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A New Two-Constant Equation of State

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The development of a new two-constant equation of state in which the attractive pressure term of the semiempirical van der Waals equation has been modified is outlined. Examples of the use of the equation for predicting the vapor pressure and volumetric behavior of single-component systems, and the phase behavior and volumetric behavior of binary, ternary, and multicomponent systems are given. The proposed equation combines simplicity and accuracy. It performs as well as or better than the Soave–Redlich–Kwong equation in all cases tested and shows its greatest advantages in the prediction of liquid phase densities.

Introduction

Ever since the appearance of the van der Waals equation in 1873 (van der Waals, 1873), many authors have proposed variations in the semiempirical relationship. One of the most successful modifications was that made by Redlich and Kwong (1949). Since that time, numerous modified Redlich–Kwong (RK) equations have been proposed (Redlich and Dunlop, 1963; Chueh and Prausnitz, 1967; Wilson, 1969; Zudkvitch and Joffe, 1970; and others). Some have introduced deviation functions to fit pure substance *PVT* data while others have improved the equation's capability for vapor–liquid equilibrium (VLE) predictions. A review of some of the modified RK equations has been presented (Tsonopoulos and Prausnitz, 1969). One of the more recent modifications of the RK equation is that proposed by Soave (1972). The Soave–Redlich–Kwong (SRK) equation has rapidly gained acceptance by the hydrocarbon processing industry because of the relative simplicity of the equation itself as compared with the more complicated BWRS equation (Starling and Powers, 1970; Lin et al., 1972) and because of its capability for generating reasonably accurate equilibrium ratios in VLE calculations.

However, there still are some shortcomings which the SRK equation and the original RK equation have in common. The most evident is the failure to generate satisfactory density values for the liquid even though the calculated vapor densities are generally acceptable. This fact is illustrated in Figure 1 which shows the comparison of the specific volumes of n-butane in its saturated states. The literature values used for the comparison were taken from Starling (1973). It can be seen that the SRK equation always predicts specific volumes for the liquid which are greater than the literature values and the deviation increases from about 7% at reduced temperatures below 0.65 to about 27% when the critical point is approached. Similar results have been obtained for other hydrocarbons larger than methane. For small molecules like nitrogen and methane the deviations are smaller.

Although one cannot expect a two-constant equation of state to give reliable predictions for all of the thermodynamic properties, the demand for more accurate predictions of the volumetric behavior of the coexisting phases in VLE calculations has prompted the present investigation into the possibility that a new simple equation might exist which would give better results than the SRK equation. In this paper, an equation is presented which gives improved liquid density values as well as accurate vapor pressures and equilibrium ratios.

Formulation of the Equation

Semiempirical equations of state generally express pressure as the sum of two terms, a repulsion pressure P_R and an attraction pressure P_A as follows

$$P = P_R + P_A \tag{1}$$

The equations of van der Waals (1873), Redlich and Kwong (1949), and Soave (1972) are examples and all have the repulsion pressure expressed by the van der Waals hard sphere equation, that is

$$P_R = \frac{RT}{v - b} \tag{2}$$

The attraction pressure can be expressed as

$$P_A = -\frac{a}{g(v)} \tag{3}$$

where $g(v)$ is a function of the molar volume v and the constant b which is related to the size of the hard spheres. The parameter a can be regarded as a measure of the intermolecular attraction force. Applying eq 1 at the critical point where the first and second derivatives of pressure with respect to volume vanish one can obtain expressions for a and b at the critical point in terms of the critical properties. While b is usually treated as temperature independent, a is constant only in van der Waals equation. For the RK equation and the SRK equation, dimensionless scaling

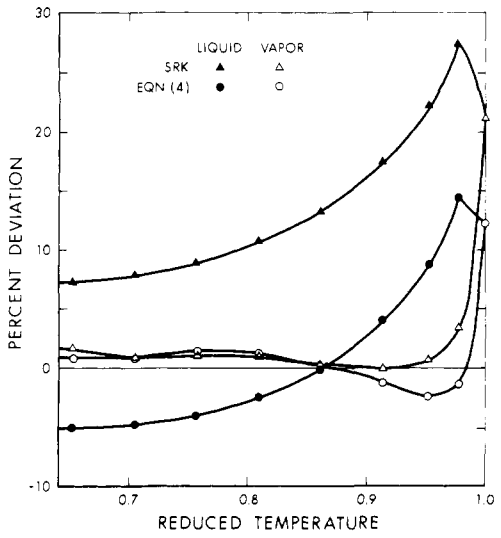

Figure 1. Comparison of predicted molar volumes for saturated n-butane.

factors are used to describe the temperature dependence of the energy parameter.

A study of the semiempirical equations having the form of eq 1 indicates that by choosing a suitable function for $g(v)$, the predicted critical compressibility factor can be made to approach a more realistic value. The applicability of the equation at very high pressures is affected by the magnitude of b/v_c where v_c is the predicted critical volume. Furthermore, by comparing the original RK equation and the SRK equation, it is evident that treating the dimensionless scaling factor for the energy parameter as a function of acentric factor in addition to reduced temperature has significantly improved the prediction of vapor pressures for pure substances and consequently the equilibrium ratios for mixtures.

We propose an equation of the form

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{4}$$

Equation 4 can be rewritten as

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{5}$$

where

$$A = \frac{aP}{R^2T^2} \tag{6}$$

$$B = \frac{bP}{RT} \tag{7}$$

$$Z = \frac{Pv}{RT} \tag{8}$$

Equation 5 yields one or three roots depending upon the number of phases in the system. In the two-phase region, the largest root is for the compressibility factor of the vapor while the smallest positive root corresponds to that of the liquid.

Applying eq 4 at the critical point we have

$$a(T_c) = 0.45724\frac{R^2T_c^2}{P_c} \tag{9}$$

$$b(T_c) = 0.07780\frac{RT_c}{P_c} \tag{10}$$

$$Z_c = 0.307 \tag{11}$$

At temperatures other than the critical, we let

$$a(T) = a(T_c) \cdot \alpha(T_r, \omega) \tag{12}$$

$$b(T) = b(T_c) \tag{13}$$

where $\alpha(T_r, \omega)$ is a dimensionless function of reduced temperature and acentric factor and equals unity at the critical temperature. Equation 12 was also used by Soave (1972) for his modified RK equation.

Applying the thermodynamic relationship

$$\ln\frac{f}{p} = \int_0^P \left(\frac{v}{RT} - \frac{1}{P}\right) dP \tag{14}$$

to eq 4, the following expression for the fugacity of a pure component can be derived

$$\ln\frac{f}{p} = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B}\ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right) \tag{15}$$

The functional form of $\alpha(T_r, \omega)$ was determined by using the literature vapor pressure values (Reamer et al., 1942; Rossini et al., 1953; Reamer and Sage, 1957; Starling, 1973) and Newton's method to search for the values of α to be used in eq 5 and 15 such that the equilibrium condition

$$f^L = f^V \tag{16}$$

is satisfied along the vapor pressure curve. With a convergence criterion of $|f^L - f^V| \leq 10^{-4}$ kPa about two to four iterations were required to obtain a value for α at each temperature.

For all substances examined the relationship between α and T_r can be linearized by the following equation

$$\alpha^{1/2} = 1 + \kappa(1 - T_r^{1/2}) \tag{17}$$

where κ is a constant characteristic of each substance. As shown in Figure 2, these constants have been correlated against the acentric factors. The resulting equation is

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{18}$$

It is interesting to note that eq 17 is similar to that obtained by Soave (1972) for the SRK equation although eq 17 is arrived at for each substance using vapor pressure data from the normal boiling point to the critical point whereas Soave used only the critical point and the calculated vapor pressure at $T_r = 0.7$ based on the value of acentric factor.

The fugacity coefficient of component k in a mixture can be calculated from the following equation

$$\ln\frac{f_k}{x_k P} = \frac{b_k}{b}(Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \times \left(\frac{2\Sigma_i X_i a_{ik}}{a} - \frac{b_k}{b}\right) \ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right) \tag{19}$$

The mixture parameters used in eq 5 and 19 are defined by the mixing rules

$$a = \sum_i\sum_j x_i x_j a_{ij} \tag{20}$$

$$b = \sum_i x_i b_i \tag{21}$$

where

$$a_{ij} = (1 - \delta_{ij})a_i^{1/2}a_j^{1/2} \tag{22}$$

In eq 22 δ_{ij} is an empirically determined binary interaction coefficient characterizing the binary formed by component i and component j. Equation 22 has been used previously by Zudkevitch and Joffe (1970) for their modified RK equation in calculating vapor–liquid equilibrium ratios.

Table I. Comparison of Vapor Pressure Predictions

Substance	No. of data points	Absolute error, psia						Relative error, %					
		AAD		BIAS		RMS		AAD		BIAS		RMS	
		SRK	Eq 4	SRK	Eq 4	SRK	Eq 4	SRK	Eq 4	SRK	Eq 4	SRK	Eq 4
C_1	28	3.08	1.82	2.82	1.72	4.31	2.83	1.44	0.66	0.47	0.38	1.57	0.77
C_2	27	1.12	0.58	0.87	−0.58	1.38	0.65	0.70	0.34	−0.10	−0.34	0.95	0.38
C_3	31	2.68	1.09	2.66	1.06	3.37	1.47	0.98	0.36	0.87	0.31	1.10	0.42
i-C_4	27	1.83	0.54	1.78	0.50	2.33	0.71	1.06	0.32	0.82	0.16	1.18	0.34
n-C_4	28	1.45	0.50	1.38	0.03	2.05	0.62	0.75	0.37	0.47	−0.22	0.86	0.42
i-C_5	15	0.64	0.95	0.22	−0.95	0.86	1.48	0.46	0.54	0.17	−0.53	0.49	0.60
n-C_5	30	1.65	0.69	1.56	0.28	2.26	0.95	0.92	0.58	0.50	−0.29	1.02	0.66
n-C_6	29	2.86	1.69	2.81	1.53	3.97	2.65	1.55	0.90	1.31	0.37	1.75	1.06
n-C_7	18	2.29	1.34	2.29	1.30	3.24	2.02	1.51	0.79	1.48	0.63	1.88	1.04
n-C_8	16	2.61	1.55	2.61	1.54	3.30	2.08	1.99	1.04	1.97	1.02	2.24	1.26
N_2	17	0.74	0.38	0.60	−0.10	1.07	0.48	0.56	0.31	0.00	−0.02	0.75	0.37
CO_2	30	2.77	1.95	2.73	−0.82	3.87	2.44	0.53	0.62	0.50	−0.49	0.63	0.71
H_2S	30	1.68	1.18	1.57	−0.53	2.52	1.42	0.66	0.96	0.34	0.42	1.00	1.48

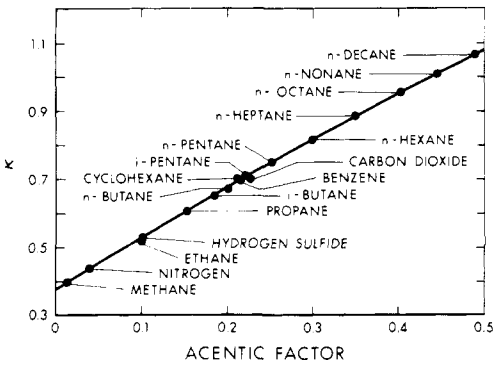

Figure 2. Relationship between characterization constants and acentric factors.

In this study δ_{ij}'s were determined using experimental binary VLE data. The value of δ_{ij} obtained for each binary was the one that gave a minimum deviation in the predicted bubble point pressures. The importance of the interaction coefficient is illustrated in Figure 3 for the binary system isobutane-carbon dioxide (Besserer and Robinson, 1973). It can be seen that the use of an interaction coefficient has greatly improved the predictions.

The enthalpy departure of a fluid which follows eq 4 is given by

$$H - H^* = RT(Z-1) + \frac{T\frac{da}{dT} - a}{2\sqrt{2}b} \ln\left(\frac{Z + 2.44B}{Z - 0.414B}\right) \quad (23)$$

This is obtained by substituting eq 4 into the thermodynamic equation

$$H - H^* = RT(Z-1) + \int_{\infty}^{v} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv \quad (24)$$

Comparisons

Since two-constant equations of state have their own purposes we do not compare the equation obtained in this study with the more complicated BWR (Benedict et al., 1940) or BWRS equations although in some circumstances these may give more accurate predictions at the expense of more computer time and computer storage space. The following comparisons are intended to show that in regions where engineering calculations are most frequently encountered better results can usually be obtained with the equation presented in this study than with the SRK equation. The symbols AAD, BIAS, and RMS are used to denote respectively the average absolute deviation, the bias, and the

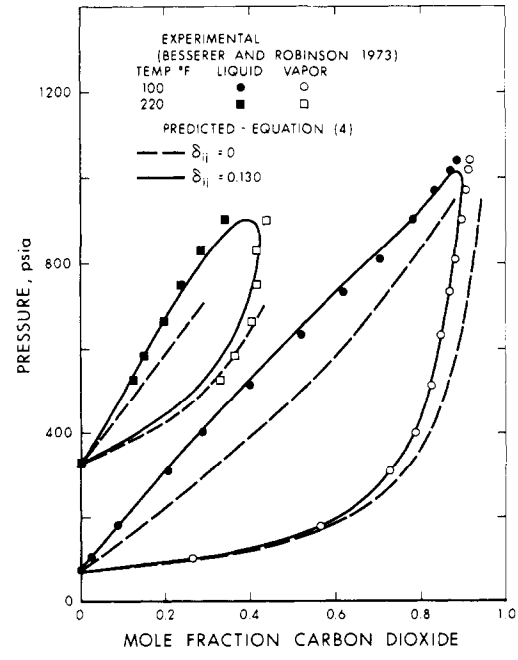

Figure 3. Pressure–equilibrium phase composition diagram for isobutane–carbon dioxide system.

root-mean-square deviation

$$\text{AAD} = \frac{\sum_{i=1}^{N} |d_i|}{N} \quad (25)$$

$$\text{BIAS} = \frac{\sum_{i=1}^{N} d_i}{N} \quad (26)$$

$$\text{RMS} = \frac{\sum_{i=1}^{N} d_i^2}{N} \quad (27)$$

where the d_i are the errors (either absolute or relative) and N is the number of data points.

Pure Substances

Vapor Pressures. Both the SRK equation and eq 4 are designed with a view to reproduce accurately the vapor pressures of pure nonpolar substances. Nevertheless eq 4 gives better agreement between calculated vapor pressures and published experimental values. A comparison of the predictions is presented in Table I for ten paraffins and

Table II. Comparison of Enthalpy Departure Predictions

Substance	No. of data points	Reference	Temperature range, °F	Pressure range, psia	Error, BTU/lb AAD SRK	AAD Eq 4	BIAS SRK	BIAS Eq 4	RMS SRK	RMS Eq 4
Nitrogen	48	(Mage, 1963)	−250–50	200–2000	0.57	1.13	0.24	−0.58	0.80	1.25
Methane	35	(Jones, 1963)	−250–50	250–2000	2.58	1.97	−1.13	−0.78	3.58	2.52
n-Pentane	160	(Lenoir, 1970)	75–700	200–1400	1.43	1.18	0.78	0.25	1.82	1.61
n-Octane	70	(Lenoir, 1970)	75–600	200–1400	2.47	2.43	2.18	2.36	3.36	3.16
Cyclohexane	113	(Lenoir, 1971)	300–680	200–1400	2.83	2.48	2.16	1.75	3.60	3.26

Table III. Compressibility Factor of the *n*-Butane–Carbon Dioxide System (Data by Olds et al., 1949)

Temp, °F	Pressure, psia	Mole fraction *n*-Butane 0.9 SRK	0.9 Eq 4	0.9 Expt	0.5 SRK	0.5 Eq 4	0.5 Expt	0.1 SRK	0.1 Eq 4	0.1 Expt
100	600	0.170	0.151	0.158			—	0.743	0.722	0.740
	1000	0.279	0.248	0.260	0.242	0.215	0.218			—
	2000	0.542	0.482	0.510	0.452	0.404	0.418	0.374	0.339	0.325
	3000	0.793	0.707	0.753	0.649	0.580	0.610	0.505	0.455	0.454
	4000	1.037	0.926	0.989	0.838	0.750	0.794	0.631	0.568	0.580
280	600				0.804	0.782	0.798	0.924	0.908	0.918
	1000	0.320	0.289	0.274	0.665	0.638	0.644	0.876	0.852	0.862
	2000	0.536	0.482	0.489	0.584	0.545	0.525	0.786	0.750	0.744
	3000	0.740	0.665	0.694	0.702	0.645	0.642	0.766	0.722	0.699
	4000	0.934	0.840	0.888	0.838	0.765	0.782	0.801	0.749	0.727
460	600	0.830	0.804	0.818	0.928	0.910	0.920	0.976	0.965	0.968
	1000	0.730	0.696	0.694	0.889	0.862	0.870	0.964	0.946	0.948
	2000	0.690	0.643	0.627	0.843	0.803	0.796	0.947	0.915	0.912
	3000	0.808	0.744	0.746	0.871	0.822	0.806	0.949	0.908	0.898
	4000	0.950	0.869	0.895	0.942	0.881	0.877	0.969	0.921	0.906

three commonly encountered nonhydrocarbons. It can be seen that the absolute errors are greatly reduced using eq 4 for all substances except isopentane. The slightly larger overall relative errors shown for carbon dioxide and hydrogen sulfide resulted from the higher percentage errors at the lower pressure regions. The consistently larger deviation shown by eq 4 for isopentane could be due to errors in the experimental results in the high-temperature region where differences between the predicted and experimental values as large as 4 psi (equivalent to 1%) occurred.

Densities. Generally, saturated liquid density values calculated from the SRK equation are lower than literature values. This is true except for small molecules like nitrogen and methane at very low temperatures where the predicted values are slightly higher. Equation 4 predicts saturated liquid densities which are higher at low temperatures and lower at high temperatures than the experimental values. As an example, the prediction for *n*-butane is presented in Figure 1. The fact that eq 4 gives a universal critical compressibility factor of 0.307 as compared with SRK's 0.333 has improved the predictions in the critical region.

The specific volumes of saturated vapors have also been compared. The results for *n*-butane are included in Figure 1. It can be seen that both equations yield acceptable values except that in the critical region better results have been obtained with eq 4. The improvement is more evident for large molecules although both equations work well for small molecules.

Enthalpy Departures. Experimental values of enthalpy departures for five pure substances have been used to compare with the values calculated from the SRK equation and from eq 4. The results are presented in Table II. It is fair to say that both equations generate enthalpy values of about the same reliability.

Mixtures

PVT **Calculations.** In order to illustrate the usefulness of eq 4 for predicting the volumetric behavior of binary mixtures in the single phase region, the *n*-butane–carbon dioxide system studied by Olds and co-workers (1949) was selected for comparison. For the SRK equation and eq 4 the interaction coefficients for this binary were 0.135 and 0.130, respectively. The compressibility factors at three temperatures and five pressures for three compositions are presented in Table III. The improvement resulting from eq 4 is evident.

VLE Calculations. One of the advantages of using simple two-constant equations of state is the relative simplicity with which they may be used to perform VLE calculations. Multi-constant equations of state, for example the BWRS equation, require the use of iteration procedures to solve for the densities of the coexisting phases while simple equations like the SRK equation and eq 4 can be reduced to cubic equations similar to eq 5 and the roots can be obtained analytically.

Vapor–liquid equilibrium conditions for a number of paraffin–paraffin binaries were predicted using eq 4. It was found that the optimum binary interaction coefficients were negligibly small for components with moderate differences in molecular size. However, systems involving components having relatively large differences in molecular size required the use of a nontrivial interaction coefficient in order to get good agreement between predicted and experimental bubble point pressures.

As an example of the use of eq 4 to predict the phase behavior of a ternary paraffin hydrocarbon system, the data of Wichterle and Kobayashi (1972) on the methane–ethane–propane system were compared to predicted values. As

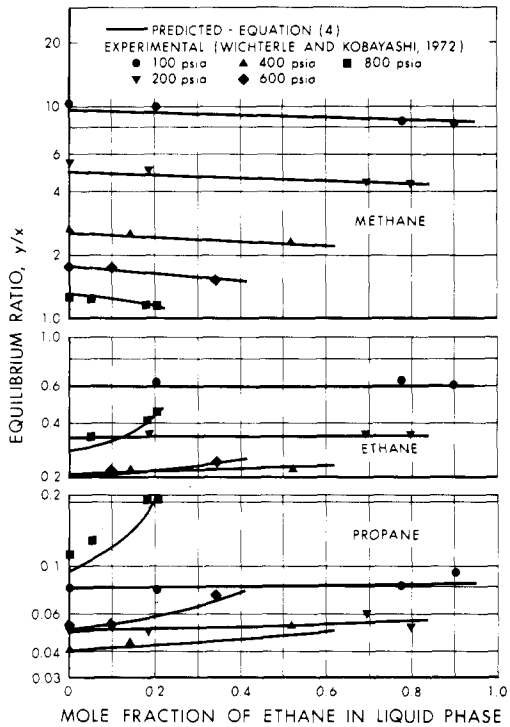

Figure 4. Comparison of equilibrium ratios for methane–ethane–propane system at −75°F.

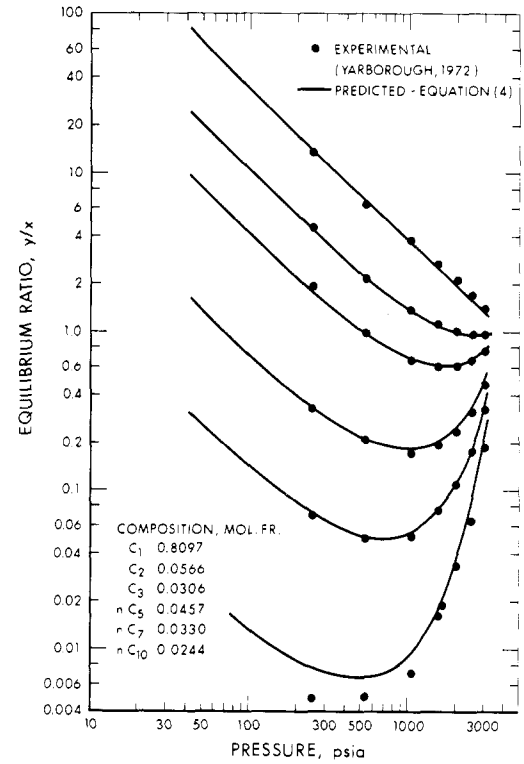

Figure 5. Comparison of equilibrium ratios for Yarborough mixture no. 8 at 200°F.

indicated in Figure 4, agreement was excellent. No interaction coefficients were used.

In a previous study (Peng et al., 1974), the binary interaction coefficients required for use with the SRK equation were determined and used to predict the phase and volumetric behavior of selected systems used in a study by Yarborough (1972). Good agreement was obtained between the predicted equilibrium ratios and the experimental values. In this study these systems have been tested using eq 4 and good results have also been obtained. The equilibrium ratios for a mixture containing only paraffins are shown in Figure 5. The volumetric behavior of this mixture is presented in Figure 6. Although both the SRK equation and eq 4 generate reliable equilibrium ratios, the new equation predicts much more accurate volumetric behavior. A paper concerning the binary interaction coefficients required for use in eq 4 for systems involving nonhydrocarbons is currently in preparation.

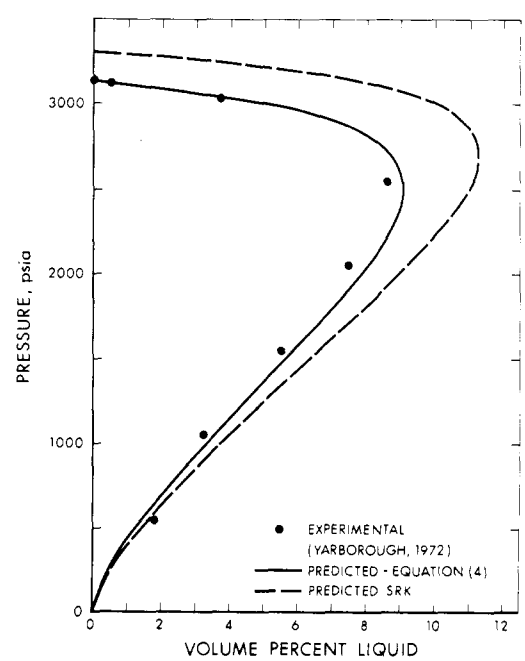

Figure 6. Volumetric behavior of Yarborough mixture no. 8 at 200°F.

Conclusions

By modifying the attraction pressure term of the semiempirical van der Waals equation a new equation of state has been obtained. This equation can be used to accurately predict the vapor pressures of pure substances and equilibrium ratios of mixtures.

While the new equation offers the same simplicity as the SRK equation and although both equations predict vapor densities and enthalpy values with reasonable accuracy, more accurate liquid density values can be obtained with the new equation. In regions where engineering calculations are frequently required the new equation gives better agreement between predictions and experimental *PVT* data.

Since two-constant equations have their inherent limitations, and the equation obtained in this study is no exception, the justification for the new equation is the compromise of its simplicity and accuracy.

Acknowledgment

The financial support provided by the Alberta Research Council and the National Research Council of Canada for this work is sincerely appreciated.

Nomenclature

A = constant defined by eq 6
a = attraction parameter
B = constant defined by eq 7

b = van der Waals covolume
f = fugacity
H = enthalpy
P = pressure
R = gas constant
T = absolute temperature
v = molar volume
x = mole fraction
Z = compressibility factor

Greek Letters

α = scaling factor defined by eq 12
δ = interaction coefficient
κ = characteristic constant in eq 17
ω = acentric factor

Superscripts

L = liquid phase
V = vapor phase
* = ideal gas state

Subscripts

A = attraction
c = critical property
R = repulsion
r = reduced property
i, j, k = component identifications

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Creation and Survival of Secondary Crystal Nuclei. The Potassium Sulfate–Water System

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Formation of secondary nuclei of K_2SO_4 was observed in a continuous flow, mixed-magma crystallizer by counting particles in the crystal effluent with a Coulter Counter. Spontaneous birth of secondary nuclei occurs over at least the 1–5 μm size range. Only a fraction of originally formed nuclei survive to populate the larger size ranges. The fraction of such surviving nuclei increases with the supersaturation level in the growing environment. The number of originally formed nuclei depends on stirrer RPM, supersaturation, and the fourth moment of the parent crystal size distribution.

Introduction

In the past several years there has been an increasing recognition of the importance of secondary nucleation as grain source in typical crystallizers of the mixed-magma type. The so-called MSMPR crystallizer with its simple distribution form (Randolph and Larson, 1971) provided a means of quantitatively measuring the effective nucleation rate under realistic mixed-magma conditions. This led to the correlation of such nucleation data in simple power-law forms of the type

$$B^0 = k_N(\mathrm{T}, \mathrm{RPM})M_T{}^j s^i \quad \text{(Class I System)} \qquad (1a)$$

or

$$B^0 = k_N(\mathrm{T}, \mathrm{RPM})M_T{}^j G^i \quad \text{(Class II System)} \qquad (1b)$$

The dependence of these kinetics on agitation level and solids concentration together with a low-order supersaturation dependence confirm a secondary mechanism which is at variance with homogeneous nucleation theory.

Clontz and McCabe (1971) conducted a now-classical experiment in which they demonstrated that nuclei could be generated in a slightly supersaturated solution by low energy metal/crystal or crystal/crystal contacts. No visible damage to the contacting crystals could be determined even after continued secondary nuclei breeding in the experiment. Ottens and de Jong (1973) and Bennett et al. (1973) take the contact nucleation mechanisms detailed by McCabe and hueristically derive the form of power-law kinetics to be expected in a mixed-magma crystallizer. These formulations were supported with additional MSMPR data.