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H. C. Li[a]; V. M. Shah[a]; H. D. Cochran[a]
[a] University of Tennessee Knoxville, Tennessee, U.S.A.

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A GENERALIZED QUARTIC EQUATION OF STATE: SIMPLIFICATION AND PERFORMANCE ON MIXTURES

H. C. Li, V. M. Shah, and H. D. Cochran

University of Tennessee Knoxville, Tennessee 37996-2200
and Oak Ridge National Laboratory, Oak Ridge,
Tennessee 37831-6224

ABSTRACT

In previous work, a generalized quartic equation of state has been developed and extended to polar fluids. There are forty general regressed coefficients used in the four parameters in the equation of state. Simplification of the quartic equation of state has been done by setting fifteen of those coefficients to zero and obtaining the remaining twenty-five coefficients from regression on the original data base of non-polar and polar fluids. The results of simplification show that the quartic equation of state can achieve similar accuracy with fewer coefficients. The quartic equation of state was tested on thirty-five binary systems and four ternary systems to see the performance of the quartic equation of state on mixtures. The results show that the performance of the quartic equation of state on mixtures is generally comparable to that of the Peng-Robinson equation of state.

INTRODUCTION

Information of phase equilibrium is very important in chemical industries, especially in separation processes. For example, to design a distillation unit, one needs to know the equilibrium compositions of the vapor and liquid phases, and an equation of state can be used for that. There are generally two approaches to deal with phase equilibrium calculations. One approach uses an equation of state to model the vapor phase and a liquid model to model the liquid phase. The other approach uses an equation of state for both vapor and liquid phases. To utilize the former approach, an arbitrary standard state needs to be picked for the liquid as a reference, and an activity coefficient model, liquid model, is also needed to describe the deviation from the reference state. Many researchers prefer the latter approach to the former one because no arbitrary reference state is needed. However, an equation of state that can model situations far from ideal gas is required in order to describe the behavior of liquids well.

Since the van der Waals equation of state, most equations of state have been cubic in volume and have consisted of two terms in the pressure expression, the repulsive and the attractive terms. Rowlinson et al. (1) showed that the repulsive term in the van der Waals equation of state might not be so correct. At the time of van der Waals, the pressure of a fluid of hard spheres was not known. Carnahan et al. (2) proposed an expression for the compressibility factor for a fluid of hard spheres. The Carnahan-Starling equation of state gave reasonably good agreement with the results from the molecular dynamic simulation (3) and Monte Carlo simulation.

No real particles will have exactly the same behavior as that of hard spheres because their intermolecular interactions other than repulsive force and the shape of the molecules are different from sphere. Perturbation theory makes it possible to extend the hard sphere equation of state to practical usage. Carnahan et al. (4) combined their hard sphere equation of state with the attractive term in the Redlich-Kwong equation of state (5) to give the CSRK equation of state, which is a great improvement over the Redlich-Kwong equation of state. It was a popular approach to combine the Carnahan-Starling equation or some other hard core equations of state with a certain attractive term to give the total expression of the equation of state. For example, Bienkowski et al. (6) used a truncated virial expansion as the attractive term and combined it with the Carnahan-Starling equation. It should be pointed out that most of these perturbed hard sphere equations of state have substantially more than three roots (often seven or more roots) because the hard sphere equations of state applied in them are usually high order equations. The presence of additional roots can lead to difficulties in choosing the correct root, particularly in automated calculations as are often used in process simulators and oil-field simulators.

A quartic equation of state, with its greater flexibility compared with cubic equations, offers another way to an improved equation of state. Kubic (7) proposed the first quartic equation of state for chain-like molecules. Kubic used a simple hard sphere equation based on the work of Beret et al. (8) with an empirical attractive term. Latter, Kubic (7) extended his four parameter quartic equation of state to mixtures by applying the van der Waals one fluid mixing rule on the parameter, a, in the attractive term and linear combination for other parameters. Soave (9) also proposed a quartic equation of state for pure compounds.

Shah et al. (10, 11) proposed a generalized four-parameter perturbed hard sphere quartic equation of state, which was extended to polar fluids by Lin et al. (12-14). The development of the generalized quartic equation of state is detailed in these prior publications. The equation of state is given as follows:

$$P = \frac{RT}{(V - k_0\beta}) + \frac{\beta\, k_1 RT}{(V - k_0\beta)^2} - \frac{aV + k_0\beta\, c}{(V(V + e)(V - k_0\beta)} \tag{1}$$

The parameter β is the hard sphere volume of the fluid. Its value at critical temperature was approximated to be $0.165V_c$, where V_c is critical volume of the pure fluid. Temperature dependence was incorporated in β by Shah (10) using the form of temperature dependence by Nezbeda et al. (15). But Shah used critical temperature as the reference for the reduced temperature instead of triple point temperature. The complete expression of β is given as follows:

$$\beta = \beta_c\{\exp[-0.03125\ln(T_I) - 0.0054[\ln(T_I)]^2]\}^3 \tag{2}$$

The temperature dependence of parameters a and c is given as follows:

$$a = a_c\alpha\,(T_r) \tag{3}$$

when $T_r \leq 1$

$$\alpha\,(T_r) = [1 + X_2(1 - \sqrt{T_r}) + X_3(1 - \sqrt{T_r})^2 + + X_4(1 - \sqrt{T_r})^3]2 \tag{4}$$

when $T_r > 1$

$$\alpha\,(T_r) = [1 + X_2(1 - \sqrt{T_r}) + X_5(1 - \sqrt{T_r})^2 + + X_6(1 - \sqrt{T_r})^3]2 \tag{5}$$

$$c = c_c\xi\,(T_r) \tag{6}$$

$$\xi\,(T_r) = [1 + X_7(1 - \sqrt{T_r})]^2 \tag{7}$$

Pitzer's acentric factor ω and the reduced dipole moment μ^*were introduced into the parameters a_c, c_c, e, and Xs to account for the substance dependence and the dipole moment by Shah et al. (10-14), respectively, as follows:

$$a_c = \frac{a_r RT_c}{\rho_c} \tag{8}$$

$$a_r = a_{r0}(1 + a_{r1}\omega + a_{r2}\omega^2 + a_{r3}\mu^* + a_{r4}\mu^{*2}) \tag{9}$$

$$c_c = \frac{c_r RT_c}{\rho_c} \tag{10}$$

$$c_r = c_{r0}(1 + c_{r1}\omega + c_{r2}\omega^2 + c_{r3}\mu^* + c_{r4}\mu^{*2}) \qquad (11)$$

$$e = \frac{e_r}{\rho_c} \qquad (12)$$

$$e_r = e_{r0}(1 + e_{r1}\omega + e_{r2}\omega^2) \qquad (13)$$

$$X_i = X_{i1} + X_{i2}\omega + X_{i3}\mu^* + X_{i4}\mu^{*2} \text{ for } i = 2, 3, 4, 5, 6 \text{ and } 7. \qquad (14)$$

$$\beta_r = \beta_c\rho_c \qquad (15)$$

$$\mu^* = \frac{0.3976\mu}{(RT_cV_c)^{0.5}} \qquad (16)$$

Note that Equations (9), (11), and (14) contain superfluous terms, since the terms linear in dipole moment do not enter into any statistical mechanical expression for equilibrium properties.

The generalized extended quartic equation of state has superior performance (13, 14) over the Peng-Robinson equation of state (16) in calculating many thermodynamic properties such as the vapor pressure, vapor or liquid density, residual enthalpy, and second virial coefficient of both non-polar and polar fluids, especially in the supercritical and compressed liquid region.

To extend an equation of state to systems of mixtures, a set of mixing rules is necessary to combine the parameters of the pure fluids to give the parameters for the mixture. The mixing rules play an important role and have great effect on the performance of the equation of state on mixtures. The simplest and most commonly used mixing rules are the linear combination and the van der Waals one fluid mixing rules. The van der Waals one fluid mixing rule is shown as follows:

$$a_m = \sum_1 \sum_j x_i x_j a_{ij} \qquad (17)$$

$$b_m = \sum_1 \sum_j x_i x_j b_{ij} \qquad (18)$$

To calculate the parameters a_{ij} and b_{ij} when $i \neq j$, combining rules are used. The most commonly used combining rules are as follows:

$$a_{ij} = \sqrt{a_i a_j}\,(1 - k_{ij}) \qquad (19)$$

$$b_{ij} = \frac{b_1 + b_i}{2}(1 - m_{ij}) \qquad (20)$$

Boublik (17) and Mansoori et al. (18) derived a mixing rule for hard sphere equations of state, which is essentially the additivity of the hard sphere volume. The Boublik-Mansoori mixing rule is as follows: Let the hard sphere equation of state be: $Z = f(\xi)$

$$\xi = \sum_{i=1}^{m} \xi_1 \tag{21}$$

$$\xi_1 = \frac{1}{6}\,\pi\,\rho\,d_i^3 x_i \tag{22}$$

APPROACH

To simplify the quartic equation of state, fifteen of the original forty coefficients were set to zero. Because of the reason previously addressed, all eight coefficients corresponding to terms linear in the dipole moment were eliminated to make the EOS better fits to the physical reality. We then did significance tests on each of the remaining coefficients to obtain the information about the effect of the removal of those coefficients on the ability of the functional expressions of the parameters to fully express the parameters. The remaining twenty-five coefficients were determined as in previous work (10-14) using the Nelder-Mead simplex algorithm (19, 20) and an adaptive nonlinear least-squares algorithm (21) to minimize the following objective function:

$$\begin{aligned} \mathrm{OBJ}_1 = {} & \sum_{i=1}^{N_1}\left[\left(\frac{\Delta P_{s,i}}{P_{s,i}}\right)^2 + \left(\frac{\Delta\rho_{sv,i}}{\rho_{sv,i}}\right)^2 + \left(\frac{\Delta\rho_{sl,i}}{\rho_{sl,i}}\right)^2\right] + \sum_{j=1}^{N_2}\left(\frac{\Delta\rho_{g,1}}{\rho_{g,j}}\right)^2 \\ & + \sum_{k=1}^{N_3}\left(\frac{\Delta H_{r,k}}{H_{r,k}}\right)^2 + \sum_{l=1}^{N_4}\left(\frac{\Delta H_{vap,1}}{H_{vap,1}}\right)^2 + \sum_{m=1}^{N_5}\left(\frac{\Delta B_{vm,}}{B_{v,m}}\right)^2 \end{aligned} \tag{23}$$

In calculations with binary mixtures, the van der Waals one fluid mixing rule was used for the attractive term and the Boublik-Mansoori mixing rule was used for the repulsive term as proposed by Lin et al. (13). Only one binary interaction parameter, k_{ij}, was used in each of the three equations of state, Peng-Robinson, original quartic equation of state, and the simplified quartic equation of state. High-pressure vapor-liquid phase equilibrium data were used in the regression for the k_{ij}. The values of k_{ij} were obtained by using the same algorithms above to minimize the following objective function:

$$\mathrm{OBJ}_2 = \sum_{n=1}^{N_6}\left[\left(\frac{P_n^{cac} - P_n^{exp}}{P_n^{exp}}\right)^2 + \left(y_n^{calc} - y_n^{exp}\right)^2\right] \tag{24}$$

For the calculations of ternary systems, the respective binary interaction parameters were obtained by the approach above. These values of k_{ij} were then used in bubble-point calculation or dew-point calculation procedures to get the vapor phase or the liquid phase compositions which were compared to the experimental data. It was not necessary to do any regression in the ternary system calculations because no adjustable parameters are involved other than the k_{ij}s obtained from binary calculations.

Data on sixteen non-polar fluids and thirty polar fluids were used in the regression to obtain the new set of coefficients for the simplified quartic equation of state. The same pure non-polar fluids as used by Shah et al. (10, 11) and the same polar fluids as used by Lin et al. (12-14) were used in the regressions. The performance of the original and simplified quartic equation of state was tested on thirty-seven binary systems and four ternary systems against that of the Peng-Robinson equation of state. The studied binary and ternary systems were picked to include different categories of systems, for example polar-polar, chain-chain, and simple-polar systems. The binary and ternary mixtures and the original data sources are presented in Table 1. Most of the binary systems are high-pressure data because it was hoped that the quartic equation of state would have superior performance over the Peng-Robinson equation of state at high-pressure range.

RESULTS AND DISCUSSION

In the original generalized quartic equation of state, there are four parameters, a and c (which are functions of temperature and depend on the fluid's critical temperature, acentric factor, and dipole moment), β (which is a function of temperature and depends on the fluid's critical temperature and critical volume), and e (which depends on the fluid's critical volume and acentric factor). These four parameters are expressed by polynomial functions of reduced temperature with forty universal coefficients. In this work, fifteen of the original forty coefficients of the generalized quartic equation of state were set to zero, and the other coefficients were obtained by nonlinear regression again. Table 2 presents the constants of both the original (40 constants) and simplified (25 constants) equations.

In Table 3 and Table 4, the overall performance of both the original and the simplified quartic equations of state are reported on the sixteen non-polar and thirty polar fluids. Table 3 shows the performance of the simplified equation on non-polar fluids is generally only slightly worse than that of the original equation in most of the calculated properties of various compounds and slightly better in some of them. The overall average performance of the original quartic equation of state is only slightly better than that of the simplified equation of state. Table 4 shows the same comparison for polar fluids. The comparison shows the generalized quartic equation of state can achieve similar accuracy with fewer regressed coefficients.

The extension of the quartic equation of state to mixtures is done by applying the Boublik-Mansoori mixing rule for parameter β and the van der Waals one fluid mixing rule for parameters a, c, and e. In this work, the mixture calculations

Table 1. Detailed Description of the Binary and Ternary Mixture Data Used for Testing the Quartic Equation of State and Their Sources

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
Acetic acid | n-Octane	323.15–43.15	0.0067–0.0291	39	(22)
Methane | 1-Propanol	313.4–333.4	1.410 –10.197	10	(23)
Methane | Ethanol	313.4–333.4	1.808 –10.464	10	(23)
Ethanol | n-Octane	343.15	0.0160–0.0722	23	(24)
Propane | Furfural	293.15–313.15	0.094–1.339	26	(25)
Propylene | Furfural	293.15–313.15	0.100–1.611	32	(25)
1-Propanol | n-Octane	358.15	0.0280–0.0628	25	(24)
n-Octane | Ethane	318.15–338.15	1.500–6.800	16	(26)
n-Octane | Ethylene	318.15–338.15	1.500–9.500	19	(26)
n-Octane | Carbon Dioxide	313.15–348.15	1.500–11.350	18	(26)
Aceto-phenone | Ethylene	318.15–338.15	3.000–19.000	19	(27)
Methyl Benzoate | Ethylene	318.15–338.15	2.500–15.000	16	(28)
Methano | Acetone	328.82–336.84	0.1013	12	(29)

(continued)

Table 1. Continued

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
Methane | n-Decane	477.59–510.93	0.1379–36.192	31	(30)
Methane | n-Pentane	176.21–273.16	0–4.1367	9	(31)
Chlorodifluoro-methane | 2-Propanol	363.7–382.8	0.819–5.273	22	(32)
Chlorodifluoro-methane | Ethanol	343.3–382.7	0.836–5.434	34	(32)
Chlorodifluoro-methane | n-Hexane	363.0–400.4	1.614–5.412	28	(32)
Chlorodifluoro-methane | Chloroform	364.3–383.0	1.485–5.379	23	(32)
Chlorodifluoro-methane | Cyclohexane	363.3–400.6	1.348–5.713	27	(32)
1,1-difluoroethane | Ethylchloride	303.2–323.2	0.466–1.047	29	(33)
Carbon Dioxide | 1-Propanol	313.4–333.4	0.518–10.822	15	(23)
Carbon Dioxide | Ethane	207.00–270.00	0.2943–3.200	44	(34)
Carbon Dioxide | Ethanol	313.4–333.4	0.514–10.654	18	(23)
Nitrogen | n-Hexane	310.93–444.26	1.7237–34.4735	39	(35)
3-Methyl-2-Butanone | n-Octane	367.44–398.76	0.1013	39	(36)

(continued)

Table 1. Continued

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
Argon | Methane	122.89	0.335–1.342	12	(37)
Benzene | 1-Propanol	323.15–333.15	0.0220 - 0.0567	60	(38)
Benzene | Cyclohexane	323.15–333.15	0.0369–0.0576	71	(38)
Cyclohexane | 1-Propanol	323.15–333.15	0.0279–0.0612	56	(38)
Cyclohexane | 3-Methyl-2-Butanone	353.87–367.44	0.1013	31	(38)
Cyclohexane | n-Heptane	353.79–371.45	0.1013	16	(39)
Cyclohexane | n-Octane	353.87–398.76	0.1013	30	(36)
Nitrogen | Argon	122.89	1.484–2.839	13	(37)
Nitrogen | Methane	122.89	0.422–2.580	10	(37)
n-Hexane | n-Heptane	341.81–371.47	0.1013	19	(39)
n-Hexane | Cyclohexane	341.79–353.75	0.1013	17	(39)
n-Hexane | Cyclohexane | n-Heptane	345.08–363.16	0.1013	29	(39)

(continued)

Table 1. Continued

System	Temperature (K)	Pressure (MPa)	No. of Data Points	Data Sources
Cyclohexane | 3-Methyl-2-Butanone | n-Octane	354.41–367.01	0.1013	39	(36)
Nitrogen | Argon | Methane	122.89	0.700–2.441	9	(37)
Nitrogen | Carbon Dioxide | Ethane	220	0.804	15	(40)

Table 2. The Regressed Constants for the Original and Simplified Generalized Quartic Equations of State

Constants	Original	Simplified	Constants	Original	Simplified
a_{r0}	1.847131	1.825716	X_{31}	−0.32379	−0.237932
a_{r1}	−0.05218	0	X_{32}	1.84591	1.022857
a_{r2}	1.06446	0.896586	X_{33}	0.39338	0
a_{r3}	−0.02730	0	X_{34}	−0.25483	0
a_{r4}	0.02048	0	X_{41}	0.14833	0.065036
β_r	0.16500	0.165000	X_{42}	−3.46693	−2.067206
c_{r0}	1.78336	1.854436	X_{43}	−0.39170	0
c_{r1}	−1.29690	0.596539	X_{44}	−0.01597	0
c_{r2}	2.78945	−1.946911	X_{51}	0.11048	0.114614
c_{r3}	0.07000	0	X_{52}	0.57743	0.678414
c_{r4}	0.01188	0.022230	X_{53}	0.41218	0
e_{r0}	0.63189	0.622480	X_{54}	−0.10676	0.131914
e_{r1}	−0.81660	0	X_{61}	0.02581	0.021573
e_{r2}	3.25246	1.316413	X_{62}	−0.02700	0.029885
k_0	1.28650	1.28650	X_{63}	0.38327	0
k_1	2.82250	2.82250	X_{64}	−0.09008	0.156664
X_{21}	0.14988	0.143600	X_{71}	−0.77357	−0.853536
X_{22}	0.97848	0.968548	X_{72}	−1.45342	−0.231363
X_{23}	−0.01390	0	X_{73}	−0.04725	0
X_{24}	0.02928	0	X_{74}	−0.09669	0

Table 3. Comparison of Various Thermodynamic Properties of Pure Nonpolar Fluids Calculated by Original and Simplified Quartic Equations of State

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Overall average	P_s	1.67	1.61	456
	ρ_{sv}	1.72	2.61	403
	ρ_{sl}	4.04	4.78	403
	ρ_g	0.75	0.89	1997
	ρ_l	4.48	4.46	129
	B_{vir}	6.31	4.86	583
	H_r	5.70	6.53	1123

AAPD(%): Average Absolute Percentage Deviation

$$AAPD(\%) = \frac{1}{N_d}\sum_{i-1}^{N_d}\left|\left(\frac{y_i^{exp} - y_i^{calc}}{y_i^{exp}}\right)\right| \times 100\%$$

have been done with the original quartic equation of state, the simplified quartic equation of state, and the Peng-Robinson equation of state to predict vapor-liquid equilibrium of thirty-seven binary systems and four ternary systems, which were not used in the development. The results are reported in Table 5 and Table 6 for the binary and ternary mixtures, respectively. Table 5 shows the performance of the simplified equation of state on binary systems is generally slightly worse than that of the original quartic equation, as on pure fluids. And both the original and simplified quartic equations of state are not superior to the Peng-Robinson equa-

Table 4. Comparison of Various Thermodynamic Properties of Pure Polar Fluids Calculated by Original and Simplified Quartic Equations of State

Compound	Properties	Original Quartic EOS AAPD (%)	Simplified Quartic EOS AAPD (%)	No. of Data Points
Overall average	P_s	2.69	3.75	956
	ρ_{sv}	4.27	6.41	334
	ρ_{sl}	2.99	3.72	956
	ρ_g	1.93	2.14	1640
	ρ_l	2.29	4.10	119
	B_{vir}	2.40	2.76	467
	H_r	4.85	5.52	830
	H_v	2.41	3.11	1003

Table 5. Comparison of Vapor-Liquid Equilibrium Calculation Results of Binary Mixtures from the Peng-Robinson, the Original, and the Simplified Quartic Equations of State

System	Properties	Original Quartic EOS	Simplified Quartic EOS	Peng-Robinson EOS	No. of Data Points
Overall	P (AAPD)	4.50	4.90	3.57	958
average	y (AAD)	0.0174	0.0204	0.0183	

AAD: Average Absolute Deviation

$$\mathrm{AAD} = \frac{1}{N_d}\sum_{i=1}^{N_d} | y_i^{exp} - y_i^{calc} |$$

tion of state as had been hoped as far as the performance is concerned. The performance is generally slightly worse than that of the Peng-Robinson equation of state on most of the tested systems. As mentioned previously, the performance of the quartic equation of state on pure fluids is superior to that of the Peng-Robinson equation of state. It is disappointing to find out the advantage is not retained upon extension to mixtures. One possible reason might be that the mixing rules are not optimal; little research has been performed to optimize mixing rules for an equation of state with an accurate repulsive term. Another possible reason might be that the quartic equation of state is more complicated than the Peng-Robinson equation of state, and it would be more difficult to combine the pure fluid parameters with only one binary interaction parameter, k_{ij}. Yet another reason might be that the quartic equation of state has superior performance when applied to calculations of thermodynamic properties other than the pressure and volumetric properties of pure fluids but is only comparable when applied to the calculations of these properties. Therefore, it is possible that the quartic equation of state might give superior performance when applied to calculation of other properties of mixtures such as heat of mixing. However, this needs to be tested. The results show the quartic equation of state or the mixing rules would need some modification to improve its performance on mixtures in order to compete with the widely used Peng-Robinson equation of state.

Table 6. Comparison of Vapor-Liquid Equilibrium Calculation Results of Ternary Mixtures from the Peng-Robinson, the Original, and the Simplified Quartic Equations of State

System	Properties	Simplified Quartic EOS	Peng-Robinson EOS	No. of Data Points
Overall	x_2 (AAD)	0.0170	0.0158	92
	y_1 (AAD)	0.0118	0.0110	
	y_2 (AAD)	0.0134	0.0103	

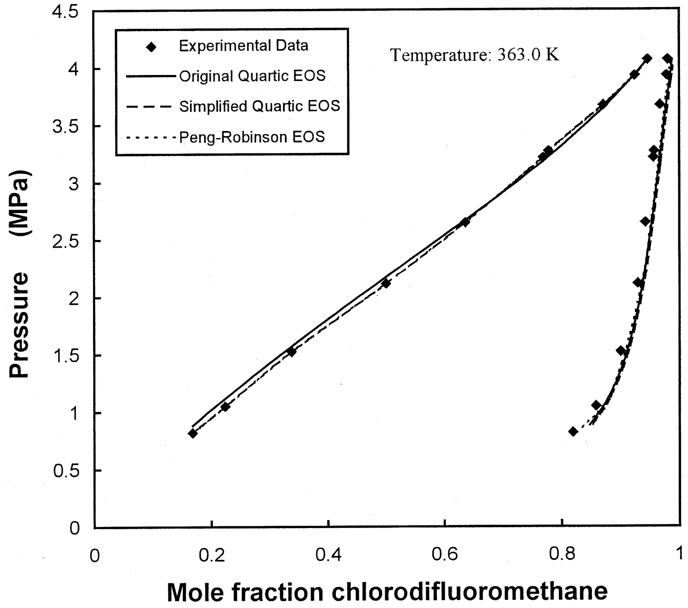

Figure 1. Comparison of the performance of the original quartic EOS, simplified quartic EOS, and Peng-Robinson EOS on the chlorodifluoromethane-2-propanol system at 363.0 K.

Figure 1 shows the comparison of the performance of the original quartic equation of state, the simplified quartic equation of state, and the Peng-Robinson equation of state on the chlorodifluoromethane-2-propanol system at 363 K. From Fig. 1, we find all three equations of state give about the same results that are very close to the experimental data. Qualitatively, this performance is typical of most binary mixture results. Figure 2 reports the comparison of the performance of the original quartic equation of state, the simplified quartic equation of state, and the Peng-Robinson equation of state on the 1-propanol-n-octane system at 358.15 K. It can be found from Fig. 2 that the original and the simplified quartic equation of state have similar performance which is better then that of the Peng-Robinson equation on this system. Figure 2 also shows that these three equations of state are not very good models for this system. A few systems showed qualitatively similar results.

Figure 3 shows the performance of the simplified quartic equation of state on the chlorodifluoromethane-n-hexane system at three different temperatures. The results show the quartic equation of state can model the system at different temperatures with a single binary interaction parameter, k_{ij}. Again, this result is qualitatively similar to what was found with most binary mixtures.

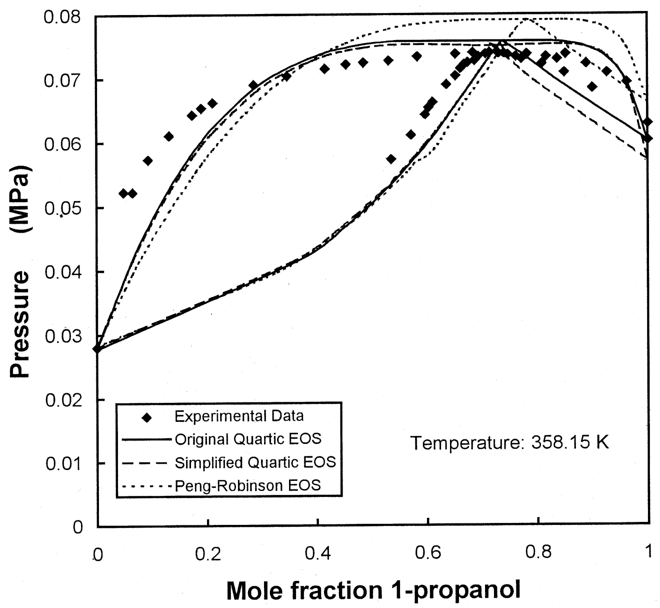

Figure 2. Comparison of the performance of the original quartic EOS, simplified quartic EOS, and Peng-Robinson EOS on the1-propanol-n-octane system at 358.15 K.

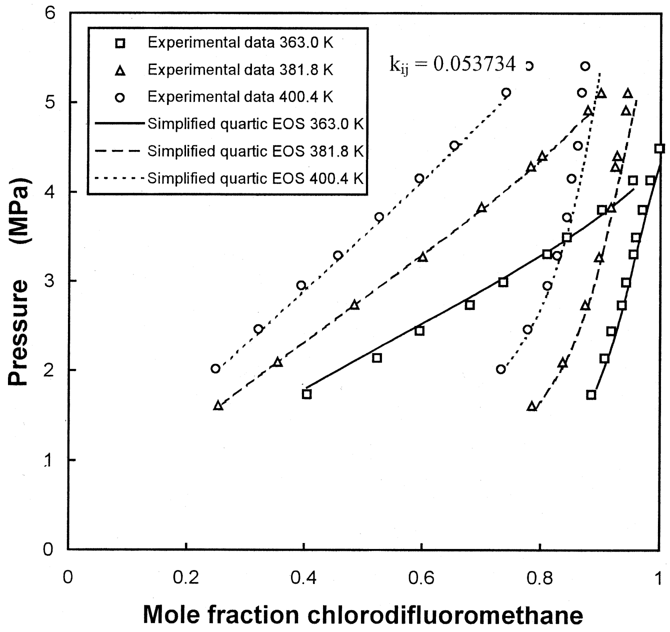

Figure 3. Comparison of the performance of the simplified quartic EOS on the chlorodifluoromethane-n-hexane system at 363.0 K, 381.8 K, and 400.4K.

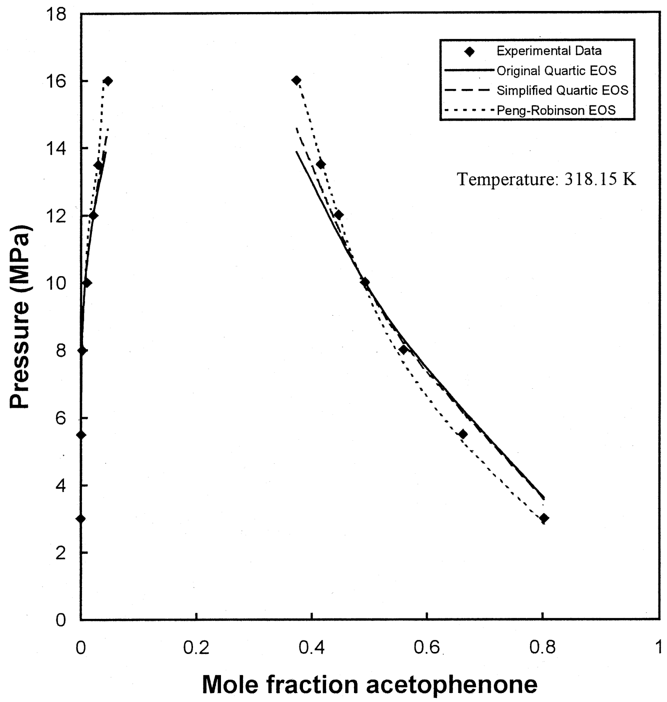

Figure 4. Comparison of the performance of the original quartic EOS, simplified quartic EOS, and Peng-Robinson EOS on the acetophenone-ethylene system at 318.15 K.

Although the performance of the original and the simplified quartic equation of state looks good on the figures, the results in the previous tables show that the quartic equation of state does not have superior performance over the Peng-Robinson equation of state for vapor liquid equilibrium calculations.

Figure 4 reports the comparison of the performance of the original quartic equation of state, the simplified quartic equation of state, and the Peng-Robinson equation of state on the acetophenone-ethylene system at 318.15 K. Figure 4 shows that the Peng-Robinson equation of state has better performance than the quartic equations of state in this system, which is the case for some of the tested systems, but for most of the tested systems the performance of the quartic equations of state is close to that of the Peng-Robinson equation of state.

CONCLUDING REMARKS

A generalized quartic equation of state with forty regressed coefficients was previously proved to have superior performance over the Peng-Robinson equation of state over large range of temperature and pressure except for the critical region when applying to pure polar and non-polar fluids. This quartic equation of state was also shown to have the two important advantages that cubic equations of state have: analytical solutions and easy specification of the roots. And only four pure fluid properties are needed to model polar fluids.

The quartic equation of state looks very complicated with forty coefficients. A new set of coefficients (fifteen less than previous work) has been obtained to show that a simplified quartic equation of state can model the polar and non-polar fluids about equally well with fewer regressed coefficients. Eight of the eliminated coefficients are the first order terms of the reduced dipole moment. The results from the regression on a data base including sixteen non-polar fluids and thirty polar fluids show that the performance of the quartic equation of state with the new set of twenty-five coefficients is only slightly worse than the original one. It should be noted that twenty-five coefficients are still a lot of coefficients. And it may be risky to use a model with too many regressed coefficients for extrapolation.

One important application of an equation of state is phase equilibrium calculation for mixtures. Since the performance of the quartic equation of state is superior to the Peng-Robinson equation of state when applying to pure fluids, it was hoped at the beginning that this advantage would remain or even increase when extending to mixtures. However, the results show that the performance with mixtures of both the original and simplified quartic equations of state (with the mixing rules used) is generally slightly worse than that of the Peng-Robinson equation of state even for systems at high pressure; and the performance of the original quartic equation of state is generally slightly better than that of the simplified one.

Beyond what has been done in this project, some further work concerning the quartic equation of state might include the following:

The work on simplification in this project did not really simplify this quartic equation of state; to really simplify it, a new and simple functional form of the attractive term must be proposed. The performance of the quartic equation of state can be improved by introducing the temperature dependency and/or composition dependency into the binary interaction parameters, using some physical relations to derive mixing rules with more physical meanings, or introducing new binary interaction parameters for parameter c and e. However, all the approaches above will make the quartic equation of state look even more complicated. The quartic equation of state is not predictive for mixtures. To make it predictive for mixtures, a group contribution method could be applied to estimate the binary interaction parameters. One important advantage of the quartic equation of state over the Peng-Robinson equation of state is that the quartic equation of state has much better performance in estimating some properties other than volumetric properties, for example, residual enthalpy (12). Therefore, it is reasonable to assume that the performance of the quartic equation of state might be better than that of the Peng-Robinson equation of state in estimating some properties such as heat of mixing for mixtures. This should be tested.

In summary, it had been hoped that a generalized quartic equation of state, with a repulsive term that accurately models the hard sphere fluid and an attractive term based on perturbation theory, would show performance superior to popular cubic equations of state while retaining their advantage of ease of identification of roots. Thus it is disappointing that this effort has, to date, shown no superiority over the Peng-Robinson equation for modeling vapor-liquid equilibrium of mixtures. Nevertheless, this effort has been the most substantial and most successful of any of its kind, and its publication can serve as a useful record to guide any future efforts.

LIST OF SYMBOLS

a = temperature and substance dependent parameter
a_c = the value of parameter a at the critical temperature of the fluid
a_{ij} = the attractive parameter for component i interacting with compound j
a_m = the attractive parameter for the mixture
a_{rj}, c_{rj}, e_{rj}, and X_{ik} for $j = 0,1,2$ and $k = 1,2$ = the actual coefficients obtained from regression
b_m = the excluded volume parameter for the mixture
b_{ij} = the excluded volume parameter for component i interacting with compound j
c = temperature and substance dependent parameter
c_c = the value of parameter c at the critical temperature of the fluid
d_i = the hard sphere diameter of the ith component
e = substance-dependent parameters
k_{ij} = binary interaction parameter
k_o = regressed constants, $k_0 = 1.2864$
k_1 = regressed constants, $k_1 = 2.8225$
m_{ij} = binary interaction parameter, m_{ij} is often set to zero
x_i = mole fraction of the component i in liquid phase
y_i = mole fraction of the component i in vapor phase
B_v = the second virial coefficient
H_r = the residual enthalpy
H_{vap} = the enthalpy of vaporization
N_1 = the number of saturation data points in the two-phase region
N_2 = the number of gas density data points in the single-phase region
N_3 = the number of residual enthalpy data points
N_4 = the number of enthalpy of vaporization data points in the two-phase region

N_5 = the number of second virial coefficient data points
N_6 = the number of vapor-liquid phase equilibrium data points
P_s = the saturated vapor pressure
$X_2, X_3, X_4, X_5, X_6, X_7$ = general constant to be determined by regression

β = the hard sphere molar volume of the fluid
βc = the hard sphere volume at the critical temperature, $\beta_c = 0.165V_c$
ρ = the number density
ΔP_s = the error in the saturated vapor pressure, $\Delta P_s = (P_s^{calc} - P_s^{exp})$
$\Delta\rho$ = the error in the density, $\Delta\rho = (\rho^{calc} - \rho^{exp})$
ΔH_r = the error in the residual enthalpy, $\Delta H_r = (H_r^{calc} - H_r^{exp)}$
ΔH_{vap} = the error in the enthalpy of vaporization, $\Delta H_{vap} = (H_{vap}^{calc} - H_{vap}^{exp})$
ΔB_v = the error in the second virial coefficient, $\Delta B_v\,(B_v^{cal} - B_v^{exp})$
subscripts:
g = single phase gas properties
r = residual properties
s = saturated properties
sv = saturated vapor properties
sl = saturated liquid properties
superscripts:
calc = calculated results
exp = experimental data

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