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A Novel Semi Empirical Equation for Prediction the Solute Solubility in Supercritical Carbon Dioxide

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Abstract: Supercritical fluid carbon dioxide with very favorable critical properties has been so important in the recent two decades as an alternative to organic solvent. In the past two decades, researchers presented many semi empirical equations for solubility prediction in supercritical carbon dioxide. In this paper, accuracy of seven semi empirical equation (consist of Chrastil, Dell Valle, Mendez, Yu, Gordillo, Jouyban, Jafari Nejad) was calculated using26 published solubility data sets. Results showed Jouyban's equation has less mean ARD (about 14.92%) than other equations .In the next step a modified form of Jouyban's equation proposed. The proposed equation is $lny_2 = B_0 + B_{1P} + B_2.P^2 + B_{3P.T} + B_{4T/P} + B_5/T + B_6 \ln \rho$ where B_0-B_6 are the coefficients of equation calculated by least square method,P(bar) is pressure of process ,T(Kelvin) is temperature of process, ρ is density of supercritical fluids and y_2 is mole fraction of solute in supercritical fluid. The mean ARD of proposed equation is 11.34%.The proposed model presents more accuracy than previously published semi empirical equation.

Key word: Solubility; Supercritical carbon dioxide; Semi empirical equation; ARD.

INTRODUCTION

In the past two decades, use of supercritical fluid as an alternative to organic solvents for extraction and separation has been increased. One of the most supercritical fluids is supercritical carbon dioxide. Because of its unique property like relative low critical temperature and pressure, special industrial application has been found. Supercritical carbon dioxide can be used to produce micro and nano scale particles, for pharmaceutical application (Coimbra *et al.*, 2005). Also ,supercritical carbon dioxide has been used to saturate the polymer with solvent for foam creating.This process occur with depressurization and heating the carbon dioxide .Through this process carbon dioxide rapidly expands and voids create within the polymer structure(Yeo and Kiran,2005).

Today, food industries use supercritical carbon dioxide for several applications like decaffeination of coffee and tea and extraction of hops and essential oils. Also, supercritical carbon dioxide can be used for environmental application (Meguro *et al*., 1996).

Relatively low critical temperature and pressure of supercritical carbon dioxide has led to many research for thermodynamic property prediction of it (Fornari *et al*., 2009).

Experimental study is very expensive and time consuming and use of mathematics for thermodynamic property prediction is very favorable. Due to chemical plant design is done based on results of mathematical models, accuracy of this model is very important. Equation of sates can be used for solubility modeling but these equations need solute properties such as critical temperature and pressure .Also complicated computation procedure isn't avoidable and errors can be increased by using solute properties.

In the past two decades, researchers presented many semi empirical equations for solubility prediction in supercritical carbon dioxide. Semi empirical equations are based on least square method and many of them have no dependency to physical properties.

In this work, a comprehensive study is done among our proposed equation and seven semi empirical equations by using published solubility data of 26 compounds. Results showed our proposed equation is more accurate than all of them.

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2. Theory:

2.1. Semi Empirical Equations:

Chrastil expressed a relation between temperature (Kelvin), density of supercritical fluid ($Kg.m^{-3}$) and concentration of solute in supercritical fluid ($Kg.m^{-3}$). k is the association number which describes the number of SCF molecules in the solvated complex, A is a function of the enthalpy of solvation and enthalpy of vaporization, B depends on the molecular weight of the solute(Chrastil,1982).

$$\ln S = k.\ln\rho + A + \frac{B}{T} \tag{1}$$

S relates to y_2 (mole fraction of solute in supercritical fluid) by means of this equation:

$$S = \frac{\mathbf{y_2}\rho M_{w\,solute}}{M_{wSCF}(1-\mathbf{y_2})} \tag{2}$$

Modified chrastil's equation proposed by Del Valle and Aguilera)Del Valle and Aguilera,1988(The Del Valle and Aguilera's equation can be expressed as follows:

$$\ln S = k.\ln\rho + A + \frac{B}{T} + \frac{C}{T^2} \tag{3}$$

Mèndez-Santiago and Teja established solubility in supercritical fluid by means of a linear equation. Unlike to previous equation, effect of pressure was considered directly (Mendez-Santiago and Teja, 2000). Their equation can be expressed as follows:

$$T\ln(\mathbf{y_2}.P) = A + B.\rho + C.T \tag{4}$$

Yu *et al* proposed, a model in which pressure and temperature appear as individual terms (Yu *et al*.,1994). This model can be expressed as follows:

$$y_2 = C_0 + C_1P + C_2P^2 \quad C_3PT(1-y_2) + C_4T + C_5T^2 \tag{5}$$

Gordillo proposed another empirical model (Gordillo *et al*., 1999). Their model has 6 parameters and model
can be expressed as follows:

$$\ln y_2 = A + B.P + C.P^2 + D.P.T + E.T + F.T^2 \tag{6}$$

Also, Jouyban proposed following equation

$$\ln y_2 = M_0 + M_1.P + M_2.P^2 + M_3.P.T + M_4.T/P + M_5.\ln\rho \tag{7}$$

Recently JafariNejad proposed a four parametric semi empirical equation (JafariNejad *et al*., 2010). Their model can be expressed as follows:

$$\ln y_2 = J_0 + J_1.P^2 + J_2.T^2 + J_3.\ln\rho \tag{8}$$

With review of many experimental solubility data we found:

1. Ln y_2 and pressure relate together with a nonlinear equation in isothermal condition.
2. Ln y_2 and temperature relate together with a nonlinear equation in isobar condition.
3. Ln y_2 and Ln ρ relate together with a linear equation.

With regard to these points, the following equation is proposed:

$$\mathrm{Ln}\, y_2 = B_0 + B_1.P + B_2.P^2 + B_3.P.T + B_4.T/P + B_5/T + B_6.\ln \rho \quad (9)$$

Where B_0 - B_6 are the coefficients of equation calculated by least square method, P (bar) is pressure of process, T (Kelvin) is temperature of process, ρ ($Kg.m^{-3}$) is density of supercritical fluids and y_2 is mole fraction of solute in supercritical fluid.

Regression can be done by several software. In this work MATLAB7.7.0 is used for programming.

2.2. Multiple Regression Least Square Method:

Multiple regression estimates the dependent variable which may be affected by more than one independent variables or there may be more than one independent variables being changed at the same time.
Consider a relation between dependent variable (Z) and independent variables (x,y) like this:

$$Z = a + bx + cy \quad (10)$$

For a given data set (x_1,y_1,z_1), (x_2,y_2,z_2),.....(x_n,y_n,z_n) where $n \geq 3$, the best fitting curve $f(x,y)$ has the least square error**.** Square error can be calculated by this equation:

$$E = \sum_{i=1}^{n} (z_i - f(x_i,y_i))^2 = \sum_{i=1}^{n} (z_i - a + bx_i + cy_i)^2 \quad (11)$$

a,b and c are unknown coefficients that must be obtained and x_i, y_i and z_i are given. To obtain the unknown coefficients following equation must be solved.

$$\frac{\partial E}{\partial a} = 2\sum_{i=1}^{n} (z_i - a + bx_i + cy_i) = 0 \quad (12)$$

$$\frac{\partial E}{\partial b} = 2\sum_{i=1}^{n} x_i(z_i - a + bx_i + cy_i) = 0 \quad (13)$$

$$\frac{\partial E}{\partial c} = 2\sum_{i=1}^{n} y_i(z_i - a + bx_i + cy_i) \quad (14)$$

RESULTS AND DISCUSSION

In present work data solubility of 26 compounds gathered from many published literature and are tabulated in Table 1.

Table 2: Data used in this study.

System no.	Solute	Number of data point	Temperature (K)	Pressure (bar)	Density ($Kg.m^{-3}$)	$y_2 * 10^6$	Reference
1	Phenazopyridine	45	327-955	122-355	308-348	4.4-202.1	Yamini *et al* (2003)
2	Propranolol	45	327-955	122-355	308-348	35.8-2396	Yamini *et al* (2003)
3	Methimazole	40	327-955	122-355	308-348	5.4-189	Yamini *et al* (2003)
4	Xanthone	16	506-927	120-300	308-328	37-470	Huang *et al* (2005)
5	Xanthene	13	260-894	80-240	308-328	67-10800	Huang *et al* (2005)
6	M-nitrophenol	49	328-1003	121.-486	308-348	132-4450	Shamsipour *et al* (2002)
7	Picric acid	50	328-1003	121-486	308-348	22-2650	Shamsipour *et al* (2002)
8	Trioctylamine	56	203.-972	80-400	308-338	50-46840	Ghaziaskar *et al* (2008)

Table 2: Continue.

9	Medroxyprogesterone acetate	40	327-955	122-355	308-348	16-413	Asghari *et al* (2004)
10	Cyproterone acetate	40	327-955	122-355	308.348	13-261	Asghari *et al* (2004)
11	N-phenylacetamide	24	356-889	104-225	308-328	290-4562	Asghari *et al* (2004)
12	Methylpheny lacetamide	21	487-889	121-225	308-328	38-480	Huang *et al* (2007)
13	Pentachlorophenol	21	245-981	150-450	313-413	10-8190	Miller *et al* (1997)
14	Atrazine	21	245-981	150-450	313-413	12-5000	Miller *et al* (1997)
15	Lovastatin	45	327-955	121-354	308-348	11-114	Hojjati *et al* (2007)
16	Rosuvastatin	45	327-955	121-354	308-348	3-244	Hojjati *et al* (2007)
17	Simvastatin	45	327-955	121-354	308-348	2-535	Hojjati *et al* (2007)
18	Fluvastatin	45	327-955	121-354	308-348	5-601	Hojjati *et al* (2007)
19	Resorcinol	32	397-975	120-400	308-338	110-973	Yamini *et al* (1998)
20	Pyrocatechol	32	397-975	120-400	308-338	660-3940	Yamini *et al* (1998)
21	1,5-naphthalene diamine	27	357-840	110-200	313-333	1.9-16.2	Khimeche *et al* (2007)
22	4,4-diaminodipheny lmethane	27	357-840	110-200	313-333	9.4-160	Khimeche *et al* (2007)
23	Hydroquinone	33	203-864	100-350	333-363	7-55.9	González *et al* (2002)
24	P-quinone	33	203-864	100-350	333-363	1300-35540	González *et al* (2002)
25	Cinnamic acid	19	546-889	123-236	308-328	35-425	Chen *et al* (2009)
26	4-methoxypheny lacetic acid	22	628-892	116-236	308-328	47-634	Chen *et al* (2009)

Different coefficients (B_0 -B_6) of our proposed equation for 26 compounds calculated by least square method are showed in Table2.

Table 2: Different parameters (B_0 -B_6) for 26 experimental dat setes produced by our model.

System. No	B_0	B_1	B_2	B_3	B_4	B_5	B_6
1	-29.09	0.0121	-3.6555E-005	4.9938E-005	1.06	-2.7833E+003	4.4792
2	-11.85	-0.0862	3.7447E-005	2.0341E-004	-1.3806	-458.45	2.5738
3	-26.80	-0.0048	-1.4732E-005	5.2739E-005	0.3614	-2.4152E+003	4.4052
4	-10.41	-0.0259	3.4765E-005	-1.2035E-006	-1.6989	-4.2466E+003	4.5332
5	-15.57	0.0660	6.4921E-006	-2.0913E-004	0.3595	-7.6272E+003	6.2768
6	-52.59	0.0154	-3.3425E-006	-3.8868E-005	1.3811	-9.5808E+003	12.0419
7	-14.90	-0.0098	-1.1028E-006	3.8154E-005	-0.2582	-678.5848	2.5816
8	-33.22	-0.0918	3.0680E-005	2.1852E-004	-1.2664	-1.0149E+003	6.8067
9	-31.71	0.0052	-4.4796E-005	9.6827E-005	1.3175	866.3968	3.1138
10	-16.80	-0.0489	2.9762E-006	1.6517E-004	-0.7620	6.9535E+003	-0.7842
11	-14.70	0.0831	-9.4061E-005	-1.2276E-004	1.0942	-1.0036E+004	5.8562
12	-5.81	-0.2342	1.3115E-004	5.1560E-004	-3.5663	4.2758E+003	0.9489
13	67.78	-0.0737	6.5081E-005	1.3034E-005	-11.7149	-3.4006E+003	-4.2529
14	21.34	0.0396	-5.8165E-005	2.2407E-005	-2.8608	-1.9867E+003	-3.2674
15	-19.37	0.0037	1.2348E-006	-1.4138E-005	0.3489	-5.0612E+003	5.0213
16	-25.46	-0.0067	1.1559E-005	-2.4546E-006	-0.3493	-6.1707E+003	6.8003
17	-34.15	-0.0157	2.8464E-007	5.3538E-005	-0.0516	-4.1495E+003	6.9481
18	-37.70	-0.0020	-5.2467E-006	2.5932E-005	0.6656	-7.5490E+003	8.7220
19	-0.67	-0.0065	-6.2111E-006	3.8422E-005	-0.1709	-2.6891E+003	1.1702
20	-5.89	0.0022	-8.1901E-006	1.2439E-005	0.1244	-3.6998E+003	2.5930
21	-23.89	0.0154	-1.2823E-004	1.0157E-004	0.1114	-555.4607	2.6565
22	-0.36	-0.0654	3.8100E-005	8.7771E-005	-2.5444	-2.1335E+003	2.4419
23	-20.66	-0.0318	3.9009E-006	8.7523E-005	0.0652	523.4818	2.4924
24	-39.79	0.0978	-4.5975E-005	-1.7283E-004	4.4087	-1.1157E+004	9.5907
25	-4.00	-0.1248	3.1094E-005	2.9501E-004	-3.4816	3.2951E+003	0.5624
26	-87.39	0.1544	-3.1560E-004	3.9937E-005	5.0460	-6.7249E+003	11.8926

In order to determination the accuracy of semi empirical equation, average relative deviation (ARD) of different equations for each compound is calculated by this equation:

$$\text{ARD} = \frac{100}{N} \times \sum_{i=1}^{N} \left| \frac{y^{exp} - y^{cal}}{y^{exp}} \right| \quad (15)$$

Also, in order to determination the relation between ARDs of different equations and compound, standard deviation of ARDs for each equation is calculated by this equation:

$$\text{Standard deviation} = \left[\frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^2\right]^{\frac{1}{2}} \quad (16)$$

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \quad (17)$$

In Table 3 ARDs of 26 experimental data set obtained by different semi empirical equation are presented.

Table 3: ARD s of seven semi empirical equations and our proposed equation..

System No.	Chrastil	Del Valle and Aguilera	Mendez Santiago Teja	Yu	Gordillo	Jouyban	Jafari Nejad	Proposed Equation
1	10	10	10	39	10	8	21	7
2	44	35	44	61	23	19	45	11
3	9	9	10	24	8	6	19	6
4	19	21	18	45	40	23	35	12
5	16	40	12	109	66	40	73	18
6	14	10	15	29	9	9	19	14
7	13	13	13	17	7	7	19	6
8	46	42	43	32	90	27	101	5
9	14	15	12	24	7	6	18	7
10	22	21	21	10	7	12	15	22
11	3	3	5	15	7	3	15	5
12	11	10	12	18	9	7	17	7
13	25	16	24	28	29	25	31	22
14	46	50	35	41	40	48	53	43
15	5	6	5	20	11	9	15	5
16	6	5	7	33	29	21	25	6
17	13	11	17	73	49	31	43	15
18	15	12	15	64	19	15	25	7
19	12	12	15	30	4	7	8	5
20	12	12	14	28	7	7	10	11
21	4	6	25	7	25	8	38	8
22	10	19	15	18	25	14	33	13
23	8	9	6	30	9	10	8	10
24	11	12	8	76	10	12	7	13
25	11	10	10	17	11	4	8	5
26	3	3	4	45	8	10	24	12
Average	15.4615	15.8461	15.9615	35.8822	21.5023	14.923	27.8852	11.3452
Standard deviation	12.2057	12.3732	10.6826	23.7054	20.9138	11.405	21.6284	8.1825

Our proposed equation is more accurate and accuracy for some compounds is very higher than previously published semi empirical equations .The mean ARD and standard deviation of ARDs for each equation are shown if Fig.1 and Fig.2.

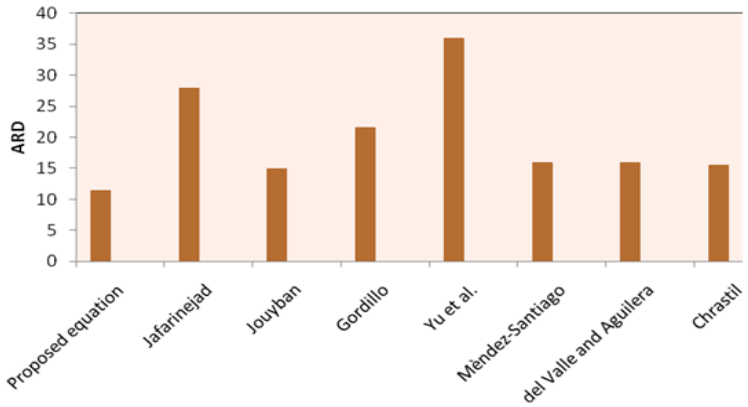

Fig. 1: ARD of different equations.

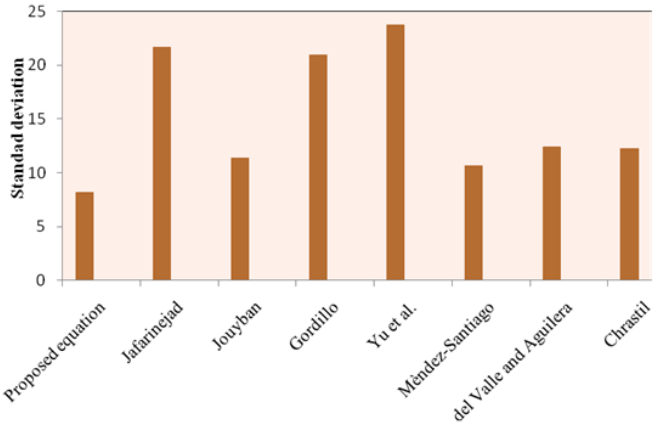

Fig. 2: Standard deviation of ARDs that obtained from different equations.

Conclusion:

In present work, we proposed a new semi empirical equation for solubility prediction of different compounds in supercritical carbon dioxide. Results showed, mean ARD of this equation is 11.34% while mean ARD of the best previously published semi empirical equation for 26 studied compound is 14.92%.

Another point is high dependency of all semi empirical equation's ARD to compound. In order to determination of this parameter, standard deviation parameter has been calculted. Results showed our proposed equation has minimum standard deviation. Probably, lack of physical property in semi empirical equation due to this problem and using physical property like molecular weight can increase the accuracy of semi empirical equations.

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