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Description of the solubilities of solids in supercritical fluids¹

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Abstract

The ability to predict the solubility of solids in supercritical fluids is very important in understanding supercritical fluid extraction. An empirical method for predicting solubility solely as a function of temperature and pressure is developed. It describes the following solid substances: anthracene, 2,3-dimethylnaphthalene, 2,6-dimethylnaphthalene, fluorene, hexachlorethane, hexamethylbenzene, naphthalene, phenanthrene, phenylbenzene, pyrene, triphenylmethane. Carbon dioxide, ethane and ethene are used as fluids. © 1997 Elsevier Science B.V.

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1. Introduction

In September 1996 there were 170 000 areas which were classified as suspiciously polluted in Germany [1]. The pollution problem in many of those areas is urgent. In the long run all these areas must be rectified step-by-step. Various thermal, microbiological and chemical-physical methods can be used to treat the polluted soil. Although there are many available methods, many pollutants could not be removed from the soil at a reasonable cost and without permanent damage to the soil. Supercritical fluid extraction (SFE), is a prospective new chemical-physical method for separations, which could not be realized until now. In order to calculate and optimize the process of high-pressure extraction for soil rectifications, a topological oriented flowsheet simulation program was developed in our Institute.

The simulator must realize the following: (i) recognize and estimate the fields of realization of this technology; (ii) carry out a feasibility study before experimental examination; (iii) reduce the time for developing the process (minimizing the costly experiments); (iv) reduce the process costs (optimization of the structure, the apparatus and the process variables); (v) evaluate the process.

One of the fundamental aspects of the model of the process is the calculation of the solubilities of solid substances in supercritical fluids. Many models have been proposed for such calculations (see Table 1). A brief description of these models is given by Johnston et al. [2].

The disadvantage of these models lies in that the corresponding properties of substances are necessary. Unfortunately, for various polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and some other substances, such data are not available or very inconsistent. Therefore, systems including those substances cannot be calculated and simulation of such systems is impossible. A possible

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Table 1
Models for the descriptions of solid–fluid systems

Model type	Ref.
Cubic equation of state	[3]
Mean field	[4]
Carnahan–Starling Van der Waals	[5]
Hard-sphere Van der Waals	[6]
Augmented Van der Waals	[7]
Density-dependent local composition mixing rules	[8]
Perturbed hard-chain theory	[9]
Kirkwood–Buff	[10]
Monte Carlo	[11]
Lattice	[12]
Correlation	[13]

way to describe solubilities is by the correlation of the measurement values. Using the model of Schmitt and Reid [13] it is possible to interpolate the experimental results with the following equation.

$$y_2 = \frac{p_2^{\text{vap}}}{p} 10^{[\alpha \rho_r + \beta + \sigma(T - T_{\text{ref}})]} \quad (1)$$

with

$$\rho_r = \frac{\rho}{\rho_c} \quad (2)$$

The parameters α , β and σ are correlated with the experimental results. The problem lies in the consideration of the vapor pressure p_2^{vap} and the density ρ . The model can not be used in general because of the large influence of the density value. The density appears in the exponent of Eq. (1), so small variations in the density lead to higher variations in the solubility. The accuracy of this model is low because only four parameters are used.

2. Results and discussion

A model can be developed on the basis of the experimental values by minimizing the average quadratic deviation. The vectors \mathbf{P} , \mathbf{T} and \mathbf{Y} are formed from the results of triplicate experiments ($n \gg 16$).

$$\text{measurement values} = \{p_i, T_i, y_i | i = 0..n - 1\} \quad (3)$$

The vector \mathbf{F} for the compensation can be built depending on p and T with sixteen components.

$$\mathbf{F}(p, T) = \left(1, e^{-\frac{p}{10}}, e^{-\frac{2 * p}{10}}, e^{-\frac{3 * p}{10}}, T, T * e^{-\frac{p}{10}}, T * e^{-\frac{2 * p}{10}}, T * e^{-\frac{3 * p}{10}}, T^2, T^2 * e^{-\frac{p}{10}}, T^2 * e^{-\frac{2 * p}{10}}, T^2 * e^{-\frac{3 * p}{10}}, T^3, T^3 * e^{-\frac{p}{10}}, T^3 * e^{-\frac{2 * p}{10}}, T^3 * e^{-\frac{3 * p}{10}} \right)^T \quad (4)$$

With the matrix \mathbf{M} (16 lines and n columns)

$$\mathbf{M}^{<i>} = \mathbf{F}(p_i, T_i) \quad (5)$$

it is possible to obtain the vector \mathbf{A} of the model parameter.

$$\mathbf{A} = (\mathbf{M}\mathbf{M}^T)^{-1} \mathbf{M}\mathbf{Y} \quad (6)$$

The final model is

$$y = \mathbf{A}^T \mathbf{F}(p, T) \quad (7)$$

The units of pressure and temperature in the equation are MPa and °C, respectively. The solubility result is to be given in 10^4 kmol/kmol. The measurement values, on which the calculation is based, are obtained from the literature [7,15–18]. The solid substances involved are shown in Fig. 1 and some correlated solid–fluid systems are shown in Tables 2–4.

The correlated results are assessed by using a naphthalene–ethane system as an example and they are shown in Table 5. It should be noted that the values compared are not those directly correlated but are the end results calculated from the correlated function. It can be seen that the maximum deviations are about -6.2% . Because the measurement errors from the literature are about 5% , the estimated solubilities by this method is very good. It is even better than the model of Schmitt and Reid which uses the literature value.

If the data of substances are unknown it is possible to predict the solubility with neural nets. An example is given in the literature [14]. The solubility models, neural nets and the correlation of the measurements are used in the simulator. Such an interdisciplinary developed simulation program, besides calculating solubilities should consider many other aspects such as: (i) description of the soil and the pollutants; (ii) development of state-models; (iii) creation of a data base with the required substance properties; (iv) development of elements (solid substances processes, SFE, substance-separation etc.); (v) development of

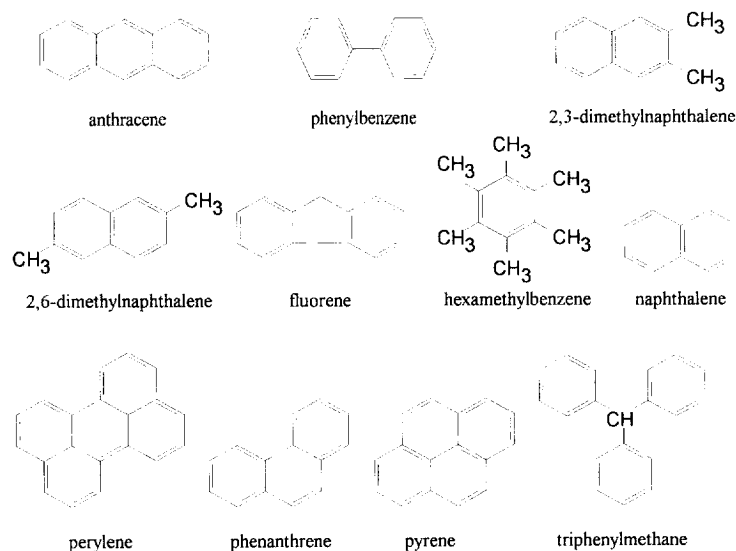


Fig. 1. Structural formulas of solid substances involved.

Table 2
Coefficients of the correlation model

	Anthracene Carbon dioxide	Anthracene Ethane	2,3-Dimethyl- naphthalene Carbon dioxide	2,6-Dimethyl- naphthalene Carbon dioxide	2,3-Dimethyl- naphthalene Ethene	2,6-Dimethyl- naphthalene Ethene	Fluorene Carbon dioxide
T_{\min} (°C)	30	30	35	35	35	35	30
T_{\max} (°C)	70	70	55	55	55	55	70
p_{\min} (MPa)	10	10.5	9.9	9.8	8	7.8	7.4
p_{\max} (MPa)	41.5	41.5	28	28	28	28	41.5
a_1	1.86451267	1.06392194	288.319817	-61.7055331	2732.15486	341.469347	-22.1627695
a_2	-37.874545	300.393389	-3406.47833	490.501649	-30848.2786	-3078.95208	1037.97234
a_3	198.015724	-2499.79824	11 104.4229	-4847.08496	111 288.046	10 255.6135	-8173.26605
a_4	-272.195185	4204.70917	-9808.20226	13 289.6490	-125 044.852	-10 968.6375	14 865.2332
a_5	-0.0804764636	-0.0322336632	-10.6.655473	2.51523815	-141.981154	-18.3112758	2.70693437
a_6	1.86294933	-19.9814400	142.721653	-3.35257430	1651.45885	191.887677	-81.8543852
a_7	-8.97643944	168.410731	-423.257852	136.920558	-6011.14797	-656.410958	612.831777
a_8	11.3578333	-288.566074	296.933194	-489.598705	6768.22578	697.409700	-1080.36758
a_9	0.00154526475	0.00153341168	0.131555435	0.0181865219	1.99384776	0.368864236	-0.0594163541
a_{10}	-0.0234796089	0.410470673	-1.50451109	-0.368345306	-22.8264357	-3.62657050	2.05233145
a_{11}	0.0949014731	-3.51614613	3.75524367	0.0298289325	82.2307167	11.7269714	-14.6359172
a_{12}	-0.106762437	6.11507706	-1.79303235	3.17860096	-91.9933327	-12.0355373	24.8114993
a_{13}	0 ^a	6.50178915 · 10 ⁻⁶	0 ^a	0 ^a	0 ^a	0 ^a	6.39584128 · 10 ⁻⁴
a_{14}	0 ^a	-0.00283258217	0 ^a	0 ^a	0 ^a	0 ^a	-0.0173048848
a_{15}	0 ^a	0.0238148157	0 ^a	0 ^a	0 ^a	0 ^a	0.110995514
a_{16}	0 ^a	-0.0418006777	0 ^a	0 ^a	0 ^a	0 ^a	-0.179105176

^a Coefficients were set 0.

Table 3
Coefficients of the correlation model

	Fluorene Ethene	Hexachlorethane Carbon dioxide	Hexamethylbenzene Carbon dioxide	Hexamethylbenzene Ethene	Naphthalene Carbon dioxide	Naphthalene Ethane	Naphthalene Ethene
T_{\min} (°C)	25	35	30	25	35	20	12
T_{\max} (°C)	70	55	70	70	55	45	45
p_{\min} (MPa)	7	10	7.4	7.5	13	5	5.5
p_{\max} (MPa)	48.5	28	35	34.5	33	20	30
a_1	100.149464	-1863.55293	34.1416373	59.8625196	1472.43997	1117.02184	-113.184005
a_2	-1081.81326	46074.2703	-716.261403	-691.368056	-11 930.9506	-17 277.7934	982.011327
a_3	4194.77923	-274 996.013	3299.19542	2756.80749	26 374.9684	72 097.8462	-2884.08942
a_4	-4924.69128	447 209.479	-3764.65150	-3159.90736	-9268.97889	-76 590.7276	3249.66372
a_5	-4.32929474	90.5294564	-1.32114654	-1.36671838	-71.2728107	-121.649607	43.5046349
a_6	59.6929289	-2193.25717	32.3349107	32.2862855	548.052174	1891.92060	-240.772296
a_7	-232.575441	13 216.6644	-132.641403	-134.948034	-970.842185	-7653.52994	637.418420
a_8	264.035947	-21 461.4743	134.912718	149.796388	-21.5430589	7992.13954	-661.176259
a_9	0.101405745	-0.951032825	0.0265689579	0.0593826107	0.996552231	-4.79819988	-1.83617233
a_{10}	-1.15922536	25.8637987	-0.362193093	-0.640435554	-6.15676812	-67.4262586	10.8274179
a_{11}	4.04142910	-157.123597	1.16790678	2.04953497	6.65459928	263.010820	-27.4419718
a_{12}	-4.30088022	253.065445	-0.964096008	-1.99870989	7.14990592	-269.427086	25.8216279
a_{13}	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	-0.0540550713	0.0317676986
a_{14}	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0.761265382	-0.170946536
a_{15}	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	-2.90083192	0.353282885
a_{16}	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	2.91241699	-0.271549955

^a Coefficients were set 0.

Table 4
Coefficients of the correlation model

	Phenanthrene Carbon dioxide	Phenanthrene Ethane	Phenanthrene Ethene	Phenylbenzene Carbon dioxide	Pyrene Carbon dioxide	Triphenylmethane Carbon dioxide	Triphenylmethane Ethane
T_{\min} (°C)	30	30	45	35	35	30	30
T_{\max} (°C)	70	60	70	55	70	50	50
p_{\min} (MPa)	10.5	15	12	15	10.5	10	7
p_{\max} (MPa)	41.5	30	28	45	48.5	41.5	27
a_1	-5.71687613	-260.300625	1098.44070	-46 663.7857	1.93502767	-47.8865784	31.5701466
a_2	-426.479983	4413.79766	-8512.70778	1 414 394.09	-46.3570678	1204.29427	126.308911
a_3	2360.47091	-36 456.5896	-93 382.8376	-10 045 621.1	213.032535	-8385.88682	688.091010
a_4	-2660.77460	87 772.5731	736 213.792	21 125 895.4	-165.424337	14 952.3092	-2287.94959
a_5	0.694837153	12.9901703	-89.5384230	3286.01888	-0.0324599940	3.24404062	0.271626866
a_6	17.9991983	-215.650803	965.341913	-98 665.9059	2.22542096	-71.5509491	-24.3451999
a_7	-94.4954546	1802.09245	2625.71965	697 349.756	-9.85559205	495.667665	32.3670617
a_8	94.0872094	-4364.30589	-36822.2125	-1 460 537.38	7.20436578	-880.377633	43.5957277
a_9	3.39338544 · 10 ⁻⁴	-0.122500835	2.17564100	-76.3412669	0.00208183717	-0.0358377293	0.0158920365
a_{10}	-0.200051976	2.28424834	-26.3497315	2269.87093	-0.0384251599	0.981830282	0.342750866
a_{11}	0.795718326	-19.7638705	-3.74165529	-15 946.8058	0.143593994	-7.03489433	-0.907457385
a_{12}	-0.556599290	48.2335685	604.205068	33 234.3724	-0.116950668	12.5011355	0.122375322
a_{13}	0 ^a	0 ^a	-0.0155200622	0.588883058	0 ^a	0 ^a	0 ^a
a_{14}	0 ^a	0 ^a	0.199719955	-17.2426449	0 ^a	0 ^a	0 ^a
a_{15}	0 ^a	0 ^a	-0.191702138	120.223872	0 ^a	0 ^a	0 ^a
a_{16}	0 ^a	0 ^a	-3.30423839	-249.090555	0 ^a	0 ^a	0 ^a

^a Coefficients were set 0.

Table 5
Comparison of the correlation results with measurement values [13]

p (MPa)	T (°C)	Literature value (10^4 kmol/kmol)	Proposed model (10^4 kmol/kmol)	Relative error (%)	Model of Schmitt and Reid (10^4 kmol/kmol)	Relative error (%)
9.15	35	197	207.4	5.26	223.3	13.38
12.05	35	230	242.4	5.38	255.6	11.12
15.08	35	256	271.8	6.16	270.9	5.8
12.05	45	346	353.4	2.14	353.7	2.22
15.07	45	408	418.6	2.60	422.9	3.64
19.90	45	474	459.4	-3.08	482.6	1.80

expenses-models; (vi) development of a graphic surface area; (vii) combination of the surface area, models and substance dependent data (e.g., realization of iterations, giving suitable initial values etc.).

3. List of symbols

a	coefficient of the correlation function (kmol/kmol)
\mathbf{A}	vector of the correlation value
i	count index (1)
\mathbf{M}	matrix
n	number of measurement values (1)
p	pressure (MPa)
p_2^{vap}	solite vapor pressure (Pa)
\mathbf{P}	vector of the pressure values
T	temperature (°C)
T_{ref}	reference temperature (°C)
\mathbf{T}	vector of the temperature values
\mathbf{Y}	vector of the solubility values
y_2	solite solubility (kmol/kmol)
α	slope parameter in the correlation (1)
β	intercept parameter in the correlation (1)
σ	splitting constant in the correlation (K^{-1})
ρ	density (kg/m^3)
ρ_c	critical density (kg/m^3)
ρ_r	reduced density (1)

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