAZ	MPR	PR	PAZ	PR	MPR	PAZ	PAZ	MPR	MPR	PR	PR	PAZ
Mix2	PAZ	MPR	PAZ	MPR	MPR	PAZ	MPR	MPR	MPR	MPR	MPR	PAZ	PAZ	PAZ	PAZ
Mix1 Klinswicez	PAZ	PAZ	PAZ	MPR	MPR	PAZ	PR	MPR	PR	MPR	MPR	MPR	MPR	MPR	PR
Mix1 Joback	PR	PAZ	PR	MPR	PR	PR	PR	MPR	MPR	PR	MPR	MPR	MPR	MPR	MPR
Mix2	MPR	MPR	MPR	MPR	MPR	MPR	MPR	MPR	MPR	MPR	MPR	MPR	MPR	PAZ	MPR

Mendez-Teja equation [29] was used to define the uncorrelated contribution of experimental data in created errors. In Table 3 and Figure 7, equation constants of Mendez-Teja with errors in each of the experimental data have been reported. It is specified that the error related to the experimental data is low in modeling by state equation with respect to the figure, in other words calculated errors are obtained from different conditions of modeling. It should be noted that Mendez-Teja equation in reference [17] has been suggested to control of experimental data correlation of solids solubility in carbon dioxide supercritical fluid.

Table 3. The values of Mendez-Teja equation constants for studied compounds

Compound	T (K)									
	308		318		328		338		348	
	A	B	A	B	A	B	A	B	A	B
AQ1	3512	0.943	2788	1.430	2936	0.932	3458	0.273	2390	1.030
AQ2	3257	1.514	3058	1.413	2993	1.145	3293	0.369	2186	1.472
AQ3	4096	1.314	3611	1.392	3582	1.116	3869	0.292	3090	0.915

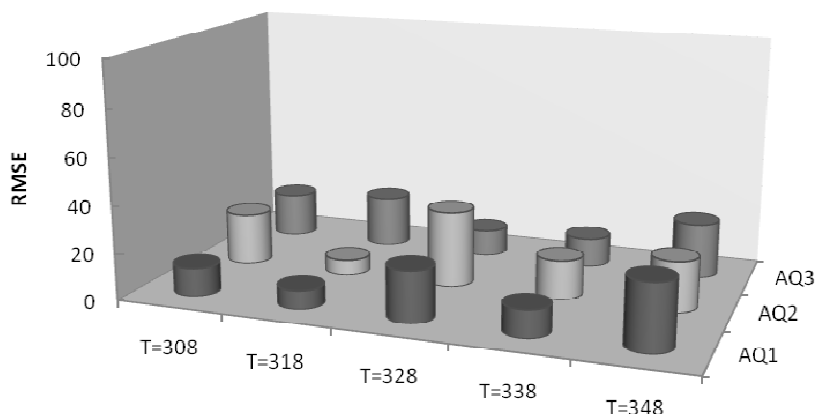


Fig. 7. The root mean square error values in solubility experimental data based on Mendez-Teja equation

Density functional method has been applied to explain obtained results. Excluded volume and interaction energy between each of the solute molecules and supercritical carbon dioxide have been calculated. For this purpose, the B3LYP method [30] with basis function of the 6-31G was used. Calculated molar volume and values of interaction energy between each of the structures and carbon dioxide for each of the dyes have been reported in Table 4. The following term was used to calculate the interaction energy.

$$E_{interaction} = E_{dye+Co2} - (E_{dye} + E_{Co2}) \quad (12)$$

Table 4. The volume and interaction energy according to relation number 12 for studied compounds

Compound	Volume ([Cm] ³ /mol)	E _{interaction} (hartree)
AQ1	186.423	0.1840422
AQ2	154.277	0.0609695
AQ3	139.614	0.0760137

Optimized structures of studied dyes have been shown in Figure 8. It is observed that hydrogen bonds have been established in AQ1 between oxygen of carbon dioxide and hydrogen of dye hydroxy group, while intramolecular hydrogen bonds have been formed in other two dyes that are in agreement with values of obtained molar volume and shows that AQ2 and AQ3 dyes have more compact structure than AQ1 dye (see Figs. 9 and 10). It can be seen that the MPR equation of state in most cases is appropriate for AQ1 material by Considering Table 2. Since in this equation, the attraction term which is related to the intermolecular forces has been modified, the obtained results of equation of state and quantum calculations are in good agreement.

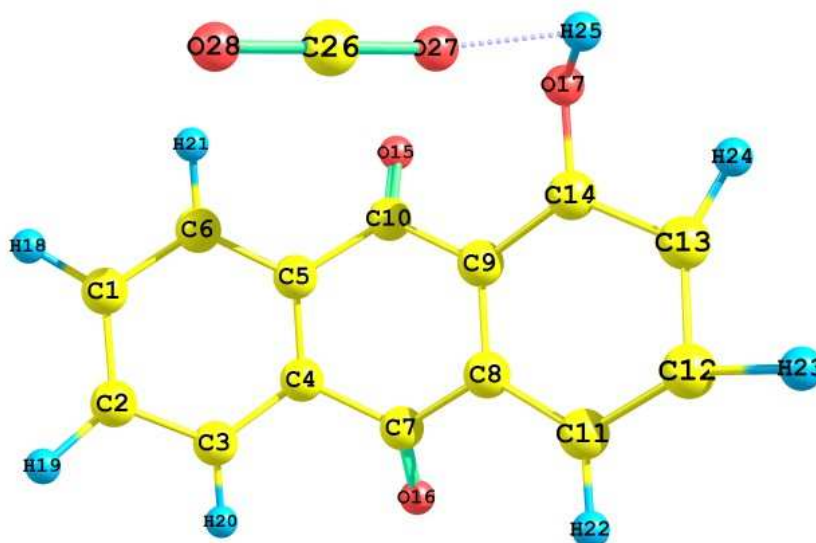


Fig. 8 optimized AQ1 structure along with carbon dioxide using B3LYP and 6-31G basis set

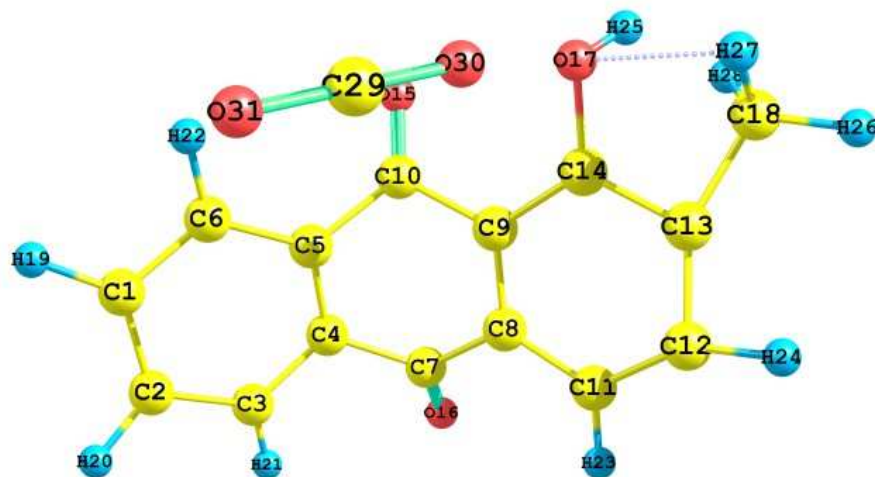


Fig. 9 same as Fig. 8 for AQ2

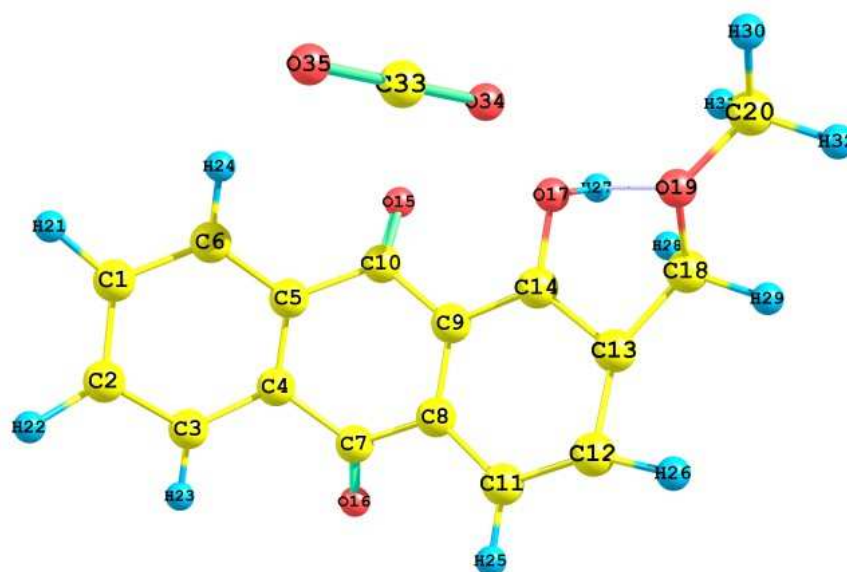


Fig. 10. Same as Fig. 8 for AQ3

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