

PREDICTION OF SOLUBILITY OF SOLID *n*-PARAFFINS IN SUPERCRITICAL FLUIDS USING MODIFIED REDLICH-KWONG EQUATIONS OF STATE

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Abstract

Three equations of state are used to predict solubilities of solid *n*-paraffins in supercritical fluids. The equations are the Redlich-Kwong, the Soave-Redlich-Kwong, and the equation proposed by Hartono *et al.* (2003; 2004). Both the last two equations were formed by modifying the Redlich-Kwong equation of state. With the binary interaction parameter, k_{ij} , equals zero, the equation proposed by Hartono *et al.* is better than both the Redlich-Kwong and the Soave-Redlich-Kwong equations of state are. Upon optimization with k_{ij} as the adjustable parameter, the equation of state proposed by Hartono *et al.* is closer to the experimental data than the other two equations are. For 142 data points of 12 systems the equation proposed by Hartono *et al.* gives the average deviation of 36.6%, while the Redlich-Kwong and the Soave-Redlich-Kwong give 66.7% and 65.8%, respectively.

Key words: equation of state, solubility, supercritical

Introduction

Supercritical fluid extraction is a separation process that uses supercritical fluid, instead of liquid, as the separating agent. This process has gained much attention during these last few decades. Its principal advantage over conventional separation process is that separation can be accomplished at moderate temperatures. In consequences it can be applied to the recovery of heat-labile substances of low volatility.

The advantages of utilizing supercritical fluid to perform extractions have been well documented (Williams, 1981; Schutz *et al.*, 1991). One of the most attractive features of supercritical fluid is that the isothermal compressibility is several orders of magnitude greater than that of liquid, and its density is nearly equal to that of liquid at normal condition. Since the solvating power of supercritical fluid is directly related to its relative density, the extraction and separation can be accomplished by slightly manipulating process conditions. In comparison with liquid solvent, the supercritical fluid has high diffusivity and low viscosity, allowing faster extraction and separation processes.

The application of extraction and separation technique using supercritical fluid needs sufficient understanding of phase behavior in the vicinity of and above the critical point. At supercritical condition, the phase behavior is highly sensitive to the temperature and pressure changes. An equation of state (EOS) can explain this phenomenon.

Equation of state

Equations of states are widely used in supercritical phase equilibria calculations, including the calculation of solubility of solid in supercritical

fluid. For the purpose of calculation, the critical temperatures and pressures of all components are needed. Experimental data of such properties for gas component are abundantly available in the literature, but not for the solid components. Such data for most solids are not available, as the experimental measurements are impossible to be carried out. One of the reasons is the instability of the compound at high temperature. However, methods for prediction of critical properties are available in the literature. Several equations of state such as the Soave-Redlich-Kwong (SRK) and the Peng-Robinson (PR) need other physical property, the acentric factor. Such data for solid compounds are hardly found. The acentric factor can be estimated using a correlation proposed by Lee and Kesler (Lyman *et al.*, 1990). However this correlation involves critical temperature and pressure which must be estimated prior to the estimation of the acentric factor.

The equations of state that are widely used in the solid-vapor equilibrium calculation are the PR and the SRK equations of state. These equations need critical temperatures, critical pressures and acentric factors data of all components. The equations of state that need only critical temperatures and pressures of the components, such as the Redlich-Kwong (RK) and the Mohsen-Nia-Moddaress-Mansoori (MMM) equations of state are sometimes used in the calculation, but the results are sometimes less accurate than those of the PR and SRK equations of state.

The MMM EOS, which is a modification of the RK EOS was proven to be more accurate than the RK and the PR equations of state to predict molar volumes of saturated liquids and supercritical *n*-paraffins (Hartono *et al.*, 1999). It is also better than the RK,

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SRK and PR equations of state to predict solubilities of solid *n*-paraffins, cholesterol and β -carotene in supercritical fluids (Hartono *et al.*, 1999; Hartono *et al.*, 2001). It proves that an EOS that needs only critical temperature and pressure can be more accurate than those that need more physical properties can. Another modification of the RK equation of state was made by Hartono *et al.* (2003; 2004). They modified the repulsive part of the RK EOS. They also modified parameter *b* of the equation by instering a new parameter, λ , as a function of temperature and molecular weight of the substance. Their modification resulted in a better equation for predicting densities of pure liquids, pure supercritical fluids, and liquid mixtures than the RK and the MMM equations of state. Their proposed EOS was also proven to be more accurate than the RK and the MMM equations of state for predicting vapor pressures of heavy substances, excess volumes of various liquid mixtures, and equilibrium vapor-liquid composition of various mixtures.

The solubilities of solid *n*-paraffins in supercritical fluids are predicted using the RK, the SRK equations of state, and the equation proposed by Hartono *et al.* (2003 and 2004), the HMS EOS. The three equations of state can be expressed in a generalized form:

$$Z = \frac{v + \gamma_1 b}{v - \gamma_2 b} - \frac{a}{RT^{(1-\theta)}(v + \gamma_3 b)} \quad (1)$$

where

$$a = a_c \kappa = \frac{\Omega_a R^2 T_c^{(2-\theta)}}{P_c} \kappa \quad (2)$$

$$b = b_c \lambda = \frac{\Omega_b R T_c}{P_c} \lambda \quad (3)$$

Parameters Ω_a , Ω_b , θ , γ_1 , γ_2 , and γ_3 are component-independent constants, while κ and λ are component-dependent constants. Parameter κ of the SRK EOS is a function of acentric factor and temperature, and is expressed as

$$\kappa = \left[1 + (1 - T_r^{0.5}) (0.48508 + 1.55171\omega - 0.15613\omega^2) \right]^2 \quad (4)$$

Parameter λ of the HMS EOS is a function of molecular weight and temperature and is expressed as

$$\lambda^{-1} = \left\{ 1 + \left[\lambda_0 + \lambda_1 (M^* - 1) + \lambda_2 (M^* - 1)^2 \right] (1 - T_r) \right\}^2 \quad (5)$$

where

$$M^* = \frac{M}{M_{He}} = \frac{M}{4.0026}$$

$$\lambda_0 = -7.0964 \times 10^{-2}$$

$$\lambda_1 = 3.0172 \times 10^{-3}$$

$$\lambda_2 = 3.7209 \times 10^{-5}$$

The parameters are all dimensionless and their numerical values for various equations of states are given in Table 1.

Table 1. Parameters of the generalized equation of state (Hartono *et al.*, 1999, Hartono *et al.*, 2004)

EOS \rightarrow Parameter \downarrow	RK	SRK	HMS ^{a)}
γ_1	0	0	0.6653
γ_2	1	1	1
γ_3	1	1	1
γ_4	0	0	0
θ	0.5	0	0.5
Ω_a	0.42748	0.42748	0.45995
Ω_b	0.08664	0.08664	0.07285
κ	1	κ_{SRK} ^{b)}	1
λ	1	1	$\lambda^c)$

a) proposed by Hartono *et al.* (2003; 2004)

b) expressed in equation (4)

c) expressed in equation (5)

In extending the EOS to mixtures, the pure-component parameter *a* and *b* of the generalized EOS are replaced with the mixture parameter a_m and b_m . The most widely used mixing rule is the vdW mixing rule,

$$a_m = \sum_i^n \sum_j^n y_i y_j a_{ij} \quad (6)$$

$$b_m = \sum_i^n y_i b_i \quad (7)$$

In these equations, a_{ij} and b_{ij} with $i = j$ are parameters corresponding to pure component, while a_{ij} and b_{ij} with $i \neq j$ are the cross parameters. The cross parameters a_{ij} and b_{ij} are related to the pure-component parameters by the combining rules as follow:

$$a_{ij} = (1 - k_{ij}) (a_i a_j)^{0.5} \quad (8)$$

Solubility of Solid in Supercritical Fluid

The solubility of solid in supercritical fluid is calculated using the following expression:

$$y_i \hat{\phi}_i^V P = \phi_i^{sat} P_i^{sat} \exp \left[\frac{v_i^S}{RT} (P - P_i^{sat}) \right] \quad (9)$$

The fugacity coefficient derived from the generalized EOS (equation 1) is (Hartono *et al.*, 1999):

$$\ln \hat{\phi}_i^V = (\gamma_1 + \gamma_2) \left[\left(\frac{b_i}{v - b_m} \right) - \ln \left(\frac{v - b_m}{v} \right) \right] - \ln Z - \frac{a_m}{b_m RT^{(1-\theta)}} \left\{ \left(\frac{b_i v}{v + b_m} \right) + \left(\frac{2}{a_m} \sum_j y_j a_{ij} - \frac{b_i}{b_m} \right) \ln \left(\frac{v + b_m}{v} \right) \right\} \quad (10)$$

Calculation Results

The HMS, the RK, and the SRK equations of state are used for calculating solubility of solid *n*-paraffins in supercritical carbon dioxide and ethane. Critical temperatures and pressures, molecular weight and acentric factors of all components involved in the calculation are needed, as well as the molar volumes and the sublimation pressures of the solid components. The critical and other physical properties of all substances are presented in Table 2. The acentric factors of all the solid *n*-paraffins are predicted using Lee and Kesler's method with vapor pressure data taken from Frenkel *et al.* (1997a). The vapor pressures of all the solid *n*-paraffins are predicted using method proposed by Pouillot *et al.* (1994).

The calculation is done in two steps. In the first calculation, the binary interaction parameter, k_{ij} equals zero. This calculation is important to know how close the predicted solubility to the experimental data is. In the second step, the optimization, the binary interaction parameter k_{ij} is used as the adjustable parameter. The parameter is determined by

minimizing the average absolute deviation (AAD) defined as

$$AAD (\%) = \frac{100}{N} \sum_{i=1}^N \frac{|y_{i,exp} - y_{i,calc}|}{y_{i,exp}} \quad (11)$$

Several results are depicted in Figures 1-4. In each figure, the solubility is plotted against pressure in semi logarithmic scale. The calculation results with k_{ij} equals zero are depicted along with the ones obtained with fitted k_{ij} . The values of k_{ij} and the AADs of all systems are presented in Table 2.

In Figure 1 the solubility of *n*-tetracosane at 308 K is plotted against pressure. With k_{ij} equals zero, the HMS EOS has the same trend as the experimental data, while both the RK and the SRK equations of state do not. Optimization with k_{ij} as the adjustable parameter results in the HMS EOS as the closest line to the experimental data. The same pattern is shown in Figure 2 which depicts the solubility of *n*-tetracosane in supercritical ethane at 308 K. The same pattern will also be found in other systems containing heavier *n*-paraffins, as it is shown in Figures 3-4. These figures depict the solubility of the heaviest *n*-paraffin available, *n*-hexatriacontane, in supercritical carbon dioxide and ethane, respectively.

The results presented in Table 3 show that for all systems, the HMS EOS is better than both the RK and the SRK equations of state. The HMS EOS is basically a modified-RK EOS. This equation needs critical temperature and pressure and molecular weight data. It is another advantage of the HMS EOS, as molecular weight can be easily calculated for any kind of substance as long as the molecular formula is known. On the other hand, the SRK EOS which involves acentric factor does not give a significant improvement over the original RK EOS. As it is shown in Table 3 that for 142 data points of 12 systems, the HMS EOS gives the AAD of 26.6%, while the RK and the SRK equations of state give 66.7% and 65.8%, respectively.

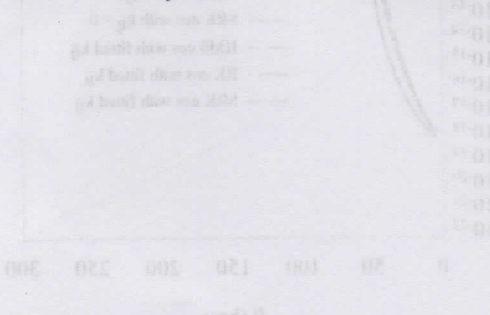


Figure 1. Solubility of *n*-tetracosane in supercritical ethane at 308 K as calculated using various equations of state and compared to the experimental data from Salinas *et al.* (1992)

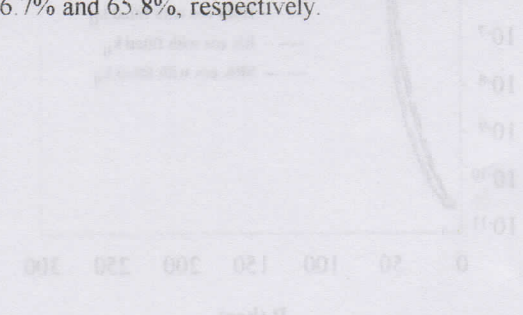


Figure 2. Solubility of *n*-tetracosane in supercritical ethane at 308 K as calculated using various equations of state and compared to the experimental data from Salinas *et al.* (1992)

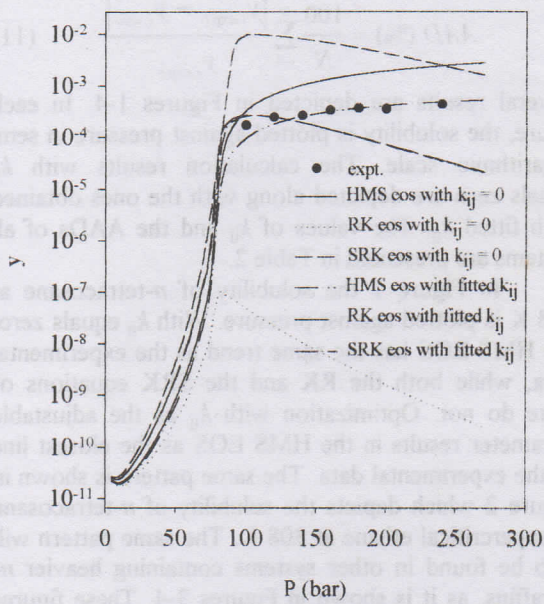


Figure 1. Solubility of *n*-tetracosane in supercritical carbon dioxide at 308 K as calculated using various equations of state and compared to the experimental data from Chandler *et al.* (1996)

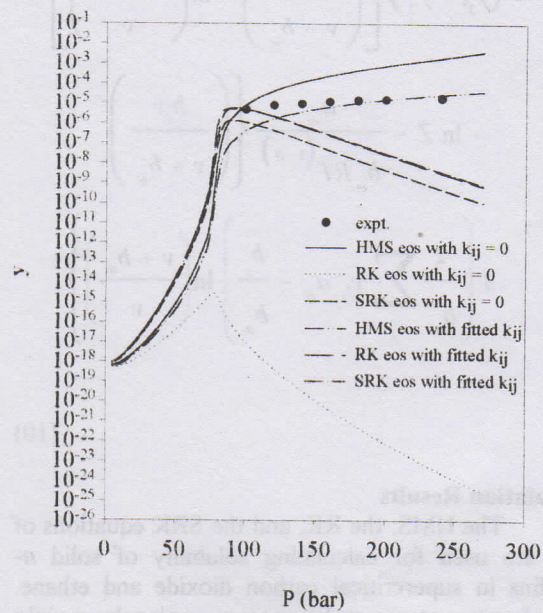


Figure 3. Solubility of *n*-hexatriacontane in supercritical carbon dioxide at 308 K as calculated using various equations of state and compared to the experimental data from Chandler *et al.* (1996)

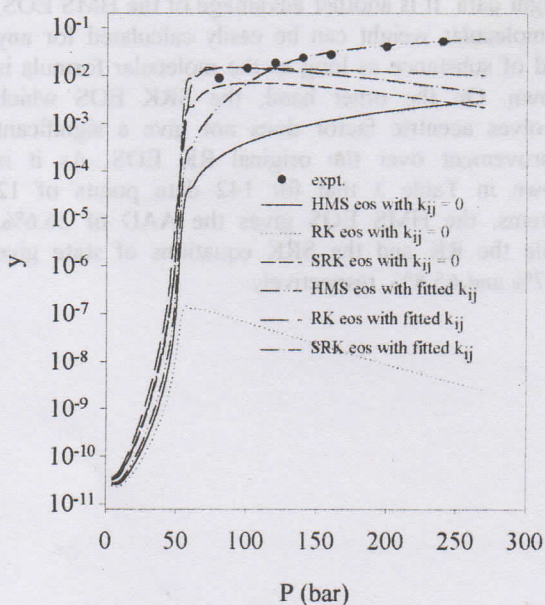


Figure 2. Solubility of *n*-tetracosane in supercritical ethane at 308 K as calculated using various equations of state and compared to the experimental data from Suleiman *et al.* (1995)

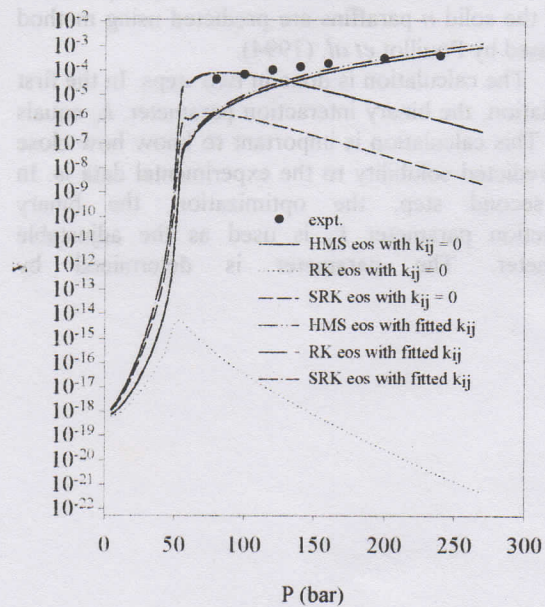


Figure 4. Solubility of *n*-hexatriacontane in supercritical ethane at 308 K as calculated using various equations of state and compared to the experimental data from Suleiman *et al.* (1995)

Table 2. Physical properties

Substance	T _c (K)	P _c (bar)	M	ω	v ^S (l/mol)	Ref.
Carbon dioxide	304.12	73.74	44.0098	0.2250		Frenkel <i>et al.</i> (1997b)
Ethane	305.32	48.72	30.0694	0.0980		Frenkel <i>et al.</i> (1997a)
<i>n</i> -Tetracosane	800.00	8.66	338.6590	1.0516 ^b	0.4246	Nikitin <i>et al.</i> (1994)
<i>n</i> -Pentacosane	806.57 ^a	8.17 ^a	352.6858	1.0852 ^b	0.4411	Himran <i>et al.</i> (1994)
<i>n</i> -Octacosane	826.00 ^a	6.91 ^a	394.7662	1.1896 ^b	0.4907	Himran <i>et al.</i> (1994)
<i>n</i> -Nonacosane	831.75 ^a	6.55 ^a	408.7930	1.2227 ^b	0.5068	Himran <i>et al.</i> (1994)
<i>n</i> -Triacontane	837.19 ^a	6.20 ^a	422.8198	1.2561 ^b	0.5236	Himran <i>et al.</i> (1994)
<i>n</i> -Dotriacontane	847.18 ^a	5.58 ^a	450.8734	1.3198 ^b	0.5562	Himran <i>et al.</i> (1994)
<i>n</i> -Tritriacontane	851.79 ^a	5.30 ^a	464.9002	1.3520 ^b	0.5728	Himran <i>et al.</i> (1994)
<i>n</i> -Hexatriacontane	864.21 ^a	4.55 ^a	506.9806	1.4414 ^b	0.6216	Himran <i>et al.</i> (1994)

^a predicted using Bolotin's method

^b predicted using Lee and Kesler's method

Table 3. Binary interaction parameters and the average deviations of various equations of state

System	T (K)	P range (bar)	No of. data pts.	k _{ij}			% AAD			Ref. ^a
				HMS	RK	SRK	HMS	RK	SRK	
<i>n</i> -C ₂₄ + CO ₂	308	100-240	7	0.0331	-0.2686	0.0747	15.2	55.0	54.4	Cha.
<i>n</i> -C ₂₅ + CO ₂	308	100-240	7	0.0648	-0.2536	0.0944	9.4	64.7	64.1	Cha.
<i>n</i> -C ₂₈ + CO ₂	308	100-240	7	0.0315	-0.3706	0.0377	24.6	70.7	69.2	Cha.
	318	120-240	6	0.0236	-0.3669	0.0372	22.4	67.6	61.2	Cha.
<i>n</i> -C ₂₈ + CO ₂	308	120-240	6	0.0677	-0.3521	0.0596	14.1	69.0	68.9	Cha.
	318	100-200	6	0.0594	-0.2708	0.0979	18.8	79.0	74.0	Cha.
<i>n</i> -C ₃₀ + CO ₂	308	90-250	9	0.0396	-0.3822	0.0459	34.8	77.4	75.2	Cha.
	318	105-200	8	0.0157	-0.3738	0.0418	34.8	68.6	60.2	Cha.
<i>n</i> -C ₃₂ + CO ₂	308	100-240	7	0.0417	-0.4539	0.0131	39.5	75.3	74.6	Cha.
	318	100-240	7	0.0319	-0.3995	0.0163	41.1	81.7	73.3	Cha.
<i>n</i> -C ₃₃ + CO ₂	308	120-240	6	0.0786	-0.4512	0.0241	25.3	74.3	74.1	Cha.
	318	120-240	6	0.0699	-0.4194	0.0402	26.9	75.5	73.7	Cha.
<i>n</i> -C ₃₆ + CO ₂	308	100-240	7	0.0549	-0.5507	-0.0206	50.0	80.7	80.4	Cha.
	318	100-240	7	0.0459	-0.4905	-0.0010	56.4	84.0	80.5	Cha.
<i>n</i> -C ₂₄ + C ₂ H ₆	308	80-240	7	-0.0670	-0.4926	-0.0153	23.5	47.1	52.3	Sul.
<i>n</i> -C ₂₅ + C ₂ H ₆	308	80-240	7	-0.0182	-0.4616	0.0114	52.3	45.9	55.3	Sul.
<i>n</i> -C ₂₈ + C ₂ H ₆	308	66-240	17	-0.0606	-0.5264	-0.0434	52.8	55.4	53.9	Kal.; Mor; Sul
	318	100-240	8	-0.0391	-0.5719	-0.0363	55.5	44.6	53.5	Sul.
<i>n</i> -C ₃₆ + C ₂ H ₆	308	80-240	7	-0.0052	-0.6080	-0.0579	62.3	72.3	72.3	Sul.
Overall			142				36.6	66.7	65.8	

^a Ref.: Cha. : Chandler *et al.* (1996)
 Kal. : Kalaga and Trebble (1997)
 Mor. : Moradinia and Teja (1986)
 Sul. : Suleiman and Eckert (1995)

Conclusions

The solubilities of solid *n*-paraffins are predicted using three equations of state, the RK, the HMS, and the SRK equations of state. Using the same mixing rule, the HMS equations of state is better than both the RK and the SRK equations of state. For 142 data points of 12 systems, the HMS EOS gives the AAD of 26.6%, while the RK and the SRK equations of state give 66.7% and 65.8%, respectively.

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Nomenclature

<i>P</i>	: pressure, bar
<i>R</i>	: universal gas constant = 0.083145 l. bar/(mol.K)
<i>R_m</i>	: molar refraction, cm ³ /mol
<i>T</i>	: absolute temperature, K
<i>v</i>	: molar volume, l
<i>y</i>	: packing fraction, dimensionless
<i>Z</i>	: compressibility factor

Greek letters

λ	: correction factor for parameter <i>b</i>
ω	: acentric factor

Subscripts

<i>c</i>	: critical
<i>r</i>	: reduced
<i>ref</i>	: reference
<i>rep</i>	: repulsive

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