A FOUR-PARAMETER CORRESPONDING STATES CORRELATION FOR FLUID COMPRESSIBILITY FACTORS

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This investigation demonstrates advantages in the use of Pitzer's acentric factor and Stiel's polar factor as the third and fourth parameters in a corresponding states correlation for compressibility factors. A generalized reduced virial equation is developed and used as the correlation framework to describe simultaneously, with a single set of generalized coefficients, the compressibility factors of sixteen fluids, ranging from noble gases to polar compounds.

In the past, the two-parameter corresponding states principle has formed the basis of many correlations in which a reduced thermodynamic or transport property for nonpolar fluids is related to the temperature and pressure or temperature and volume. More recently, third and fourth parameters have been introduced into corresponding states correlations to predict the behavior of wider ranges of fluids, including polar fluids. The accuracies of correlations using third and fourth parameters have varied, with the degree of success depending primarily on the parameters used.

Four-Parameter Correlation Development

The work of van der Waals about 1873 used the critical temperature and critical pressure to characterize a substance. According to van der Waals, the simple theorem of corresponding states indicated that substances at equal reduced conditions should behave identically. However, it was shown that this behavior results only for fluids having small, spherical, weakly interacting molecules.

To correct for the effects of molecular size and shape, various third parameters were added to the simple theorem. Among those advancing third parameters were Su and Viswanath (1), Meissner and Seferian (2), Lyderson, *et al.* (3), Riedel (4-6), and Pitzer, *et al.* (7-13). Definite improvements were obtained for correlations for nonpolar fluids. The most widely used and most reliable third parameter was the Pitzer acentric factor, ω . The name "acentric factor" was used to imply that the factor roughly measures the deviation of the intermolecular potential function from that of the simple fluids. Expressed in terms of its defining vapor pressure relation, the acentric factor is a measure of vapor pressure deviation from simple fluid behavior due to size-shape, polarity, association, and quantum effects. Pitzer showed that the acentric factor can be used to correlate real fluid properties by using the following expression to correct (to first order) for deviations from simple fluid properties,

$$Y = Y^{(0)} + \omega Y^{(1)} \qquad \textbf{Eq. 1}$$

where Y is any correlatable reduced property, $Y^{(0)}$is the simple fluid contribution, and $Y^{(1)}$ is the correction term.

With the success of the acentric factor in correlating properties of nonpolar fluids, the next step was to define a suitable fourth parameter to take into account polar effects. Eubank and Smith (14) were one of the first to define a fourth parameter in terms of dipole moment. Their fourth parameter was made an arbitrary function of a reduced dipole moment, and an extra term was added to Equation 1 in their approach. The acentric factor of each polar material was taken to be that of its hydrocarbon homomorph, which limited the correlation to organic materials. The use of the dipole moment or reduced dipole moment has been previously criticized by Hildebrand and Scott (15), Riedel (6), and Pitzer and Curl (9).

The first really satisfactory development of a fourth parameter was made by Thompson (16). Thompson succeeded in separating size-shape effects from polarity effects in developing his fourth parameter. He defined a so-called "true acentric factor" and an association factor, and related them by

$$\omega = \bar{\omega} + \tau \qquad \textbf{Eq. 2}$$

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with ω = Pitzer's acentric factor, ϖ = true acentric factor, τ = association factor
The true acentric factor was correlated with the molecular radius of gyration, and the association factor was determined by the difference between ω and ϖ. Using these parameters, Thompson proposed the relation

$$Y = Y^{(0)} + \bar{\omega}Y^{(1)} + \tau Y^{(2)} + \bar{\omega}\tau Y^{(3)} \quad \text{Eq. 3}$$

where $Y^{(1)}$, $Y^{(2)}$, $Y^{(3)}$ are the correction terms due to the true acentric factor, the association factor, and their cross product, respectively.

Since the radius of gyration is difficult to determine, Harlacher (17) modified Equation 3 by using the molecular parachor, P, as the fourth parameter. The parachor is a function of liquid molar volume, and Harlacher (17) showed that the liquid molar volume is a function of the molecular radius of gyration. Based upon Harlacher's development, Equation 3 becomes

$$Y = Y^{(0)} + PY^{(1)*} + \omega Y^{(2)} + P\omega Y^{(3)*} - P^2Y^{(3)**} \quad \text{Eq. 4}$$

with
$$Y^{(1)*} = Y^{(1)} - Y^{(2)}$$
$$Y^{(3)*} = aY^{(3)}$$
$$Y^{(3)**} = a^2Y^{(3)}$$

where <u>a</u> is the slope of the line representing the locus of zero association effects on a plot of parachor versus acentric factor.

The parachor was shown by Harlacher and Braun (18) to be a reliable fourth parameter for correlating vapor pressures of polar materials. However, the nature of the expansion in Equation 4 is such that a value of the parachor is required even when nonpolar, normal fluids are being considered. One advantage of Pitzer's acentric factor as a third parameter is that it becomes zero when working with simple fluids. A fourth parameter would have a similar advantage if it became zero when the fluid considered is not polar.

In a series of papers, Halm and Stiel defined a fourth parameter for polar fluids through the vapor pressure and showed that their approach was applicable for the entropy of vaporization (19), density of saturated liquids and vapors (20), and second virial coefficients (21). Their fourth parameter, referred to as the polarity factor, x, may be represented by

$$x = \log p_r^*\big|_{T_r=0.6} + 1.70\omega + 1.552 \quad \text{Eq. 5}$$

with ω being Pitzer's acentric factor and p_r^* the reduced vapor pressure at $T_r = 0.6$. Using x as the fourth parameter, the four-parameter extension of Equation 1 becomes

$$Y = Y^{(0)} + \omega Y^{(1)} + xY^{(2)} + \omega x Y^{(3)} \quad \text{Eq. 6}$$

with $Y^{(2)}$ the contribution due to the polarity correction and $Y^{(3)}$ the cross product correction term if molecules of the material are very large or highly associated, or both. Recently, Peng and Stiel (22) have considered two alternative parameters, ω' and x'. These are related to ω and x by

$$\omega = \omega' + x' \quad \text{Eq. 7} \qquad x = 0.14\,x' - 1.1\,\omega' x' \quad \text{Eq. 8}$$

with ω' and $x' \geq 0$. These equations allow for a degree of separation of ω into shape and polarity contributions, while ω' and x' remain positive for all substances. This is an advantage over the parameter x, which was found to be negative for several of the higher-molecular-weight alcohols, for example.

In the present investigation, Pitzer's acentric factor, ω, and the polarity factor, x, were selected as the most suitable parameters to be used in a four-parameter corresponding states correlation. Both parameters have the advantage that they are calculable from reliable vapor pressure data and approach zero values when simple fluid behavior is approached.

CORRELATION DEVELOPMENT

One of the reduced thermodynamic properties which can be correlated using the corresponding states principle is the compressibility factor, Z. The compressibility factor can be expressed by the reduced virial equation of state, which has the form

$$Z = \sum_{n=1}^{N} B_n \rho_r^{n-1} \quad \text{Eq. 9}$$

where ρ_r the reduced density, is

$$\rho_r = \frac{\rho R T_c}{P_c} \quad \text{Eq. 10}$$

Vernick (23) has shown that the coefficients B_n in Equation 9 may be expressed by expansions in $1/T_r$. The coefficients may be represented as

$$B_n = \sum_{s=0}^{S} A_{ns} T_r^{-s} \qquad \text{Eq. 11}$$

with $T_r = T/T_C$.

In order to characterize the behavior of normal fluids, it is possible to express the coefficients A_{ns} from Equation 11 in terms of an expansion in ω , shown by.

$$A_{ns} = \sum_{a=0}^{A} D_{nsa} \omega^a \qquad \text{Eq. 12}$$

For polar materials, the coefficients D_{nsa} in Equation 12 may be expressed in terms of expansion in x, given by

$$D_{nsa} = \sum_{b=0}^{B} C_{nsab} x^b \qquad \text{Eq. 13}$$

By combining Equations 9 through 13 one arrives at a general expression for the compressibility factor given by Eq.14

$$Z = \sum_{b=0}^{B} \sum_{a=0}^{A} \sum_{s=0}^{S} \sum_{n=1}^{N} C_{nsab} x^b \omega^a T_r^{-s} \rho_r^{n-1}$$

Thus, Equation 14 represents a means of obtaining the compressibility factor of a material by knowing the values of $\rho_{r'}$, $T_{r'}$, ω', and x.

In order to calculate compressibility factors from Equation 14, the maximum index of each summation must be specified and the values of the coefficients C_{nsab} must be determined. This was accomplished in this investigation by using a computer program known as ORNOR, which is an orthogonal least-squares technique. Hall and Canfield (24) developed the ORNOR program, which will choose, in a least-squares sense, the best polynomial to approximate an infinite series. It will also select the polynomial coefficients which have a minimum variance from the series coefficients. In this investigation, values were assigned to the indices in Equation 14 to specify the maximum number of terms with which the ORNOR program was to perform computations. The computer program then used experimental compressibility factor data to determine the best polynomial fit for each degree polynomial up to and including the maximum number of terms in the summation. For each polynomial fit, the program determined the average absolute deviation of calculated compressibility factor values from the experimental values and the values of the coefficients C_{nsab} in the summation. Analyses of the orthonormalization process have been presented elsewhere (24, 25).

DISCUSSION OF RESULTS

P-V-T data were collected for twenty-one fluids studied in this investigation. These fluids ranged from noble gases to strongly polar materials. Superheated vapor data were obtained for each gas; saturated liquid and vapor data were obtained where available. Accurate values for molecular weight, critical temperature, critical pressure, criti-

TABLE 1. *Values of Molecular Weight,* T_c, P_c, Z_c, ω , x, *and Sources of P-V-T Data for Selected Fluids*

Substance	M. Wt.	T_c (°R)	P_c (psia)	Z_c	ω	X	Sources of P-V-T Data
Argon	39.95	271.8	705.4	0.290	0	0	26
Krypton	83.80	377.2	196.9	0.291	0	0	27
Xenon	131.30	521.6	852.4	0.290	0	0	28
Methane	16.04	343.6	673.1	0.290	0.013	0	29, 30, 31, 32
Ethane	30.07	549.9	711.5	0.285	0.099	0	33, 34, 35
Propane	44.09	665.9	617.4	0.277	0.150	0	35, 36, 37, 38, 39, 40
Butane	58.12	765.4	550.6	0.274	0.201	0	34, 35, 39, 41, 42
Pentane	72.15	845.7	489.5	0.269	0.254	0	34, 39
Ethylene	28.05	509.0	739.8	0.270	0.087	0	34, 35, 43, 44
Benzene	78.11	1012.3	714.3	0.274	0.215	0	45, 46
Nitrogen	28.02	227.1	492.6	0.291	0.040	0	34, 47, 48, 49
Carbon monoxide	28.01	239.7	507.6	0.294	0.046	0	43, 50, 51
Carbon dioxide	44.01	547.6	1071.3	0.274	0.420	0	34
Hydrogen sulfide	34.08	672.4	1306.5	0.268	0.100	0	52, 53, 54
Propylene	42.08	657.0	667.5	0.274	0.142	0.002	55
Nitric oxide	30.01	323.9	946.9	0.251	0.577	−0.045	56
Nitrous oxide	44.02	557.4	1051.0	0.273	0.160	−0.003	57, 58
Sulfur dioxide	64.06	775.2	1142.9	0.268	0.252	0.006	59, 60
Methyl chloride	50.49	749.3	986.3	0.276	0.152	0.007	58, 61
Ethylene oxide	44.05	842.0	1043.4	0.255	0.207	0.012	62
Ammonia	17.03	730.2	1641.0	0.242	0.252	0.013	43, 63, 64

cal compressibility factor, acentric factor, and polarity factor were gathered from the literature for each of the materials studied. These values are presented in Table 1 along with the literature citations for the P-V-T data.

The data for each individual fluid were fitted to a polynomial to determine the self-consistency of the data and to establish the limits for the index on each summation. The limits which were finally established were N = 7, S = 1, A = 1, and B = 1. Values larger than 1 for S did not improve the accuracy of the resulting data fit. Values of A and B equal to 2 and greater produced terms in ω^2, ω^3,... and x^2, x^3, ... which offered negligible contributions. The contributions of the cross product terms $\omega\ x$ and $(\omega\ x)^2$ were also negligible and were eliminated from the correlating equations.

Using the four parameters $\rho_{r'}$, $T_{r'}$, ω', and x, the coefficients in Equation 14 were determined by the ORNOR program for one equation for predicting saturated vapor and liquid compressibility factors and a second equation for predicting superheated vapor compressibility factors. These correlations were based upon the data for 16 materials, including 5 polar materials. The average absolute deviation from experimental values of the predicted compressibility factors for the saturated vapor and liquid equation was 1.87%, and for the superheated vapor equation was 2.92%. The coefficients for these two equations are given in Table 2 together with the range of data used. Deviations for individual substances are given in Table 3.

TABLE 2. *Coefficients C_{nsab} in Generalized Correlation*

The general equation for the compressibility factor is: $Z = \sum_{b=0}^{1} \sum_{a=0}^{1} \sum_{s=0}^{1} \sum_{n=1}^{7} C_{nsab}\, x^b\, \omega^a\, T_r^{-s}\, \rho_r^{n-1}$

Coefficient	Saturated vapor and liquid	Superheated vapor with ω and x	Superheated vapor with ω' and x'
C_{1000}	0.860582650	0.954048455	0.972791791
C_{1100}	0.075710773	0.062849879	0.032091185
C_{2000}	0.205989122	0.420237720	0.241056740
C_{2100}	−0.462107062	−0.767798960	−0.403009772
C_{3000}	−0.025237545	−0.401667178	0.177534580
C_{3100}	0.011164818	0.435857952	−0.552089393
C_{4000}	−0.003318009	0.290118635	−0.154963732
C_{4100}	0.023606755	−0.282660365	0.523571491
C_{5000}	−0.000707319	−0.088654816	0.017654218
C_{5100}	−0.003335397	0.081065237	−0.162066758
C_{6000}	0.000202248	0.010880917	0.009247009
C_{6100}	0.000132202	−0.007969588	0.01613895
C_{7000}	−0.000010291	−0.000340795	−0.001647658
C_{1010}	1.307934761	−0.106720328	−1.823885918
C_{1110}	−0.695210636	−0.127976894	1.502427101
C_{2010}	7.362009048	−0.465414047	9.384355545
C_{2110}	−7.206141624	0.794676423	−9.082871437
C_{3010}	−3.06127264	3.404707504	−16.19099426
C_{3110}	2.600443940	−3.797091484	16.36482239
C_{4010}	0.516537189	−2.269314766	9.128727913
C_{4110}	−0.306062126	2.585428238	−9.372029305
C_{5010}	−0.051010318	0.530812561	−2.041124344

C_{5110}	0.012195520	−0.646206915	2.110067368
C_{6010}	0.003265619	−0.037198722	0.158676743
C_{6110}	−0.000022699	0.054571766	−0.164424837
C_{7010}	−0.000101819	−0.000865158	——
C_{1001}	−23.85057068	89.78648376	7.366435051
C_{1101}	12.34868240	−81.24546814	−6.780570030
C_{2001}	−98.52748108	−27.41287231	−16.41654968
C_{2101}	96.74450684	64.60748291	14.71321106
C_{3001}	46.32156372	477.4396973	21.84963989
C_{3101}	−36.63549805	−513.1188965	−20.06927490
C_{4001}	−8.553021431	−503.6542969	−7.690523148
C_{4101}	3.966945648	480.4921875	6.635499001
C_{5001}	0.957946479	178.8093567	0.606222093
C_{5101}	−0.073547423	−147.1973572	−0.310671210
C_{6001}	−0.071554959	−24.59184265	0.042634919
C_{6101}	−0.005570989	14.57466984	−0.072088778
C_{7001}	0.002520135	0.987864613	——
Average Absolute Deviation	1.87%	2.92%	3.84%
Range of Data	Liq. T_r = 0.64-0.99 Vap. T_r = 0.61-0.99	T_r = 0.64-3.3 ρ_r = 0.01-4.8	T_r = 0.64-3.3 ρ_r = 0.01-4.8

TABLE 3. *Deviations of Calculated Compressibility Factors from Experimental Data*[a]

	Average absolute deviation, percent			
	Saturated conditions			
Substance	Vapor	Liquid	Superheated vapor with ω and x	Superheated vapor with ω' and x′
Argon	b	b	1.3	0.7
Krypton	b	b	0.7	1.0
Xenon	b	b	(1.6)	b
Methane	0.4	0.9	1.1	1.7
Ethane	0.4	2.0	0.6	2.8
Propane	0.7	b	1.1	2.5
Butane	0.5	2.2	1.5	1.5
Pentane	b	b	2.0	3.5
Ethylene	0.8	1.3	1.6	3.9
Benzene	(1.1)	(4.2)	(2.2)	b
Nitrogen	0.8	5.8	0.6	0.9
Carbon monoxide	b	b	(2.7)	b
Carbon dioxide	0.5	1.4	1.6	4.2
Hydrogen sulfide	1.5	1.6	1.1	2.6
Propylene	0.5	1.4	3.5	3.7
Nitric oxide	b	b	b	4.5
Nitrous oxide	b	b	b	7.4
Sulfur dioxide	0.6	5.7	7.9	7.8
Methyl chloride	0.3	3.1	7.6	6.6
Ethylene oxide	0.8	2.2	7.3	7.2
Ammonia	0.4	6.7	9.8	10.7

[a] Substances with deviations in parentheses were not included in determinations of coefficients.
[b] Deviations were not determined for these cases.

Two of the materials used in this investigation, nitrous oxide and nitric oxide, have negative values of x and could not be included in the existing correlation. However, using the alternative parameters ω' and x', a second superheated-vapor equation was developed with a resulting average absolute deviation in the data of 3.84%. Deviations for individual substances are given in Table 3. The coefficients for this equation are given in Table 2. Since the first superheated-vapor equation is slightly more accurate, use of the second equation is recommended only when the compressibility factor of a material with a negative value of x is desired. A prior four-parameter correlation of saturated polar vapor and saturated polar liquid densities (20) treated each phase individually through separate expressions. The single equation developed here representing both saturated vapor and liquid compressibility factors is of advantage when self-consistent vapor and liquid properties are needed.

An important feature of the structure of the equations resulting from adopting the form of Equation 14 is the manner in which the equations simplify themselves as a material approaches simple fluid behavior from the direction of polar behavior. For polar materials the equations contain 39 terms. If the material is nonpolar, the polar terms vanish and the equations contain 26 terms. If the material is a single fluid, the acentric factor terms vanish and the equations contain 13 terms. Thus, the utility of the equations has been increased by selecting third and fourth parameters whose values become zero when the behavior characterized by that particular parameter is absent.

The four-parameter correlational approach developed in this investigation has the potential of being applicable to other polar materials. For water, and for highly associated alcohols such as the propanols and butanols, the cross product terms in (ω x), which in the present study were negligible, will probably have to be added to the correlation to account for high association effects. However, until experimental data for wide ranges of conditions are available for fluids having large polar molecules, such as the alcohols, their behavior can be estimated using the present equations with significantly higher deviations to be expected. Since several of the values of x for the alcohols are negative, this will necessitate using the alternative parameters ω' and x' to correlate compressibility factors of these materials.

CONCLUSIONS

The investigation presented here shows that when Pitzer's acentric factor is used as the third parameter in corresponding states correlations, Stiel's polar factor is a logical choice for the fourth parameter when polar fluids are to be included. With these choices for the third and fourth characterization parameters, a generalized reduced virial equation has been developed. This equation reduces to the virial equation for nonpolar fluids when the polar factor is zero and reduces to the virial equation for simple fluids when both the polar factor and acentric factor are zero. This generalized virial equation has been used to describe the compressibility factors of sixteen fluids including noble gases, normal fluids, and polar fluids.

NOTATION

P_c = critical pressure
p_r^* = reduced vapor pressure
P = molecular parachor
R = gas constant
T_c = critical temperature
T_r = reduced temperature
x = polarity factor
x' = alternative polarity factor
Y = any correlatable property
$Y^{(1)}, Y^{(2)}, Y^{(3)}$, etc. = correction terms to simple fluid behavior
Z = compressibility factor
$\rho_r{}'$ = reduced density
τ = association factor
ω = acentric factor
ω' = alternative acentric factor
$\bar{\omega}$ = "true" acentric factor

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