Thermochimica Acta 519 (2011) 16–21

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

An improved density-based model for the solubility of some compounds in supercritical carbon dioxide

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ARTICLE INFO

Article history:
Received 2 November 2010
Received in revised form 17 January 2011
Accepted 14 February 2011
Available online 23 February 2011

Keywords:
Solubility
Carbon dioxide
Supercritical fluid
Density-based models
AARD

ABSTRACT

The ability to correlate the solubility of solutes in supercritical fluids (SCF) is of great importance for the design and evaluation of any supercritical process. The empirical equations are quite successful in correlating the solubility of compounds in the SCF. In this work, a new density-based semi-empirical model was proposed to correlate some compounds in supercritical carbon dioxide. Solubility data from 54 different compounds were collected from literature published in the last ten years and the different empirical models (Chrastil, Adachi-Lu, del Valle-Aguilera, Kumar-Johnston, Méndez Santiago-Teja, Gordillo, Jouyban, Sparks, Garlapati-Madras, and Ch-Madras) were evaluated. The results showed that, the proposed model produced the least global average absolute relative deviation (5.91%) compared to all other empirical models considered in this study.

1. Introduction

In recent years, supercritical fluid technology has been becoming increasingly popular in petroleum, food, pharmacy and chemical industries. This is because the supercritical fluid (SCF) has a large density, a low viscosity and a high diffusivity, which can be very adequate for extraction. Carbon dioxide is the most commonly used supercritical fluid. The critical properties of carbon dioxide are respectively low (T_c = 304.2 K and P_c = 7.38 MPa) and it is non-toxic, non-flammable, non-explosive and readily available at low cost [1,2]. In this work, the solubility of some compounds in the supercritical carbon dioxide (SC-CO_2) has been considered.

In an extraction or reaction process, it is crucial to obtain the solubility of solutes in the SCF in order to determine the optimal operating conditions. The experimental determination of solubility of compounds in the SCF at various temperatures and pressures is expensive and time-consuming. Therefore, correlation and prediction of solubility is essential [3]. In general, there are two sorts of models used to correlate and predict the solubility. One is based on theoretical models such as equations of state, another is semi-empirical equations. Theoretical models like cubic equation of state need complicated computational procedures and the knowledge of solute critical properties, acentric factor and sublimation pressures [4–6]. However, semi-empirical models, which are based on simple error minimization using least-square methods, do not need solute properties, and they only need temperature, pressure, density of solvent such as SC-CO_2 and solubility data. The most common semi-empirical equations are based on solvent density.

In this study, our focus was on correlating the solubility of some compounds in SC-CO_2 using the 11 most common semi-empirical models [7–15,52] and a new density-based model was proposed. The model parameters for each equation were also presented. The accuracy of the new and previously published semi-empirical models were evaluated using solubility data of 54 different compounds in SC-CO_2, which were collected from the literatures published in the last ten years. The results showed that the proposed model provided the least global average absolute relative deviation compared to all existing models considered in this study.

2. Review of density-based models

Chrastil [7] assumed that a solvate complex was formed between the solute and solvent molecules at equilibrium and presented the first density-based model as follows:

$$c_2 = \rho_1^k \exp\left(\frac{a}{T} + b\right) \quad (1)$$

where c_2 is the solute solubility in the solvent in kg m^{-3}, ρ_1 is the density of the solvent in kg m^{-3}, k is the average association number, a is a function of the enthalpy of solvation and enthalpy of vaporization, b is a function of the average association number and molecular weight of the solute and solvent, and T is the operating temperature in K.

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doi:10.1016/j.tca.2011.02.023

However, Chrastil's model has some limitations. For example, it is not applicable to the higher solubility (greater than 100–200 kg m^{-3}) and a wide range of temperatures [10,16]. Therefore, there were several modified forms of Chrastil's equation.

Adachi and Lu [8] correlated the average association number k to a second-order polynomial of the solvent density, achieving a lower error in the correlation of the solute solubility. The Adachi-Lu model can be shown as follows:

$$c_2 = \rho_1^{(e_0+e_1\rho_1+e_2\rho_1^2)} \exp\left(\frac{a}{T}+b\right) \tag{2}$$

where e_0, e_1, and e_2 are model parameters, respectively, which can be obtained by the fitting of experimental data.

On the basis of Eq. (1), del Valle and Aguilera [9] took into consideration the change in the enthalpy of vaporization with temperature and obtained the following modified equation:

$$c_2 = \rho_1^{k} \exp\left(\frac{a}{T}+b+\frac{m}{T^2}\right) \tag{3}$$

where m is the model parameter.

Since the Adachi-Lu equation (Eq. (2)) corrected the effect of density on solubility and the del Valle-Aguilera equation (Eq. (3)) corrected the effect of temperature on solubility, Sparks et al. [10] conducted a combination of Eq. (2) and Eq. (3) and proposed the following equations, respectively.

$$c_2 = \rho_1^{(e_0+e_1\rho_1)} \exp\left(\frac{a}{T}+b+\frac{m}{T^2}\right) \tag{4}$$

$$c_2 = \rho_1^{(e_0+e_1\rho_1+e_2\rho_1^2)} \exp\left(\frac{a}{T}+b+\frac{m}{T^2}\right) \tag{5}$$

The latest Chrastil's modification was done by Garlapati and Madras [11]. They found a linear relation between $\ln y_2$ and $\ln(\rho_1 T)$ in a certain range of density and temperature and presented the following equation:

$$\ln\ y_2 = e_0 \ln\rho_1 + e_1\rho_1 \ln\rho_1 + e_2 \ln(\rho_1 T) + \frac{a}{T} + b \tag{6}$$

where y_2 is the solubility of the solute in the SCF in mole fraction.

Kumar and Johnston [12] presented a new density-based model according to a linear relationship between $\ln y_2$ and ρ_1:

$$\ln y_2 = k\rho_1 + \frac{a}{T} + b \tag{7}$$

A widely used density-based model based on the theory of dilute solutions was proposed by Méndez-Santiago and Teja [13]. This model is excellent for determination of consistency of solubility data across different isotherms. However, the model must need previously the knowledge of solute sublimation pressure. In many instances, the sublimation pressure of the solute is not available. In order to solve this problem, a two-constant Antoine equation for solute sublimation pressure is substituted and the final model can be expressed as follows:

$$\ln(Py_2) = k\frac{\rho_1}{T} + \frac{a}{T} + b \tag{8}$$

where P is the system pressure in MPa.

Another different density-based model was presented by Jouyban et al. [14]. Though the use of this model was low [16], the model was in good agreement with experimental solubility data, which can be confirmed in the ensuing text. The Jouyban model can be written as

$$\ln\ y_2 = m_0 + m_1 P + m_2 P^2 + m_3 PT + m_4\frac{T}{P} + m_5 \ln\ \rho_1 \tag{9}$$

where m_i (i = 0, 1,. . .,5) are the model constants.

Based on the theory of response surface, Gordillo et al. [15] proposed another empirical model which contained only temperature and pressure:

$$\ln\ y_2 = m_0 + m_1 P + m_2 P^2 + m_3 PT + m_4 T + m_5 T^2 \tag{10}$$

Based on the association theory, Ch and Madras [52] have presented a four parameter model very recently:

$$y = \left(\frac{P}{P^*}\right)^{(k-1)} \exp\left(\frac{a}{T}+m\rho_1+b\right) \tag{11}$$

where P^* is a reference pressure, and P^* = 0.1 MPa.

3. Improved density-based model

Reviewing published experimental solubility in SC-CO_2 and previously presented empirical models indicate the existence of:

(a) Non-linear relationship between $\ln c_2$ and $\ln\rho_1$ over a wide range of temperatures and pressures.
(b) Non-linear relationship between $\ln c_2$ and temperature in isopycnic condition.
(c) When the system temperature increases under isobaric conditions, the average association number k will certainly decrease due to the increase of the thermal motion of its molecules; on the other hand, when the system pressure increases under isothermal conditions, k will increase as a result of shortening distance as well as increasing collision between molecules. Once k changes, the enthalpy of solvation and enthalpy of vaporization will change.

Taking into account all the above factors and in order to provide a better correlation, the following density-based empirical equation is proposed for the solubility of some compounds in SC-CO_2:

$$c_2 = \rho_1^{(e_0+e_1\rho_1+e_2/\ln T)} \exp\left(\frac{a+m\rho_1}{T}+b\right) \tag{12}$$

4. Methodology

In this study, the density of SC-CO_2 for all models was determined with PR EoS [17]. Solubility of a solute is calculated by means of Eq. (13):

$$c_2 = \frac{\rho_1 MW_2 y_2}{MW_1(1-y_2)} \tag{13}$$

where MW_2 is molar weight of the solute in g mol^{-1}, MW_1 is the molar weight of CO_2 in g mol^{-1}, the other symbols are the same as stated above.

The model parameters for each compound with each equation were determined by using MATLAB 7.01 by the minimization of experimental and calculated solubility data with the following objective function:

$$\mathrm{OF} = \sum_i^N \left|\frac{y_i^{\mathrm{calc}} - y_i^{\mathrm{exp}}}{y_i^{\mathrm{exp}}}\right| \tag{14}$$

where N is the number of solubility data points, y_i^{calc} and y_i^{exp} is the calculated and experimental solubility for experimental point i, respectively.

The goodness of the calculations was evaluated by the absolute average relative deviation defined as follows:

$$\mathrm{AARD}\ (\%) = \frac{100}{N}\sum_i^N \left|\frac{y_i^{\mathrm{calc}} - y_i^{\mathrm{exp}}}{y_i^{\mathrm{exp}}}\right| \tag{15}$$

Table 1
Details and references of the solubility of some compounds in SC-CO_2.

No.	Compound	T (K)	P (MPa)	ρ (kg m^{-3})	N_i	Refs.
1	Naphthalene	308.2–318.2	8.05–29.92	286.3–960	18	[18]
2	α-Naphthol	308–318	10.6–15.2	530–818	11	[19]
3	B-Naphthol	308–328	10.6–15.2	329–805	16	[19]
4	2-Nitroanisole	313.2–333.2	8–20	196.4–829.2	18	[20]
5	3-Phenyl-1-propanol	313.2–333.2	8–20	196.4–829.2	18	[20]
6	Troeger'sbase (1)	308–328	8–19	208.9–849	15	[21]
7	Blackcurrantseedoil	313.2–333.2	12–28	688.3–899.3	13	[22]
8	Capsaicin	308.2–328.2	12–24.99	469–911.5	23	[23]
9	Diazepam	308–348	12.2–35.5	327–955	45	[24]
10	Codeine	308–348	12.2–35.5	327–955	45	[24]
11	p-Quinone	333–363	10–35	203–864	33	[25]
12	Methylgallate	313–333	10–50	295–992	27	[26]
13	TCMTB	323.2–333.2	10–30	266.5–874.4	12	[27]
14	Caffeicacid	313–333	15–50	607–992	24	[28]
15	Ferulicacid	313–333	10–50	295–992	27	[28]
16	Phenazopyridine	308–348	12.2–35.5	327–955	45	[29]
17	Propranolol	308–348	12.2–35.5	327–955	45	[29]
18	Methimazole	308–348	12.2–35.5	327–955	40	[29]
19	Cyp	308–348	12.2–35.5	327–955	40	[30]
20	C.I.Disperseorange30	312.2–393.2	11.46–32.67	194.5–916.7	45	[31]
21	BDP	338–358	21.3–38.5	593–867	21	[32]
22	BUD	338–358	21.3–38.5	593–867	21	[32]
23	Artemisinin	308.2–328.2	10.4–25.2	539.2–900.4	16	[33]
24	n-Hexadecane	308–323	9.2–20.37	249–864.4	19	[34]
25	Apricotkerneloil	313.2–333.2	15–60	603–1032	15	[35]
26	RPI	308.2–328.2	8.83–24.2	325.1–895.2	24	[36]
27	DADPM	313.2–333.2	11–20	357.9–840.7	27	[37]
28	1,5-NDA	313.2–333.2	11–20	357.9–840.7	27	[37]
29	Fluvastatin	308.2–328.2	10.1–25.6	327–955	45	[38]
30	Astaxanthin	303–333	8–30	191.7–982	49	[39]
31	Pelargonicacid	313.2–333.2	10–30	290–909.9	14	[40]
32	Irgacure2959	308.2–328.2	10.1–25.6	326.9–901.8	21	[41]
33	CBU	308.2–328.2	12–24	506. 6–895.2	17	[42]
34	CBE	308.2–328.2	12–24	506.6–895.2	17	[42]
35	Cinnamicacid	308.2–328.2	12.3–23.61	546.7–889.5	19	[43]
36	4-Mpa	308.2–328.2	11.61–23.47	628.7–892.8	22	[43]
37	N-Hexyl-N-octanamide	313–333	9.3–13.4	444–616	15	[44]
38	N-Pfoa	313–333	10.2–24.9	639–796	18	[44]
39	Peperine	313–333	10–30	289.8–840.6	18	[45]
40	Tributylphosphate	303.2–363.2	15–25	372–923	24	[46]
41	Triphenyltinchloride	308.2–328.2	15–30	653.8–929.6	12	[47]
42	Triphenylmethylchloride	308.2–338.2	15–40	555.5–972.8	18	[47]
43	Acetamide	308.2–323.2	9–40	289–1011	30	[48]
44	Acrylamide	308.2–323.2	9–40	289–1011	28	[48]
45	Triclocarban	313.2–333.2	10.93–38.96	509.1–986.6	24	[49]
46	Lycopene	323.2–353.2	20–40	595.4–923.8	20	[50]
47	ANA	308–348	12.2–35.5	327–955	45	[51]
48	Propyphenazone	308–328	9–19	260.5–849	18	[52]
49	Isoniazid	308–313	13–18.5	744–853	18	[53]
50	Naphthalene	308.2–318.2	8.8–25	287.2–865.8	12	[54]
51	Octadecanoicacid	308–338	12.85–22.65	418.1–889.7	20	[55]
52	Hexadecanoicacid	308–328	12.85–22.65	518.3–889.7	15	[55]
53	Co(thd)3	313–343	10–19.8	357.3–818.3	33	[56]
54	Cr(thd)3	313–343	10.1–18	346–818.3	19	[56]

RPI: Racemic Paroxetine Intermediate; N-Pfoa: N-(4-Pyridyl) pentadecafluorooctanamide; 4-Mpa: 4-Methoxyphenylaceticacid.

5. Results and discussions

To illustrate the usefulness of the proposed model in calculation of solubility of the solute in SC-CO_2, solubility data from 54 compounds, collected from literature published in the last ten years, were compared with the previously published models. The details of the experimental data for each compound are indicated in Table 1. Different model parameters, obtained for each compound with each published equation and the proposed equation by the minimization of the objective function (Eq. (14)), were presented in an appendix (see Tables A-1–10).

Table A-1 demonstrates that the average association number k from Chrastil and del Valle-Aguilera are almost identical. The reason is that the slope for the same group of ($\ln c_2$, $\ln \rho_1$) is the same for the Eqs. (1) and (3). Table 2 shows the AARD for 54 solubility data sets produced by each equation studied. The lowest error of each compound for various models is marked with a red asterisk (*). The overall AARD values for 54 data sets for each equation are listed in Fig. 1.

Careful examination of Table 2 and Fig. 1 reveals that the Gordillo model with 6 adjustable parameters produces the highest error, and the overall AARD (%) is 13.51. We found that this conclusion was inconsistent with that from Tabernero et al. whose conclusion was that the Gordillo equation was the second best model among 9 common used models [16]. The error might be caused by the two much higher AARD (AARD were 55.46 and 42.34 for No. 15 and No. 12, respectively.). However, for 3 of the 54 compounds, Gordillo model provides the lowest individual AARD.

Among all the equations with 3 adjustable parameters, Chrastil model produces highest accuracy. The second is Kumar-Johnston

Table 2
AARD (%) of each equation with each compound.

No	Empirical model											
	1	2	3	4	5	6	7	8	9	10	11	12
1	17.98	6.39	17.99	8.72	6.37	8.72	28.87	18.63	13.51	30.51	16.68	5.70*
2	2.33	1.55	2.27	1.94	1.53	2.08	1.96	4.60	1.32	2.30	1.94	0.75*
3	4.69	4.41	4.61	4.77	4.31	4.73	9.24	8.92	4.59	6.78	8.25	4.24*
4	3.46	1.18	3.48	1.18	1.18	1.18	12.53	12.01	4.33	9.86	10.52	1.05*
5	6.83	2.29	6.99	2.28	2.14*	2.27	23.00	22.51	4.45	17.41	18.97	2.15
6	15.79	15.22	16.01	15.69	14.81	15.83	20.12	22.01	9.14*	12.41	19.88	9.49
7	2.49	2.13*	2.52	2.51	2.15	2.54	3.72	3.50	2.83	4.42	2.38	2.48
8	10.53	10.04	4.96	4.34	2.87	4.78	11.26	11.78	10.12	3.35	10.91	2.33*
9	18.40	12.56	17.95	12.24	12.60	12.23	11.97	15.17	10.82	13.35	12.57	10.68*
10	17.91	12.67	17.49	12.29	12.78	12.29	12.15	16.37	10.69*	11.61	12.63	10.71
11	12.37	8.05	12.41	8.90	7.99	8.87	9.83	8.13	10.57	13.34	7.56*	7.71
12	11.24	8.18	11.82	8.29	8.23	8.32	12.20	9.04	16.22	42.34	9.1	6.36*
13	31.36	14.60	31.36	17.61	14.58	17.47	18.51	19.93	10.67	32.35	18.55	9.95*
14	29.95	24.98	29.96	26.69	25.11	26.67	28.06	28.46	11.82	13.45	24.99	11.62*
15	9.62	7.62	7.45	7.49	6.28	9.36	22.29	9.68	14.85	55.46	8.57	5.02*
16	16.38	7.44	16.11	8.31	7.40	8.30	8.76	13.13	7.20	10.25	8.78	6.60*
17	22.52	13.71	22.79	13.82	13.74	13.80	15.35	20.71	5.72*	8.41	14.37	8.84
18	18.98	14.05	19.04	14.10	14.25	14.04	13.74	18.13	9.07*	11.33	13.82	10.00
19	27.69	11.05	27.76	10.74	10.27	10.52	18.48	26.08	10.25	4.52*	11.89	7.54
20	16.22	6.36	15.68	6.83	5.35*	6.84	7.32	14.48	5.38	6.41	5.49	6.62
21	11.95	9.82	11.34	9.52	9.20	9.39	11.20	11.81	6.53	7.02	10.64	5.79*
22	13.14	10.27	12.60	10.22	10.07	10.26	12.00	12.79	6.12	6.98	11.05	5.75*
23	8.36	5.09	8.63	5.45	4.98	5.45	6.85	11.43	3.63*	4.09	5.51	5.00
24	24.63	14.94	22.94	12.02	11.31	11.48	17.66	25.85	11.05	10.66*	13.48	11.82
25	8.35	6.42	8.62	6.74	6.70	7.31	16.44	12.56	8.31	19.91	9.87	5.77*
26	6.80	4.05	6.74	3.92	3.90	3.92	5.52	8.01	3.26	12.88	4.9	3.01*
27	10.04	9.24	8.37	8.25	8.18	8.34	11.52	8.95	6.28	11.91	10.09	3.90*
28	7.44	7.17	6.61	6.74	6.54	6.58	9.08	7.30	5.56	10.22	7.94	3.15*
29	15.77	8.30	15.61	10.11	8.25	10.10	9.89	11.64	6.95	13.96	9.45	4.40*
30	12.36	12.17	11.34	11.44	11.43	11.14*	14.14	18.71	16.69	21.79	13.47	11.20
31	30.81	7.02	30.81	6.85	7.01	6.85	47.89	36.37	13.11	46.94	18.99	1.89*
32	3.37	2.49	2.78	2.19	2.14*	2.20	10.37	4.68	5.24	21.47	5	2.19
33	4.87	4.37	2.75	2.53	2.50*	2.62	7.78	5.93	7.70	12.54	5.14	2.52
34	6.19	5.09	6.06	5.91	5.02*	5.91	9.27	6.52	6.29	14.18	5.48	5.46
35	9.43	7.11	9.12	6.76	6.53	6.66	7.84	8.11	2.43*	6.76	7.67	5.20
36	4.10	3.48	3.97	4.09	3.33*	4.11	5.05	4.15	3.92	4.56	3.79	4.10
37	5.87	3.57	4.59	3.88	3.19	3.89	5.18	4.06	2.32*	3.17	3.52	2.85
38	1.48	1.14	1.40	1.38	1.12*	1.46	1.61	2.26	1.45	2.02	1.58	1.40
39	21.14	13.51	21.11	14.03	13.76	14.02	14.60	18.83	10.02	7.00*	13.41	7.20
40	7.14	3.89	6.93	4.61	3.84*	4.60	7.34	7.37	5.64	6.29	6.47	4.00
41	6.80	4.60	6.87	4.78	4.47	4.74	8.28	5.10	2.56*	4.99	4.07	3.50
42	5.75	5.38	6.01	5.86	5.83	5.94	8.86	5.75	6.70	11.39	5.87	5.35*
43	7.94	4.00	7.89	3.97	3.97	3.98	15.60	6.55	8.46	19.73	5.98	3.82*
44	5.72	5.12	4.48	4.20	3.80	4.14	12.04	6.32	7.19	17.77	6.43	3.58*
45	5.19	5.16	4.98	4.92	5.09	5.05	9.02	5.95	3.92	12.14	6.03	3.76*
46	5.48	4.21	4.31	3.23	3.34	3.37	5.31	7.03	2.59	2.39	4.16	2.12*
47	11.01	7.22	9.10	7.35	6.34*	7.35	9.51	6.78	10.16	17.27	6.63	7.40
48	8.36	7.29	7.82	7.74	7.58	7.82	20.14	18.46	5.71*	15.38	12.22	5.79
49	8.63	8.45	13.18	10.87	10.67	13.05	8.32	8.58	6.51	5.79	8.31	5.39*
50	12.71	2.13	12.73	2.21	2.12	2.21	24.44	16.68	6.29	25.01	9.04	1.84*
51	7.16	6.97	6.62	6.66	6.66	6.73	9.82	9.29	9.89	7.24	7.42	6.29*
52	4.47	0.86	4.46	0.85	0.59*	0.90	8.11	5.59	5.72	5.59	1.77	0.80
53	7.27	3.66	6.84	3.77	3.59	3.82	17.6	16.74	5.45	9.54	9.24	2.60*
54	15.16	9.42	9.62	7.38	7.07	8.01	27.93	30.22	13.93	18.95	24.18	6.92*

model (global AARD = 12.81), and the worst is Méndez Santiago-Teja model (global AARD = 13.02). The fitting accuracies were improved with Chrastil's subsequent derivations and the increase in the model parameters number, reducing the global AARD from 12.50 to 7.59. It can be observed that in many cases, the del Valle-Aguilera model with 4 adjustable parameters provides a slightly better fit than Chrastil model. Commonly, the Adachi-Lu model with 5 adjustable parameters performs better than del Valle-Aguilera model (overall AARD = 11.98), but it does not perform as well as the del Valle-Aguilera model for No. 27, 30, and 33, especially for No. 8. The results might not be compensated for the effect of temperatures. Further, the Valle-Aguilera model is worse than the Ch-Madras model (AARD = 9.78). The reason may be that the latter considered the influence of pressure on the solubility. In addition, a comparison between Adachi-Lu model and Sparks model (Eq. (4)) both with 5 adjustable parameters demonstrates that, in many cases, the former provides lower errors than the latter except for No. 8, 24, 27, 33, 46 and 54. We assumed that these might be caused by the higher effect of the SC-CO_2 density and lower effect of the temperature in the studied systems. Compared to the other models with 5 adjustable parameters, the Garlapati-Madras model does not improve the correlated accuracy for the solubility data in this study.

It also can be seen from Table 2 that, the Sparks model (Eq. (5)) with 6 adjustable parameters is superior to the Adachi-Lu model for most of compounds, with the exception of the No. 25, 42, 48, and 49. The reason is that Eq. (5) conducted a combination of the Adachi-Lu and del Valle-Aguilera equation, correcting the effect of both density and temperature on solubility. Moreover, Eq. (5) is also superior to Eq. (4) for majority of compounds. In addition, the

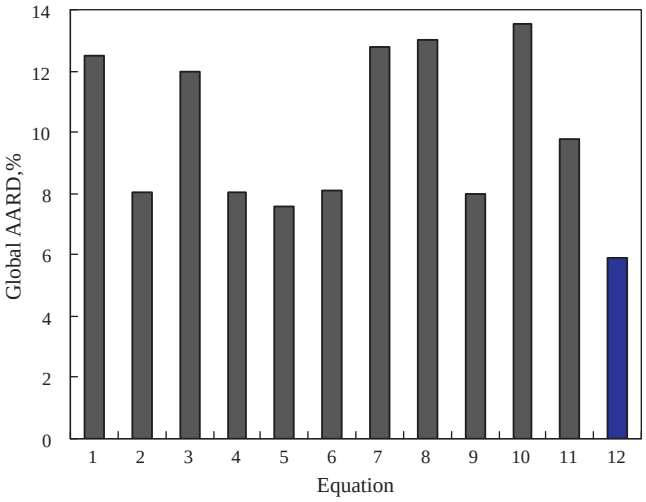

Fig. 1. Overall AARD of different models. 1: Chrastil model; 2: Adachi-Lu model; 3: del Valle-Aguilera model; 4: Sparks model; 5: Sparks model; 6: Garlapati-Madras model; 7: Kumar-Johnston model; 8: Méndez Santiago-Teja model; 9: Jouyban model; 10; Gordillo model; 11: Ch-Madras model; 12: The proposed model.

equation proposed by Jouyban et al. (Eq. (9)) is superior to the existing models except for Sparks model (Eq. (5)), in line with previous work [11].

From Table 2 and Fig. 1, it is important to notice that, although the newly proposed model has 6 adjustable parameters, it does correlate the solubility of compounds in SC-CO_2 better than that of all existing model considered in this study. Herein, for 29 of the 54 compounds, the proposed model produced the best fit, for 10 of the 54 compounds, the Sparks model (Eq. (5)) provided the best fit, and for 9 of the 54 compounds, the Jouyban model obtained the best fit. That is, the presented equation is the best empirical model, and the Sparks equation (Eq. (5)) or Jouyban equation could be used instead of the proposed equation for some compounds. The reason is because the presented model considered the effect of temperature and density not only on the average association number, but also on the enthalpy of solvation and enthalpy of vaporization. It should be also noticed that some data sets (such as No. 9, 10, 14 and 24) produced relatively higher AARD values for all models.

In a word, the proposed equation is the best for correlation of solubility of compounds in SC-CO_2 compared to other equations in this study, the following order is Sparks equation (Eq. (5)), Jouyban equation, Adachi-Lu equation, Sparks equation (Eq. (4)) and Garlapati-Madras equation. And the corresponding mean AARDs are 5.91, 7.59, 7.96, 8.04, 8.05, and 8.12, respectively. The other models are relatively poor.

6. Conclusions

The 11 most common empirical models used in correlation of solubility in SC-CO_2 were evaluated for 54 compounds. Among previously published models, Sparks model (Eq. (5)) produced the lowest mean AARD, the second was the Jouyban model, while the worst was Gordillo model. In addition, a new density-based formulation was proposed here in which the effect of temperature and density both on the average association number and on the enthalpy of solvation and vaporization are considered. The newly presented model was found to correlate the solubility better than all the existing empirical models considered.

Acknowledgements

The authors wish to acknowledge anonymous reviewers for constructive comments and suggestions for improving this paper. The authors also wish to thank the anonymous Associate Editor for his handling of the manuscript and additional suggestions. This work was supported by National Science and Technology Major Project of PR China (No. 2008ZX05016-001) and National Natural Science Foundation of China (No. 50774062).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2011.02.023.

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