

## **Solubility of solids in supercritical fluids using equations of state - excess Gibbs free energy models.**

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### **ABSTRACT**

Solubilities of several organic solids in four supercritical fluids are calculated with Soave and Peng-Robinson equations of state, incorporating excess Gibbs free energy into the mixing rules, with Heidemann-Kokal, Wong-Sandler and MHV2 procedures. Three excess Gibbs free energy models are used in the mixing rules: NRTL, UNIQUAC and UNIFAC. Furthermore, a comparison between these mixing rules and conventional two-binary-parameter form and modification of the excluded volume parameter in the MHV2 procedure is also presented. The best result were obtained with NRTL model and the Wong-Sandler mixing rule.

keywords: equation of state, supercritical fluids, mixing rules.

### **1. INTRODUCTION**

The design and development of supercritical extraction processes depend on the ability to model and predict the solubilities of solid solutes in supercritical solvents. The prediction is usually difficult due to the large differences in sizes and molecular interactions between the solvent and solute molecules.

Cubic equations of state (EOS), which have been extensively applied in vapor-liquid equilibrium calculations, have been also used in computing the solubilities of solids in supercritical fluids by Johnston et al. (1), Haselow et al. (2). They suggested that there is a need to develop new mixing rules. The prediction for phase equilibria using the EOS- $G^E$  models, combining excess free energy ( $G^E$ ) models and EOS at zero pressure standard state has been actively studied. These mixing rules have been extensively discussed for vapor-liquid equilibria calculations. There have been only scattered attempts to apply these mixing rules to supercritical calculations (Sheng et al. (3)).

The aim of this paper is to explore the feasibility of the three mixing rules: Wong-Sandler (4), Heidemann-Kokal (5) and MHV2 (Dahl-Michelsen (6)) to the solid-fluid equilibria occurring in the binary systems composed of a organic solid and four supercritical fluids, with the calculations of solubility and density of the mixture.

## 2. MIXING RULES

The SRK (Soave (7)) and PR (Peng-Robinson (8)) equations of state, have been used for all mixing rules investigated. The three different mixing rules are extensively described in the references. The results are compared to those using the traditional Van der Waals mixing rules suggested by Soave (9). A modification for the mixing rules of the excluded volume parameter in the MHV2 mixing rule, have been presented. In this case a deviation of the linear combination is considered, with two additional parameters.

The different mixing rules and nomenclature used are described in table 1. The simplex algorithm modified by Nelder-Mead (10) is used to fit the model parameter to experimental solubility.

Table 1  
Models used to compare mixing rules

method	mixing rule	G <sup>E</sup> model	EOS
M1	Wong-Sandler	NRTL	SRK
M2	Wong-Sandler	NRTL	PR
M3	MHV2	NRTL	SRK
M4	MHV2	NRTL	PR
M5	MHV2	UNIFAC	SRK
M6	MHV2	UNIFAC	PR
M7	MHV2	UNIQUAC	SRK
M8	MHV2	UNIQUAC	PR
M9	Heidemann-Kokal	NRTL	SRK
M10	Heidemann-Kokal	NRTL	PR
M11	Heidemann-Kokal	UNIFAC	SRK
M12	Heidemann-Kokal	UNIFAC	PR
M13	Heidemann-Kokal	UNIQUAC	SRK
M14	Heidemann-Kokal	UNIQUAC	PR
M15	Empirical Rules	-	SRK
M16	Empirical Rules	-	PR
M17	MHV2*	NRTL	SRK
M18	MHV2*	NRTL	PR

\* quadratic mixing rules for the covolume-parameter

## 3. RESULTS

In the present study, we tested the validity of the EOS-G<sup>E</sup> models by applying different treatments for 21 binary solid/supercritical fluid systems listed in table 2. In those systems, the supercritical component is one of the following fluids: carbon dioxide, ethane, fluoroform and chlorotrifluoromethane; and the solid component is either a nonpolar compound

(naphthalene, biphenyl or phenanthrene) or a polar compound (acridine, benzoic acid or 1,4-naphthoquinone).

Table 2  
Summary of binary systems studied <sup>a</sup>

mixture (1) / (2)	data points	T (K)	mixture (1) / (2)	data points	T (K)
CO <sub>2</sub> / Phenanthrene	5	318	C <sub>2</sub> H <sub>6</sub> / Acridine	6	308
CO <sub>2</sub> / Benzoic acid	9	308		10	318
	12	318		9	328
	12	328	CClF <sub>3</sub> / Phenanthrene	4	318
	7	343		4	328
CO <sub>2</sub> / 1,4-Naphthoquinone	6	318	CClF <sub>3</sub> / Naphthalene	7	308
	6	328		7	318
	6	343		7	328
CO <sub>2</sub> / Acridine	6	308	CClF <sub>3</sub> / Benzoic acid	6	318
	8	318		7	328
	7	328	CClF <sub>3</sub> / 1,4-Naphthoquinone	6	318
	7	343		6	328
C <sub>2</sub> H <sub>6</sub> / Phenanthrene	6	318	CClF <sub>3</sub> / acridine	5	318
	6	328		5	328
C <sub>2</sub> H <sub>6</sub> / Naphthalene	15	308	CHF <sub>3</sub> / Phenanthrene	4	318
	12	318		4	328
	14	328	CHF <sub>3</sub> / Naphthalene	6	308
C <sub>2</sub> H <sub>6</sub> / Biphenyl	5	308		6	318
	5	318		6	328
C <sub>2</sub> H <sub>6</sub> / Benzoic acid	8	308	CHF <sub>3</sub> / Benzoic acid	5	318
	8	318		5	328
	7	328	CHF <sub>3</sub> / 1,4-Naphthoquinone	6	318
	7	343		6	328
C <sub>2</sub> H <sub>6</sub> / 1,4-Naphthoquinone	7	308	CHF <sub>3</sub> / Acridine	6	318
	7	318		6	328
	7	328	CHF <sub>3</sub> / Anthracene	3	328
	7	343		3	343

<sup>a</sup> Data source: Schmitt-Reid (11)

The pressure range of about 60-360 bar and temperature range from 35-70 °C are involved. Table 3 reports the results of the solubility calculations with 18 selected models. An important point must be emphasized: the Wong-Sandler mixing rule coupled with the UNIQUAC model generated a serious instability such that it was impossible to converge. Table 4 illustrates the variation of solid solubility and mixture density for a typical binary mixture.

Table 3

Average absolute deviation (percent) of solute solubility ( $y$ ) and mixture density ( $\rho$ )

Model	% $y$	% $\rho$	Model	% $y$	% $\rho$
M1	7.25	11.31	M10	23.42	5.78
M2	6.74	5.50	M11	22.09	10.56
M3	26.79	10.78	M12	21.38	8.57
M4	29.55	6.28	M13	20.52	10.88
M5	26.61	11.54	M14	23.60	4.60
M6	29.07	10.59	M15	24.10	10.37
M7	16.64	11.51	M16	26.65	5.59
M8	17.28	6.55	M17	19.36	8.96
M9	21.95	10.42	M18	12.94	3.11

Table 4

CO<sub>2</sub>/ACRIDINE - performance for solute solubility ( $y$ ) and mixture density ( $\rho$ )

Model	% $y$	% $\rho$	Model	% $y$	% $\rho$
M1	4.45	14.61	M10	13.68	3.86
M2	4.26	5.10	M11	13.63	18.81
M3	11.56	14.42	M12	14.05	3.86
M4	17.62	5.07	M13	13.06	8.87
M5	13.62	10.80	M14	20.76	3.32
M6	17.78	5.07	M15	13.74	14.30
M7	10.83	8.86	M16	14.38	5.17
M8	16.15	4.06	M17	8.96	10.81
M9	13.51	14.41	M18	7.41	3.84

#### 4. CONCLUSIONS

The following comments summarize our observations on the performance of these mixing rules:

1. The most successful method is M2, with a 6.4% mean deviation in solid solubility;
2. Regarding the solid solubility, the EOS influence is inconclusive (for some mixing rules Peng-Robinson was the best, while for others ones, Soave);
3. Soave equation gives rather deviations in mixture density with all mixing rules;
4. Wong-Sandler mixing rule is extremely sensitive to the initial parameters estimation, such that with the UNIQUAC method it was not capable to converge in most of the mixtures;
5. In order to use the UNIQUAC pure parameters in all the mixing rules, it was necessary to regress them, because its value obtained from group contribution did not perform well;

6. Attempts to use the  $G^E$  interaction parameters available in literature did not work, neither as initial estimation;
7. We use the quadratic mixing rule for the covolume parameter in the MHV2 method, instead of the original linear development. This modification largely increases the performance, as can be noticed on table 4, when we compared the prediction of M3 and M17 methods, as well as M4 and M18 methods;
8. Comparing two adjustable parameters only, the classical mixing rules (M15, M16 methods) give the same performance as more complicated rules (M9, M10, M3 and M4 methods);
9. It should be noted that as temperature increases, it does not mean a corresponding increase in the average absolute deviation solubility;
10. The results given in table 3 clearly indicate the lack of relationship between mixture density and solid solubility quality calculations;
11. To attempt phase equilibria predictions in regions where experimental results are not available, methods with no adjustable parameters for each binary system can be analyzed (M5, M6, M11 and M12). The M12 method provides better predictions.

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