

VAN DER WAALS MIXING RULES FOR THE REDLICH-KWONG EQUATION OF STATE. APPLICATION FOR SUPERCRITICAL SOLUBILITY MODELING

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Abstract

A solid-supercritical fluid system is highly asymmetric in terms of the size and energy differences of the components. The key point in extending a cubic equation of state to such system is on the choice of proper mixing rules. New mixing rules for the Redlich-Kwong equation of state are developed. The development is based on the statistical-mechanical theory of the van der Waals mixing rules. The Redlich Kwong equation of state with the proposed mixing rules along with the original ones is used to predict solubilities of solids in supercritical fluid. The prediction is done with k_{ij} equal zero, as well as with optimized k_{ij} . The results show superiority of the proposed mixing rules over the original ones. For most of the systems considered, the proposed mixing rules with the k_{ij} equal zero are closer to the experimental data than the original ones do. For 28 systems with 521 data points taken from various sources, the original and the proposed mixing rules give the overall AAD of 13.4%, while the original mixing rules give 45.9%.

Keywords: mixing rule; solubility; supercritical

Introduction

Cubic equations of state are widely used in phase-equilibrium calculations because of their simplicity and accuracy. Most of the equations need the critical properties data, including critical pressure and temperature, of the compounds involved in the calculations. Several equations need additional data, such as acentric factor, molar refraction, or molecular weight. Redlich-Kwong (RK) equation of state (eos) is one of the simplest form that needs only critical pressure and temperature:

$$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)} \quad (1)$$

where $a = \Omega_a R^2 T_c^{2.5} / P_c = 0.42748 R^2 T_c^{2.5} / P_c$

$$b = \Omega_b R T_c / P_c = 0.08664 R T_c / P_c$$

However, this equation is not accurate enough for phase-equilibria calculations, including vapor pressures and solubility of solids in supercritical fluids (Hartono *et al.*, 1999; 2001; 2005; Ratnawati, 2004). A solid-supercritical fluid system is highly asymmetric, in terms of the size and energy differences between the components. It is reflected for instance in the critical properties of the components. In extending the eos to mixtures, the pure-component parameters a and b are replaced with the mixture parameters a_m and b_m . The key point in extending the eos to such mixtures is on the choice of a proper mixing rule to determine the mixture parameters. The

most widely used mixing rules are the van der Waals mixing rules,

$$a_m = \sum_i^n \sum_j^n y_i y_j a_{ij} \quad (2)$$

$$b_m = \sum_i^n \sum_j^n y_i y_j b_{ij} \quad (3)$$

with the combining rules

$$a_{ij} = (1 - k_{ij}) (a_{ii} a_{jj})^{0.5} \quad (4)$$

$$b_{ij} = (1 - l_{ij}) \frac{b_i + b_j}{2} \quad (5)$$

where k_{ij} and l_{ij} are known as the binary interaction parameters, 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. If $l_{ij} = 0$ and equation (5) is substituted in equation (3), the expression for b will reduce to one-summation form,

$$b_m = \sum_i y_i b_i \quad (6)$$

According to Reid and Leland (1965), the derivation of the quadratic form of the mixing rules for the a and b parameters (equations 2 and 3) in an eos is based on the assumption that the properties of a fluid can be rederived from any pair interaction potential function $\Gamma(r)$ having the form:

$$\Gamma(r) = \varepsilon f\left(\frac{r}{\sigma}\right) \quad (7)$$

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The final result given by Reid and Leland (1965) for the expansion of the pair and the intermolecular radial distribution functions around a hard sphere distribution function in powers of (ε/kT) , after performing the required integration in the eos for the dense fluid is:

$$\sigma_m^3 f_0(\rho_m \sigma_m^3, T) + \sigma_m^3 \frac{\varepsilon_m}{kT} f_1(\rho_m \sigma_m^3, T) + \dots = \sum_i \sum_j y_i y_j \sigma_{ij}^3 f_0(\rho_m \sigma_m^3, T) + \quad (8)$$

$$\sum_i \sum_j y_i y_j \sigma_{ij}^3 \frac{\varepsilon_{ij}}{kT} f_1(\rho_m \sigma_m^3, T) + \dots$$

Equation (8) should valid at all temperatures and mixture densities and, thus, the coefficients of the function f_0, f_1, f_2, \dots of both sides must be equal. This equality results in the equations for the mixture energy and co-volume parameters:

$$\sigma_m^3 \varepsilon_m = \sum_i \sum_j y_i y_j \sigma_{ij}^3 \varepsilon_{ij} \quad (9)$$

$$\sigma_m^3 = \sum_i \sum_j y_i y_j \sigma_{ij}^3 \quad (10)$$

Coefficients a and b of the van der Waals eos are proportional to $\varepsilon \sigma^3$ and σ , respectively, according to the following expression (Kwak and Mansoori, 1986):

$$a = 1.1250 RT_c v_c \propto N_0 \varepsilon \sigma^3 \quad (11)$$

$$b = 0.3333 v_c \propto N_0 \sigma^3 \quad (12)$$

Hence equations (2) and (3) can be obtained from equations (9) and (10), respectively.

Another form of the combining rule for parameter b has been derived (Kwak and Mansoori, 1986; Coutinho *et al.*, 1994). For cross parameter σ_{ij} , a combining rule with a theoretical basis, is the one which assumes the additivity of diameters for hard-sphere molecules:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (13)$$

This gives the following expression of b_{ij} :

$$b_{ij} = (1 - l_{ij}) \left(\frac{b_i^{1/3} + b_j^{1/3}}{2} \right)^3 \quad (14)$$

with $l_{ij} = 0$ for spherical molecules.

Proposed Mixing Rules

As parameter a of the RK eos has dimension different from that of the vdW eos, the mixing rule will be different. To derive new mixing rule for parameter a , a new parameters, α , having dimensions as that of parameter a and b of the vdW eos is introduced.

$$\alpha = \frac{\Omega_a R^2 T_c^2}{P_c} \quad (15)$$

The mixing rule for this new parameter is:

$$\alpha_m = \sum_i \sum_j y_i y_j \alpha_{ij} \quad (16)$$

with the combining rule:

$$\alpha_{ij} = (1 - k_{ij}) (\alpha_i \alpha_j)^{0.5} \quad (17)$$

Parameter b has the dimension of a molar volume, hence the mixing rule for b is the same as that of the vdW eos, i.e. equation (14). Most of the combining rules use only one interaction parameter, k_{ij} . However, for highly asymmetric system such as solid-supercritical fluid system, the second interaction, l_{ij} , is needed (Coutinho *et al.*, 1994).

Parameter a_m of the RK equations of state for mixture is related to parameter α_m as follows.

$$a_m = \left(\frac{\Omega_a \alpha_m}{\Omega_b R b_m} \right)^{0.5} \alpha_m \quad (18)$$

The RK eos with the original and the proposed mixing rules are then used to predict solubilities of solids in supercritical fluids.

Assuming that the solid phase remains pure, the solubility of solid in supercritical fluid can be calculated using the following expression:

$$y_i = \frac{P_i^{sat}}{\hat{\phi}_i^V P} \exp \left[\frac{v_i^S}{RT} (P - P_i^{sat}) \right] \quad (19)$$

The fugacity coefficient of solid solute in supercritical phase, $\hat{\phi}_i^V$, derived from the RK eos is:

$$\ln \hat{\phi}_i^V = \left[\left(\frac{1}{v - b_m} \right) \frac{\partial (nb_m)}{\partial n_i} - \ln \left(\frac{v - b_m}{v} \right) \right] - \ln Z \quad (11)$$

$$- \frac{a_m}{b_m RT^{1.5}} \frac{v}{(v + b_m)} \frac{\partial (nb_m)}{\partial n_i}$$

$$- \frac{a_m}{b_m RT^{1.5}} \left\{ \frac{1}{a_m} \left[\frac{1}{n} \frac{\partial (n^2 a_m)}{\partial n_i} \right] - \frac{1}{b_m} \frac{\partial (nb_m)}{\partial n_i} \right\} \ln \left(\frac{v + b_m}{v} \right) \quad (20)$$

The derivatives of a_m and b_m of the proposed mixing rules with respect to n_i are

$$\frac{1}{n} \frac{\partial (n^2 a_m)}{\partial n_i} = \left(\frac{\Omega_b \alpha_m}{\Omega_a R b_m} \right)^{0.5} \left[3 \sum_{j \neq i}^n y_j \alpha_{ij} - \left(\frac{\alpha_m}{b_m} \right) \sum_{j \neq i}^n y_j b_{ij} \right] \quad (21)$$

$$\frac{\partial (nb_m)}{\partial n_i} = 2 \sum_{j \neq i}^n y_j b_{ij} - b_m \quad (22)$$

Results and Discussion

The RK eos with the original and the proposed mixing rules is used to predict the solubilities of various solids in supercritical fluids. The results are compared to the experimental data taken from various sources. First, the calculation is done with k_{ij} and l_{ij} equal zero, then k_{ij} is optimized while $l_{ij} = 0$. The results are presented in Figures 1 to 6. The figures show that with k_{ij} and l_{ij} equal to zero, the proposed mixing rules resulted in predicted solubilities having the same trend as the experimental data.

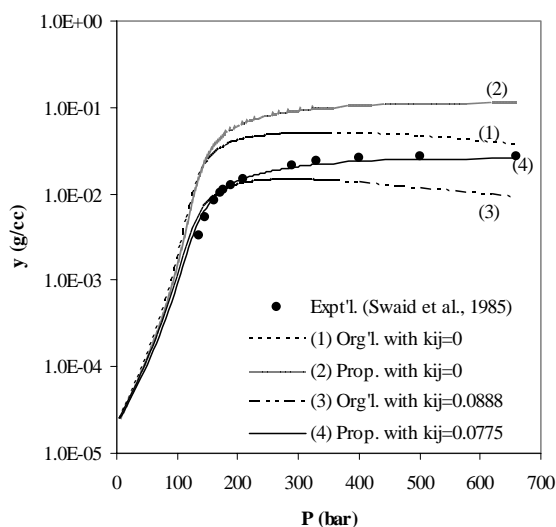


Figure 1. Solubility of adamantane in supercritical carbon dioxide at 343 K as calculated using the RK eos with the original and proposed mixing rules

In Figure 1, the solubility of adamantane in supercritical carbon dioxide is plotted against pressure. With both k_{ij} and l_{ij} equal to zero, the solubilities calculated using the original mixing rules, represented by line 1, are closer to the experimental data than those calculated using the proposed mixing rules are (line 2). However, the solubilities predicted using the proposed mixing rules have the same trend as the experimental data. It is very important for a model to give the same trend as the experimental data, as upon optimization, such model gives better results. Upon optimization, the best fitted k_{ij} for the original and the proposed mixing rules are 0.0888 and 0.0775, respectively. The predicted solubilities using original and proposed mixing rules with optimized k_{ij} are shown as line 3 and 4, respectively. The proposed mixing rules give closer solubility to the experimental data than the original mixing rules do. Similar results were obtained by Ratnawati (2005).

The solubilities of anthracene in supercritical carbon dioxide at 343 K are depicted in Figure 2. With k_{ij} equals zero, the proposed mixing rules (line 2) predict the solubility of anthracene having similar trend to the experimental data taken from Johnston *et al.* (1982), while the original ones (line 1) do not. Best fitting of the model to the experimental data give smaller value of k_{ij} for the proposed mixing rules (line 4) with better agreement with the experimental data than the original mixing rules (line 3). Similar results are obtained for other systems, as it is shown in Figures 3 to 6. Due to page limitation, only six figures are presented in this paper.

In Figure 3 the solubility of hexamethyl benzene in supercritical carbon dioxide is depicted as a function of pressure. It is shown that the predicted solubility using original mixing rules, with k_{ij} equal zero and 0.0026 (best fitted value), as represented by

line 1 and 3, respectively, are far from the experimental data. The proposed mixing rules, even with k_{ij} equals zero, predict the solubility having the same trend as the experimental data taken from Johnston *et al.* (1982). It is represented by line 3. With best fitted value of k_{ij} , 0.015, the proposed mixing rule accurately predict the solubility (line 4).

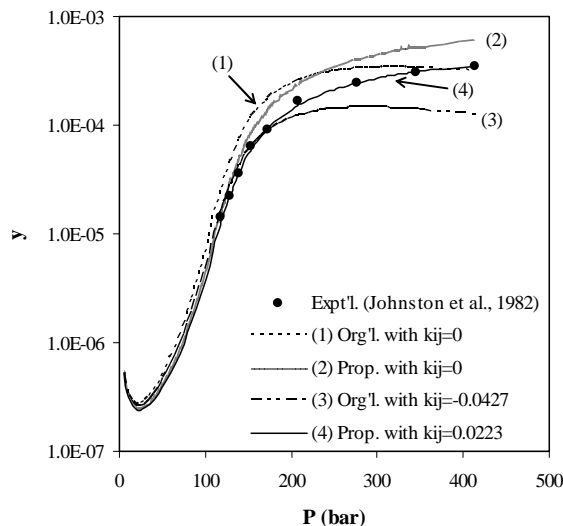


Figure 2. Solubility of anthracene in supercritical carbon dioxide at 343 K as calculated using the RK eos with the original and proposed mixing rules

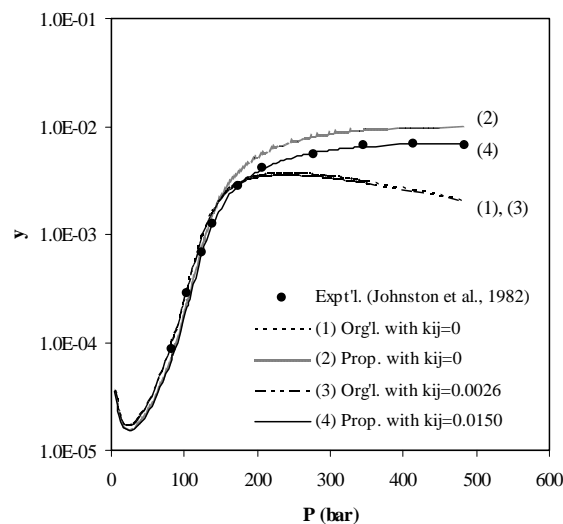


Figure 3. Solubility of hexamethylbenzene in supercritical carbon dioxide at 343 K as calculated using the RK eos with the original and proposed mixing rules

The superiority of the proposed mixing rules over the original ones is more obviously shown in Figure 4 where the solubility of hexatriacontane in supercritical carbon dioxide is plotted against pressure. The original mixing rules with k_{ij} equals zero predict the solubility which is not only far from the

experimental data, but also having different trend, as it shown as line 1. With best fitted value of k_{ij} , 0.4854, the original mixing rules predict the solubility which declines as pressure rises above 100 bar (line 3), while the experimental data shows different direction. The proposed mixing rules with k_{ij} equals zero (line 2) is far from the experimental data taken from Chandler *et al.* (1996), but it has the same trend as the experimental data.

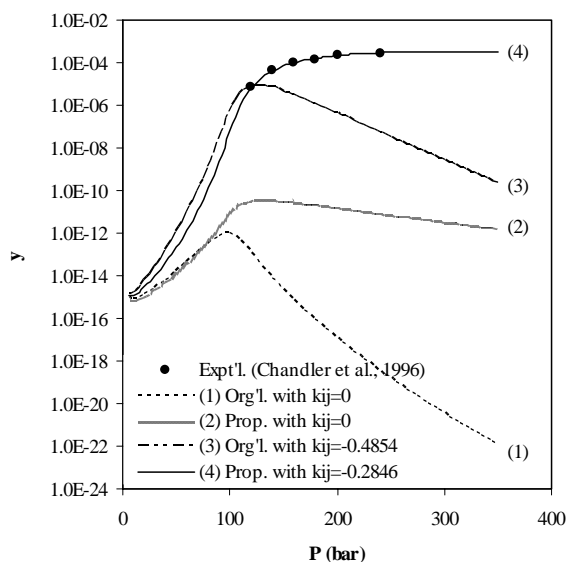


Figure 4. Solubility of hexatriacontane in supercritical carbon dioxide at 328.2 K as calculated using the RK eos with the original and proposed mixing rules

The four figures shown above depict the solubility of nonpolar solids in supercritical fluids. The RK eos with both the original and the proposed mixing rules are used to predict the solubility of polar solids in supercritical fluids as well, where similar results are obtained. In Figure 5 the solubility of cholesterol in supercritical ethane is plotted against pressure. The proposed mixing rules with zero and best fitted k_{ij} 's (line 2 and 4, respectively) are much better than the original ones (line 1 and 3, respectively).

The solubility of another polar solid, i.e. stigmaterol, in supercritical carbon dioxide is depicted in Figure 6. Again, the proposed mixing rules are much better than the original ones.

The solubilities of other solids in various supercritical fluids are also predicted using the RK eos with both zero and best fitted value of k_{ij} 's. The optimized values of k_{ij} of both the original and proposed mixing rules for various systems are presented in Table 1. It is shown in this table that for most of the system, the proposed mixing rules give k_{ij} values closer to zero than the original ones. It is important to be pointed out that if both mixing rules give the same %AAD (% of average absolute

deviation), the closer the value of k_{ij} the more accurate the mixing rules are. The most important point that can be concluded from the table is that the proposed mixing rules give smaller %AAD for all of the systems considered. For 521 data points of 28 systems, the original and the proposed mixing rules give the overall AAD of 45.9% and 13.4%, respectively.

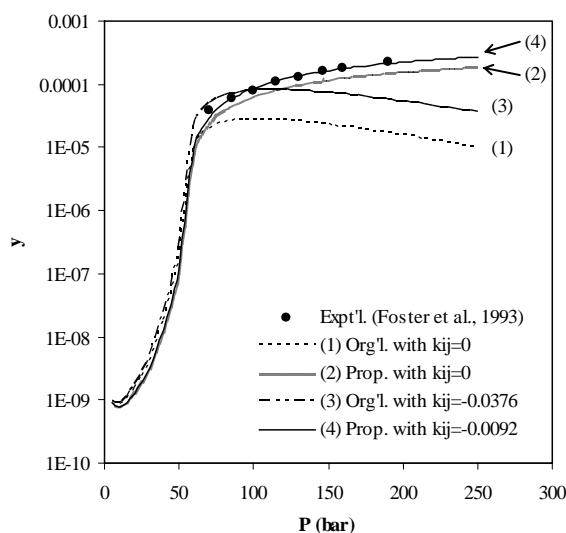


Figure 5. Solubility of cholesterol in supercritical ethane at 313.2 K as calculated using the RK eos with the original and proposed mixing rules

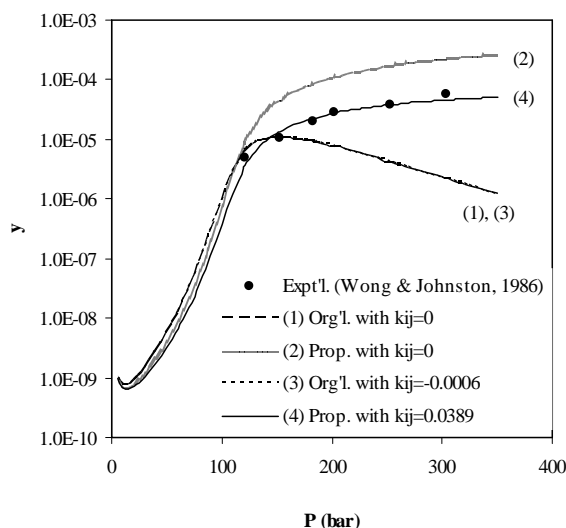


Figure 6. Solubility of stigmaterol in supercritical carbon dioxide at 333.2 K as calculated using the RK eos with the original and proposed mixing rules

Table 1. Binary interaction parameter (k_{ij}) for the original and the proposed mixing rules

SCF	Solut	T	N ^a	k_{ij}		%AAD ^b		Ref.
				Org'l.	Prop.	Org'l.	Prop.	
CO ₂	Octacosane	308.2	6	-0.3761	-0.1706	64.0	6.8	Chandler <i>et al.</i>
		318.2	6	-0.3332	-0.1693	70.1	7.3	
	Nonacosane	308.2	7	-0.4128	-0.2038	71.6	13.7	Chandler <i>et al.</i>
		318.2	7	-0.2862	-0.1646	81.3	5.9	
	Triacontane	308.2	9	-0.3531	-0.1970	79.4	8.0	Chandler <i>et al.</i>
		318.2	9	-0.3621	-0.2027	73.5	13.7	
	Dotriacontane	308.2	7	-0.4446	-0.2314	76.4	12.9	Chandler <i>et al.</i>
		318.2	7	-0.3868	-0.2287	82.3	11.6	
		328.2	7	-0.3528	-0.2232	80.0	11.8	
	Tritriacontane	308.2	6	-0.4534	-0.2180	74.7	8.1	Chandler <i>et al.</i>
		318.2	6	-0.4209	-0.2145	76.0	9.1	
	Hexatriacontane	308.2	6	-0.5705	-0.2918	76.6	7.2	Chandler <i>et al.</i>
		318.2	6	-0.5351	-0.2891	78.2	10.2	
		328.2	6	-0.4854	-0.2846	80.0	4.3	
	Adamantane	343.0	12	0.0888	0.0775	32.0	9.8	Swaid <i>et al.</i>
		362.2	19	0.0948	0.0792	31.4	14.8	
		382.0	31	0.0906	0.0758	35.7	16.6	
		402.0	12	0.1032	0.0890	21.0	12.4	
	Anthracene	313.2	7	0.0308	0.0417	34.6	17.8	Johnston <i>et al.</i>
		323.2	18	0.0330	0.0343	54.7	26.8	
		333.2	8	0.0260	0.0334	32.0	24.7	
		343.2	9	0.0427	0.0223	26.5	4.7	
	Biphenyl	318.6	8	-0.0394	-0.0145	11.9	11.6	McHugh & Paulaitis
		322.7	8	-0.0481	-0.0175	19.2	8.4	
	Fluorene	323.2	9	0.0151	0.0151	22.4	11.2	Johnston <i>et al.</i>
		343.2	8	0.0129	0.0136	26.0	7.8	
	Hexamethylbenzene	323.2	10	-0.0110	0.0130	27.5	21.7	Johnston <i>et al.</i>
		343.2	10	0.0026	0.0150	33.3	5.5	
	Phenanthrene	323.2	6	0.0198	0.0212	31.4	14.5	Kurnik <i>et al.</i>
		343.2	7	0.0375	0.0308	52.6	29.5	
	Pyrene	308.2	7	0.0282	0.0210	27.0	17.0	Johnston <i>et al.</i>
		323.2	7	0.0306	0.0193	47.7	5.0	
		343.2	8	0.0384	0.0166	55.8	16.6	
	Triphenylmethane	313.2	5	0.0155	-0.0023	65.2	21.6	Johnston <i>et al.</i>
		323.2	7	-0.0390	-0.0027	34.1	30.6	
	Cholesterol	313.2	6	0.0258	0.0436	73.7	13.8	Singh <i>et al.</i>
323.2		6	0.0861	0.0959	78.9	60.8		
333.2		5	0.0657	0.0610	72.3	35.7		
Stigmasterol	308.2	7	0.0574	0.0726	78.1	18.4	Wong & Johnston	
	323.2	6	0.0551	0.0596	76.1	40.4		
	333.2	6	-0.0006	0.0389	57.4	14.1		
C ₂ H ₆	Octacosane	308.2	11	-0.5410	-0.3072	44.9	11.4	Suleiman & Eckert
		318.2	8	-0.5591	-0.2898	45.4	16.0	
	Nonacosane	308.2	6	-0.3100	-0.1791	69.2	9.4	Suleiman & Eckert
		318.2	7	-0.3093	-0.1534	64.5	5.0	
	Triacontane	308.2	5	-0.5200	-0.3050	37.3	11.2	Suleiman & Eckert

Concluded

SCF	Solut	T	n ^a	k _{ij}		%AAD ^b		Ref.
				Org'l.	Prop.	Org'l.	Prop.	
	Dotriacontane	308.2	6	-0.5732	-0.3537	57.6	16.2	Suleiman & Eckert
		318.2	8	-0.6237	-0.3399	55.7	7.4	
	Tritriacontane	308.2	5	-0.5844	-0.3323	49.9	11.7	Suleiman & Eckert, Moradinia & Teja
		318.2	10	-0.5619	-0.3189	59.5	9.3	
	Hexatriacontane	308.2	6	-0.5994	-0.3568	72.4	10.2	Suleiman & Eckert
		318.2	7	-0.7087	-0.3847	50.9	7.9	
	Anthracene	308.2	4	-0.0098	-0.0244	24.1	10.6	Johnston <i>et al.</i>
		323.2	10	-0.0288	-0.0396	18.7	7.5	
		343.2	7	-0.0679	-0.0680	19.1	3.1	
	Triphenylmethane	313.2	5	-0.1140	-0.0921	14.4	9.7	Johnston <i>et al.</i>
		323.2	5	-0.1199	-0.1048	12.5	12.6	
	Cholesterol	313.2	8	-0.0376	-0.0092	38.9	5.4	Foster <i>et al.</i>
323.2		8	-0.0293	-0.0082	44.1	5.9		
333.2		7	-0.0273	-0.0043	44.2	7.9		
C ₂ H ₄	Fuorene	343.2	11	-0.0879	-0.0977	18.0	8.4	Johnston <i>et al.</i>
	Phenanthrene	308.2	5	-0.0793	-0.0893	9.8	6.9	Kurnik <i>et al.</i>
		318.2	5	-0.0818	-0.0952	19.8	8.3	
		328.2	5	-0.0783	-0.0943	17.9	11.9	
	Pyrene	318.2	8	-0.0668	-0.0771	21.9	11.9	Johnston <i>et al.</i>
348.2		7	-0.0787	-0.0849	20.9	9.7		
Total			521			45.9	13.4	

^a n : number of data points

$$\%AAD = \frac{1}{n} \sum_{i=1}^n \left| \frac{y_i^{calc} - y_i^{exp}}{y_i^{exp}} \right| \times 100\%$$

Conclusion

New mixing rules, for the RK eos, based on the statistical mechanical theory are proposed. The RK eos with the proposed mixing rules along with the original ones are used to predict solubilities of various solids in supercritical fluids. The results show that the proposed mixing rules are better than the original ones. For 28 systems with 521 data points, the original and the proposed mixing rules give overall AAD of 13.4%, while the original mixing rules give 45.9%.

Nomenclature

- a* equation of state parameter
b equation of state parameter
c concentration [g/cm³]
f fugacity
k Boltzman constant
P pressure [bar]
r intermolecular distance
R universal gas constant
T temperature [K]
v molar volume [l/mol]
y mole fraction
z compressibility factor
 α parameter in the proposed mixing rules

 ε energy parameter in potential function ϕ fugacity coefficient**References**

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