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Modified mass action law-based model to correlate the solubility of solids and liquids in entrained supercritical carbon dioxide

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Abstract

The solubility of solids and liquids in supercritical CO₂ with added entrainers was modeled with a modified version of the equation of Chrastil to include the effect of entrainers. By considering the formation of the solute–entrainer–solvent complexes an equation is obtained which predicts an exponential increase of solubility with fluid density and/or entrainer concentration. The correlating model was tested by non-linear regression through a computerized iterative process for several systems where an entrainer was present. Four experimental parameters are easily regressed from experimental data, hence the corresponding properties of components such as chemical potentials or critical parameters are not needed. Instead of its simplicity, this thermodynamical model provided a good correlation of the solubility enhancement in the presence of entrainer effect. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermodynamic parameters; Solubility; Mathematical modelling; Supercritical fluid extraction

1. Introduction

The design and optimization of supercritical fluid extraction processes depend on knowledge of solubility data, hence correlation and predictive techniques are needed to model solubility behavior. Currently used models include the application of the solubility parameter concept [1–3], equation of state methods [4–8], computer simulations [9,10], neural

networks [11] and an array of thermodynamic models [12–14], in addition to purely empirical methods [15,16] to account for the solubility behavior of a solute in pure supercritical fluids. Considerable success has been achieved by applying the solubility parameter concept for structurally-simple solutes, because the use of many equation of state (cubic and virial) methods requires many physical parameters of pure components that are currently unknown. Among the other methods used to correlate solubility data is the association law-based method of Chrastil [13,17,18] because of its simplicity and agreement with experimental data.

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A further challenge for modeling these systems has emerged because of the special advantages of adding cosolvents to supercritical carbon dioxide: Low concentrations of cosolvents added to the supercritical fluid specifically interact with the solute improving the selectivity and economics of the extraction process. However to date, just a few models have been developed to explain the solubility behavior in supercritical fluids with entrainers. Some equation of state-based models have been combined with chemical association or intermolecular potential (computer simulation) premises, but the solution to such equations requires pure component parameters which are usually unknown for the solutes [6,7,10,19]. The same drawback is observed in other approaches where a theoretical rigorous treatment is not very useful for practical extraction of natural substances with entrained supercritical fluids [20].

In this paper, the thermodynamical method of Chrastil based on the mass-action law was adapted to include the effect of using entrainer solvents. Although the Chrastil equation results are limited to low solubility and temperature intervals (lower than 100 K), it has the advantage of avoiding the determination of the difficult to obtain parameters for equations of state, especially for high-molecular-mass solutes. Despite these limitations, we have used the solubility data of the toxin okadaic acid and other substances in supercritical carbon dioxide modified with entrainers and fit it to the above-described model.

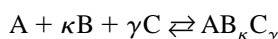
2. Methods

The fitting of the data to the theoretical model was done with the software package STATISTICA 5.0 (StatSoft, Tulsa, OK, USA). The theoretical model was specified and the iterative process was run to get a minimum in the squared differences between the experimental and the predicted values (loss function). The estimation lied in the minimization of the loss function by means of the very effective method of Hooke–Jeeves [21] followed by quasi-Newton type iterations. The standard error of the parameters was estimated via finite difference approximation of the second-order partial derivatives. The program

checks the ‘responsiveness’ of the loss function to small changes in the parameter values.

3. Theoretical

Solubilization of the solute in supercritical carbon dioxide modified with entrainer is assumed to occur because each molecule of solute associates with κ molecules of carbon dioxide and γ molecules of entrainer C:



where A = solute, B = carbon dioxide and C = entrainer. This model assumes that there is not a significant solubilization in the absence of the entrainer, or that the solubility in pure carbon dioxide is negligible with respect to that in the presence of entrainer.

The equilibrium constant for the process is:

$$K = \frac{[AB_{\kappa}C_{\gamma}]}{[A][B]^{\kappa}[C]^{\gamma}} \quad \text{or} \quad \ln K + \ln [A] + \kappa \ln [B] + \gamma \ln [C] = \ln [AB_{\kappa}C_{\gamma}] \quad (1)$$

where [A] is the molar vapor concentration of solute, [B] the molar concentration of carbon dioxide and [C] the molar concentration of entrainer and $[AB_{\kappa}C_{\gamma}]$ is the molar concentration of the solvato complex formed.

The equilibrium constant can be expressed as:

$$\ln K = -\frac{\Delta G_{\text{solvation}}}{RT} + q_s$$

where $\Delta G_{\text{solvation}}$ = Gibbs free energy of solvation, R = gas constant and T = Temperature, if no high temperature or a constant variation of entropy are assumed, K can be finally approximated as:

$$\ln K \cong -\frac{\Delta H_{\text{solvation}}}{RT} + q_s$$

where $\Delta H_{\text{solvation}}$: Enthalpy of solvation, or

$$K \cong e^{\left(\frac{\Delta H_{\text{solvation}}}{RT}\right)} + q_s \quad (2)$$

where q_s is a constant. The molar vapor concentration of solute term, [A], can be approximated by the Clausius–Clapeyron equation for the solid–gas equilibrium where a constant value of $\Delta H_{\text{vaporization}}$

was assumed (valid assumption for a limited range of temperature, not higher than 100 K):

$$\ln [A] \cong \frac{\Delta H_{\text{vaporization}}}{RT} + q_v \quad (3)$$

where q_v is a constant.

Substitution of Eqs. (2) and (3) in Eq. (1):

$$-\frac{\Delta H_{\text{total}}}{RT} + q + k \ln [B] + \gamma \ln [C] = \ln [AB_\kappa C\gamma]$$

where ΔH is the total reaction enthalpy; $q = q_s + q_v$.

If all concentrations are converted to g/l:

$$-\frac{\Delta H_{\text{total}}}{RT} + q + (k \ln d - k \ln M_B - k \ln \gamma M_C) + \gamma \ln m = \ln s - \ln (M_A + kM_B + \gamma M_C)$$

where s = solubility of the solute (g/l), d = density of carbon dioxide (g/l), m = concentration of entrainer (g/l) and M_A , M_B and M_C are the molecular mass of A, B and C.

Hence

$$\ln s = -\frac{\Delta H_{\text{total}}}{RT} + q + k \ln d - k \ln M_B - k \ln \gamma - k \ln M_C + \gamma \ln m + \ln (M_A + kM_B + \gamma M_C)$$

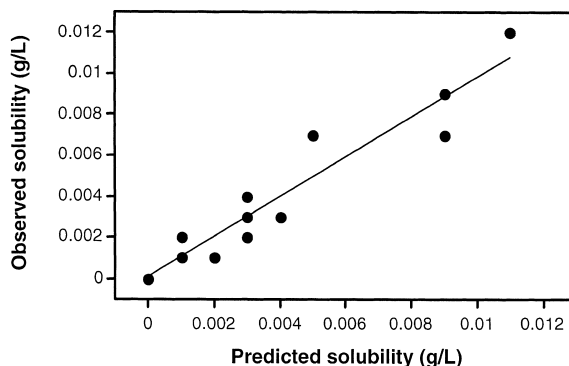
and thus

$$s = d^k m^\gamma e^{(a/T+b)}$$

where $a = \Delta H_{\text{total}}/R$, $b = q - k \ln M_B - k \ln \gamma - k \ln M_C + \ln (M_A + kM_B + \gamma M_C) = \text{constant}$, k = association number of carbon dioxide and γ = association number of entrainer

4. Results

This model was initially developed to explain the solubility behavior of the polyether toxin okadaic acid in CO₂–methanol [22]. Since this solute showed a negligible solubility in the absence of the entrainer, the model hypothesis of the participation of the entrainer in the solvato complex described by Chras-til seemed appropriate. The solute solubility increases exponentially with the density of the supercritical fluid and the concentration of methanol. Estimated parameters and their statistical significance are shown along with a predicted versus observed solubility plot (Fig. 1). The estimated value of the

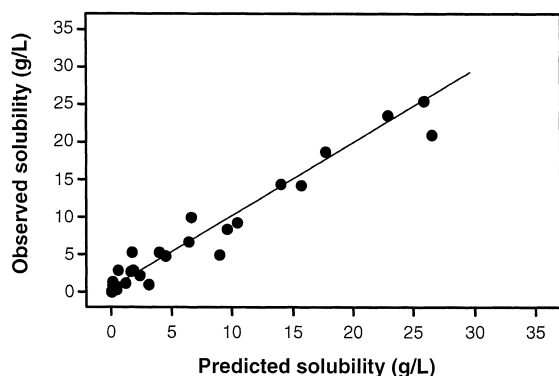


	κ	γ	a	b
Estimate	3.15552	2.23308	5951.617	-54.392
Std.Err.	0.04722	0.09673	121.241	0.499
t(13)	66.81987	23.08470	49.089	-108.974
p-level	0.00000	0.00000	0.000	0.000

Fig. 1. Regression summary and model constants for the okadaic acid–methanol–CO₂ system. The regression equation is $y = 9.1171 \cdot 10^{-5} + 0.97281x$, $R = 0.95732$.

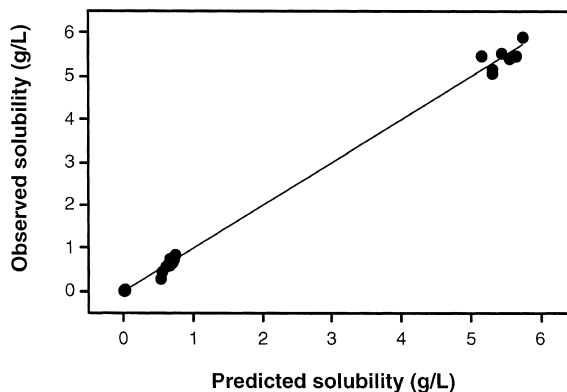
parameter $a = \Delta H_{\text{total}}/R$ is equivalent to a total variation of enthalpy of -49 ± 1 kJ/mol (exothermic) is in accordance with the observation of lower solute solubility at higher temperature in the range studied. The parameter $a + \Delta H_{\text{total}}/R$ has always been negative (endothermic process) for other substances in entrainer-free solvents [13]. Nevertheless, the process could obviously become exothermic with a strong (exothermic) interaction solute–entrainer, as is expected in this case where a strong enhancement was observed in the presence of the entrainer. Unfortunately there is no other independent literature solubility data of this solute for comparison.

The general application of the model was tested later with data from other authors. Solubility data was obtained over a significant range of temperature, CO₂ density and entrainer concentration for the acridine–CO₂–methanol [23], stearic acid–CO₂–methanol [12] and hydroquinon–CO₂–TBP systems [7] (TBP tri-*N*-butyl phosphate). In every case, experimental data agreed well with predicted solubilities as is demonstrated by the linear correlation between predicted and experimental values in Figs. 2–4. The observation that in the acridine–CO₂–methanol system virtually all the acridine molecules



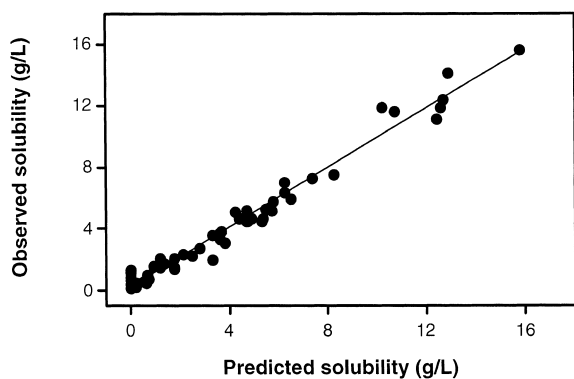
	κ	γ	a	b
Estimate	7.2209	0.279636	-2261.21	-39.7535
Std.Err.	0.0084	0.087595	954.67	4.8306
t(25)	859.7540	3.192363	-2.37	-8.2295
p-level	0.0000	0.003786	0.03	0.0000

Fig. 2. Regression summary and model constants for the acridine–methanol–CO₂ system. The regression equation is $y = 0.56076 + 0.969251x$, $R = 0.97494$.



	κ	γ	a	b
Estimate	-0.95303	1.92828	-1451.09	17.52492
Std.Err.	0.23060	0.07236	675.50	3.02392
t(31)	-4.13292	26.64884	-2.15	5.79544
p-level	0.00025	0.00000	0.04	0.00000

Fig. 4. Regression summary and model constants for the hydroquinone–TBP–CO₂ system. The regression equation is $y = 0.0096126 + 0.99791x$, $R = 0.9988$.



	κ	γ	a	b
Estimate	1.854705	1.43738	-6614.23	6.098376
Std.Err.	0.255421	0.05715	881.73	2.312877
t(49)	7.261365	25.15160	-7.50	2.636706
p-level	0.000000	0.00000	0.00	0.011183

Fig. 3. Regression summary and model constants for the stearic acid–ethanol–CO₂ system. The regression equation is $y = 0.27415 + 0.965581x$, $R = 0.98818$.

are interacting in methanol–acridine complexes [20,23], is in accordance with this model (Fig. 2). The reported stearic acid solubility data from two authors [12,24] (at different temperatures) were pooled and regressed with this model. Stearic acid solubility in pure CO₂ is quite significant but the large enhancement observed in the presence of the ethanol gives validity to the correlating performance of the proposed model when the entrainer is present (Fig. 3). The strong enhancement of hydroquinone solubility in CO₂ with TBP was attributed to the formation of a complex hydroquinone–TBP₂; Similar estimates and good correlation were obtained with the model proposed in this paper, which suggest no participation of CO₂ ($\kappa=0$) although in this case the estimation was more questionable since the data were not well distributed for the regression to be robust (Fig. 4).

Table 1 shows the results obtained with four entrained systems. Further solubility data from the literature [12,15,23] obtained at constant temperature were used to partially validate this action law-based model by reducing the exponential term of the equation to a constant. In this way, only the effect of

Table 1

Experimental conditions, model constants and fitting performance of the modified model for four entrained systems^a

Compound	Entrainer	Entrainer range (g/l)	Density range (g/l)	Temperature range (K)	κ	γ	a	b	V. expl (%)	A.A.R.D. (%)	Ref.
Okadaic acid ($N=17$)	Methanol	0–67	495–913	313–343	3.1	2.2	6000	–45	95.2	23.4	[22]
Acridine ($N=29$)	Methanol	2.4–25.4	336–897	323–343	7.2	0.3	–2200	–39	94.8	40.6	[23]
Hydroquinone ($N=35$)	TBP	$3 \cdot 10^{-5}$ – $9.6 \cdot 10^{-2}$	587–965	308–333	0	1.8	–900	9	99.6	37.3	[7]
Stearic acid ($N=53$)	Ethanol	0–53	462–863	308–318	1.8	1.4	–6000	6	97.4	26.9	[24,12]

^a N : Number of solubility data points. V. expl.: Variance of the data explained by the model. A.A.R.D.: Average absolute relative deviation.

CO₂ density and entrainer concentration were considered and the enthalpic parameter **a** and the constant **b** could not be estimated. The fitting performance of the truncated model is summarized in Table 2. Statistical significance of the obtained parameters is not available due to the limited data to be regressed. The systems that are best described by the model (top of the table) are those that show higher solubility enhancement when the entrainer is present (Fig. 5) e.g., palmitic and stearic acid with methanol or octane (polar or hydrophobic interac-

tions respectively occurs); stearyl alcohol with ethanol; phenanthrene, fluorene and 9-fluorenone with acetone.

The model shows the worst correlating behavior in those systems (bottom of Table 2) where the entrainer did not cause a significant increase in solubility (Fig. 6). An exception to this rule was the system squalene–CO₂–methanol. A significant entrainer effect was observed but the abnormal positive deviation of an extreme value negatively affected the fitting performance of the regression of only 10

Table 2

Experimental conditions and fitting performance of the model at isothermal conditions^a

Compound	Entrainer	Entrainer range (g/l)	Density range (g/l)	κ	γ	V.expl (%)	A.A.R.D (%)	Ref.
Palmitic acid ($N \sim 22$)	Ethanol	0–53	710–863	0.6	1.7	98.6	22.5	[12]
Palmitic acid ($N=22$)	Octane	0–134	710–863	0.2	1.9	98.3	25.5	[12]
Stearic acid ($N=20$)	Octane	0–154	710–863	2.2	1.5	97.9	25.0	[12]
Phenanthrene ($N=14$)	Acetone	6–30	431–946	4.0	0.7	96.7	18.4	[23]
Stearyl alcohol ($N=22$)	Ethanol	0–81	710–863	1.9	1.2	95.9	26.5	[12]
Spiny dogfish ($N=12$)	Ethanol	29–72	724–832	5.8	1.0	95.4	14.7	[15]
Fluorene ($N=13$)	Acetone	6–30	449–898	4.0	0.6	95.3	22.0	[23]
Dibenzofuran ($N=13$)	Methanol	2–16	336–897	6.0	0.1	94.8	31.2	[23]
9-Fluorenone ($N=13$)	Acetone	6–28	433–897	6.2	0.7	94.8	31.5	[23]
Acridine ($N=25$)	Acetone	0–30	431–915	5.8	0.0	94.0	53.4	[23]
Phenanthrene ($N=23$)	Methanol	3–25	431–897	6.0	0.9	93.7	43.8	[23]
Cod liver oil ($N=12$)	Ethanol	30–78	724–832	5.9	1.0	93.0	20.1	[15]
Stearyl alcohol ($N=20$)	Octane	0–134	710–863	1.2	0.9	92.1	20.8	[12]
Dibenzofuran ($N=13$)	Acetone	6–30	432–897	4.2	0.1	90.1	31.9	[23]
Orange roughy ($N=12$)	Ethanol	0–81	724–832	5.8	1.1	89.7	31.6	[15]
Cetyl alcohol ($N=18$)	Octane	0–86	710–863	2.0	0.6	88.3	20.2	[12]
Squalene ($N=10$)	Ethanol	29–87	724–812	6.2	1.0	85.5	14.4	[15]
Cetyl alcohol ($N=15$)	Ethanol	0–31	710–863	3.7	0.3	78.9	18.5	[12]
9-Fluorenone ($N=22$)	Methanol	0–16	336–915	5.9	0.4	43.8	58.9	[23]
Phenazine ($N=14$)	Acetone	0–30	432–897	Estimation did not converge				[23]
Phenazine ($N=14$)	Methanol	0–16	431–897	Estimation did not converge				[23]

^a The effect of temperature was unknown in the reference data sets. (N : Number of solubility data points. V. expl.: Variance of the data explained by the model. A.A.R.D.: Average absolute relative deviation).

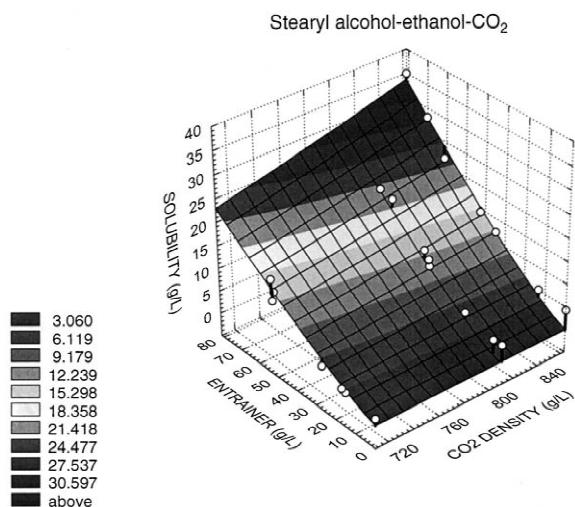


Fig. 5. The entrainer effect in the system stearyl alcohol–ethanol–CO₂.

solubility measurements. Examples of the systems well described by the proposed model are: 9-fluorenone with methanol or dibenzofuran with acetone. However, strong conclusions cannot be reached from this data set due to the limited availability of the data to be regressed. However, such

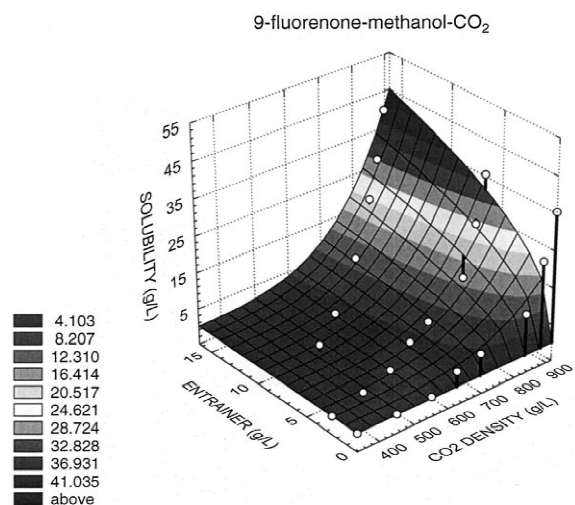


Fig. 6. Effect of methanol concentration and CO₂ density on 9-fluorenone solubility. No entrainer effect is observed.

systems support the usefulness of the model and its ability to correlate solubility data from systems where a strong interaction entrainer–solute produces significant solubility enhancement.

5. Discussion

Modeling solubility behavior in supercritical fluids requires additional study. Predictive models are useful tools in theoretical research but their applicability is very limited in real systems consisting of complex solutes and entrainers. Among the diverse array of correlating models, the thermodynamical method of Chrastil based on the mass-action law has been useful for modeling solute solubility in non-entrained supercritical fluids. The modification of this model presented here showed also a good ability correlation in systems where the entrainer caused a significant enhancement of solute solubility, i.e. systems with a strong solute–entrainer interaction.

The above model combines the usually observed log fluid density dependence of solubility with the exponential relationship between solubility and cosolvent concentration that has also been previously shown [6,25]. Obviously, this is not a universal model and its suitability is restricted to supercritical systems with entrainer effect and in a limited range of temperature. We agree with those authors that sometimes had questioned the physical significance of the parameters of the Chrastil model [26], particularly the meaning of the enthalpic parameter *a*. Nevertheless, the main hypothesis of the model, the formation of clusters or solvato complexes between the solute, the entrainer and also the solvent agrees with the negative contribution of temperature to the solubility of okadaic acid. This is also true for the complexing of hydroquinone with TBP and the spectroscopically-observed interaction of acridine and methanol. Therefore, the model is not expected to yield good correlations in systems where the cosolvent added to CO₂ just acts as a cosolvent but without displaying the entrainer effect that could otherwise enhance both the solubility and the selectivity of the extraction.

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