Saturated-Liquid and Vapor Densities for Polar Fluids

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Relationships have been developed for the saturated-liquid density and the compressibility factor of saturated vapors by an extension of Pitzer's acentric factor approach. The fourth parameter for polar fluids defined previously by the authors in terms of the vapor pressure was utilized. For the saturated-liquid density and the critical compressibility factor quadratic terms were necessary to accurately represent the data for a wide range of normal and polar fluids including large polar molecules. Comparisons for substances not used in the development of the relationships indicate that good results can be obtained for polar fluids by the method of this study.

Halm and Stiel (*13*) have extended Pitzer's acentric factor approach to the calculation of the vapor pressure and entropy of vaporization of polar fluids. A fourth parameter was defined in terms of the vapor pressure and shown to be applicable for other thermodynamic properties. In the present study this approach has been used to develop relationships for the calculation of the saturated-liquid and vapor densities of polar fluids.

For saturated polar fluids, the functional dependence of the compressibility factor on temperature and molecular properties is

$$z = f_1\left(\kappa T/\epsilon, \frac{a}{\rho_0}, \frac{\mu^2}{\epsilon\,\rho_0^3}\right) \tag{1}$$

Equation (1) corresponds to the use of an intermolecular potential function containing four characteristic parameters, such as the superposition of the Kihara spherical core potential with a term accounting for dipole-dipole interactions,

$$\psi(r) = 4\epsilon\left[\left(\frac{\rho_0}{r-2a}\right)^{12} - \left(\frac{\rho_0}{r-2a}\right)^{6}\right] - \frac{\mu^2}{r^3}g(\theta) \tag{2}$$

where ρ_0 is the shortest distance between molecular cores at the potential minimum, r is the distance between molecular centers, a is the radius of the core, and $g(\theta)$ represents the angular dependence of the dipole-dipole interaction. Only little theoretical progress has been made in the use of an intermolecular potential of this type for the calculation of the thermodynamic properties of polar fluids. O'Connell and Prausnitz (*23*) have obtained an expression for the second-virial coefficient of polar gases for spherical cores.

Halm and Stiel (*13*) defined the reduced vapor pressure of a polar fluid as

$$\log P_R = (\log P_R)^{(0)} + \omega(\log P_R)^{(1)} + x(\log P_R)^{(2)} \tag{3}$$

where ω is Pitzer's acentric factor (25). At $T_R = 0.7$, $\log P_R^{(0)} = -1.00$, $\log P_R^{(1)} = -1.00$, and the polar correction $\log P_R^{(2)} = 0$ for $T_R \geqq 0.7$, so that ω has the same definition as for a normal fluid, and the values of $(\log P_R)^{(0)}$ and $(\log P_R)^{(1)}$ are the same as tabulated by Pitzer, et al. for $T_R = 0.56$ to 1.00. Log $P_R^{(2)}$ was also defined to be 1.00 at $T_R = 0.6$ so that the fourth parameter is

$$x = \log P_R|_{T_R=0.6} + 1.70\,\omega + 1.552 \tag{4}$$

Values of the normal fluid functions $\log P_R^{(0)}$ and $\log P_R^{(1)}$ were established for $T_R = 0.44$ to $T_R = 0.56$ and of $\log P_R^{(2)}$ for $T_R = 0.44$ to 0.70. With the functions defined in this manner $\log P_R^{(2)} = 0$ for $T_R = 0.70$ to 1.0. Halm and Stiel also defined the entropy of vaporization of polar fluids as:

$$\Delta S = \Delta S^{(0)} + \omega\,\Delta S^{(1)} + x\,\Delta S^{(2)} \tag{5}$$

Values of $\Delta S^{(2)}$ were established for $T_R = 0.56$ to $T_R = 0.72$. These functions enable ω and x to be calculated for a polar fluid from two vapor pressure values below $T_R = 0.7$, or from the vapor pressure and entropy of vaporization at the normal boiling point.

THE CRITICAL COMPRESSIBILITY FACTOR OF POLAR FLUIDS

If the conditions of the critical point are applied to Equation (1), the following relationship results:

$$z_c = f_2\left(\frac{a}{\rho_0}, \frac{\mu^2}{\epsilon\,\rho_0^3}\right) \tag{6}$$

In terms of the macroscopic parameters ω and x, Equation (6) becomes

$$z_c = f_3(\omega, x) \tag{7}$$

In Figure 1 values of the critical compressibility factor are plotted against ω for polar fluids. It can be seen that for small polar fluids such as water and ammonia a single line results, distinct from the normal fluid relationship. This line corresponds to the use of an intermolecular potential function for polar fluids which excludes shape effects, such as the Stockmayer potential [Equation (2) with $a = 0$]. Therefore, from Equation (6), z_c for small polar substances to a good approximation is only a function of one dimensionless macroscopic parameter characterizing the reduced dipole group. However, it can be seen from Figure 1 that for larger polar fluids such as the alcohols for which shape effects are important a fourth macroscopic parameter is required, as indicated by Equation (7). The combined effects of polarity and dispersion

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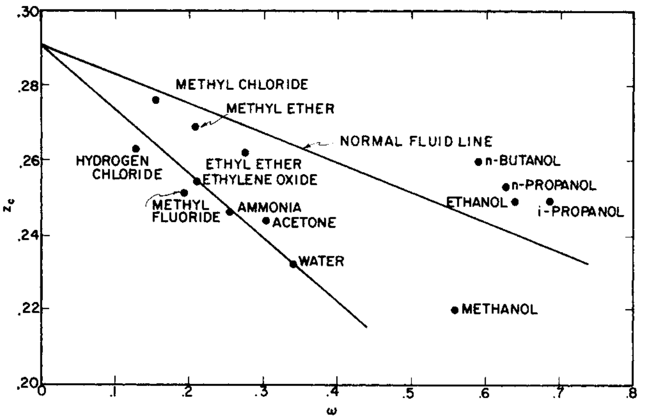

Fig. 1. Relationship between z_c and ω for normal and polar fluids.

result in z_c for ethanol being close to the normal fluid line, which is confirmed by its small value of x. The negative values of x for large polar molecules result from the fact that in the defining equation for ω and x only linear terms are retained so that polarity and shape effects are not segregated.

Values of the critical compressibility factor for 15 normal and 15 polar fluids were related to ω and x by a least squares procedure. The polar substances are listed in Table 1 along with the values of z_c, ω, and x used. It was found that quadratic terms in the Taylor series expansion of Equation (7) were necessary. The resulting relationship is

$$z_c = 0.291 - 0.114\omega - 1.42x + 0.069\omega^2 - 7.05x^2 + 1.51\omega x \qquad (8)$$

In Figure 2 values of $z_c - z_{cn} - 1.51\omega x$ are plotted against x for the polar fluids considered. A statistical significance test suggested by Chou (*5*) was applied to the coefficients of Equation (8) and they were all determined to be highly significant. In Table 1 the per cent errors between z_c values calculated from Equation (8) and the corresponding experimental values are presented for the fifteen substances. The per cent errors resulting from the use of Pitzer's normal fluid equation

$$z_{cn} = 0.291 - 0.08\omega \qquad (9)$$

are also included. The average deviation for the fifteen polar substances is 1.38% for Equation (8) and 5.99% for Equation (9). Per cent errors were also calculated for methyl fluoride, *n*-butane, acetic acid, and *n*-propanoic acid which were not included in the establishment of Equation (8), and the results are included in Table 1.

SATURATED-LIQUID DENSITIES FOR POLAR FLUIDS

Pitzer, et al. (*25*) tabulated values of $z^{(0)}$ and $z^{(1)}$ for the saturated liquid compressibility factor for $T_R = 0.56$ to $T_R = 1.00$. Lyckman, Eckert, and Prausnitz (*18*) found that large errors can result from these tables and have presented an improved correlation for saturated liquids in terms of the reduced volume, as follows:

$$v_R = v_R^{(0)} + \omega v_R^{(1)} + \omega^2 v_R^{(3)} \qquad (10)$$

where $v_R^{(0)}$, $v_R^{(1)}$, and $v_R^{(3)}$ are tabulated functions of the reduced temperature. A relationship between reduced density and acentric factor for saturated liquids can also be obtained by combining Riedel's equation (*27*) in terms of α_c with the linear relationship between α_c and ω for normal fluids to obtain

$$\rho_R = 1 + 0.85\,(1 - T_R) + (1.692 + 0.986\omega)\,(1 - T_R)^{1/3} \qquad (11)$$

Lydersen, Greenkorn, and Hougen (*19*) have used the critical compressibility factor as a third parameter combining both shape and polarity effects to develop tables for the reduced density and compressibility factor of saturated liquids for values of z_c of 0.23, 0.25, 0.27, and 0.29. Yen and Woods (*35*) have presested analytical relationships between the reduced density and the reduced temperature and critical compressibility factor for saturated liquids. Barile and Thodos (*3*) developed relationships between z/z_c and reduced pressure and critical compressibility factor for saturated nonpolar and polar liquids. A graphical relationship of this type has been presented by Hobson and Weber (*14*). Goyal and Doraiswamy (*12*) have presented an equation for the group $T_c\rho/P_c$ as a function of reduced temperature and z_c for nonpolar and polar fluids.

The use of z_c as a third parameter results in loss of accuracy for both nonpolar and polar fluids. In Figure 3 values of the reduced density for nonpolar and polar saturated liquids at $T_R = 0.9$ are plotted against the critical compressibility factor. The line resulting from the correlation of Lydersen, Greenkorn, and Hougen (*19*) is a good approximation for all the fluids. However, improvement for both normal and polar fluids can be obtained by the use of ω and x as third and fourth parameters, as indicated by Equation (1) which contains separate dimensionless groups representing shape and polarity effects.

For liquids the compressibility factor is not a desirable quantity since it is more a measure of the vapor pressure divided by the temperature than of the density (*15*). Also, the reduced density requires ρ_c, accurate values of which are not usually available. Therefore, in the present study the quantity $P_c v/RT_c$ for saturated liquids has been related to ω and x by the use of experimental density data for normal fluids (*2, 4, 9, 10, 32, 33*) and for the 14 polar fluids listed in Table 1 (nitric oxide was not included).

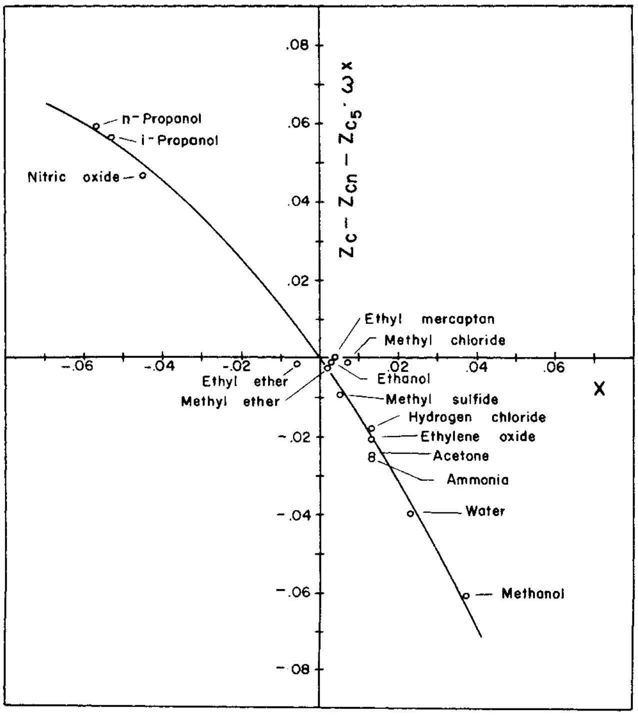

Fig. 2. Correlation for critical compressibility factor of polar fluids.

TABLE 1. VALUES OF z_c, ω, AND x, PER CENT ERRORS AND SOURCES OF DENSITY DATA FOR POLAR FLUIDS

Substance	z_c	ω	x	% Error, Equation (8)	% Error, Equation (9)	Sources of Density Data
water	0.232	0.344	0.023	+1.43	+13.37	*17*
ammonia	0.246	0.252	0.013	+2.47	+10.08	*4, 10, 16*
acetone	0.244	0.304	0.013	+2.13	+ 9.30	*16, 32, 33*
methyl ether	0.269	0.206	0.002	−0.26	+ 2.05	*16*
ethyl ether	0.262	0.275	−0.003	+2.29	+ 2.67	*16, 32, 33*
methyl sulfide	0.264	0.190	0.005	+0.71	+ 4.39	*16, 32*
ethyl mercaptan	0.274	0.186	0.004	−2.34	+ 2.12	*16, 32*
hydrogen chloride	0.263	0.125	0.013	−0.72	+ 7.01	*16, 31*
methyl chloride	0.276	0.152	0.007	−3.38	+ 1.03	*16, 32*
nitric oxide	0.256	0.577	−0.045	+1.08	− 4.38	
ethylene oxide	0.254	0.207	0.012	+0.85	+ 8.05	*6, 22, 34*
methanol	0.220	0.556	0.037	−0.73	+12.16	*30, 32, 33*
ethanol	0.249	0.639	0.003	−1.44	− 3.71	*8, 26, 32*
n-propanol	0.253	0.626	−0.057	−0.59	− 4.94	*1, 7, 8, 32, 33*
iso-propanol	0.249	0.663	−0.053	−0.40	− 4.53	*1, 32, 33*
methyl fluoride	0.251	0.191	0.012	+2.37	+ 9.70	
n-butanol	0.259	0.590	−0.07	−3.47	− 8.22	
acetic acid	0.200	0.444	0.047	+1.75	+27.74	
n-propanoic acid	0.243	0.537	0.013	+0.86	+ 2.06	

Last four substances not included in development of Equation (8).

The sources of the density data are included in Table 1. The Taylor series expansion in ω and x was truncated after quadratic terms, as follows:

$$v^* = \frac{P_c v}{RT_c} = v^{*(0)} + \omega v^{*(1)} + x v^{*(2)} + \omega^2 v^{*(3)} + x^2 v^{*(4)} + \omega x v^{*(5)} \quad (12)$$

The values of $v^{*(0)}$, $v^{*(1)}$, $v^{*(2)}$, $v^{*(3)}$, $v^{*(4)}$ and $v^{*(5)}$ established are presented in Table 2. In Figure 4 values of $v^* - v_n^* - v^{*(5)}\,\omega x$ at $T_R = 0.7$ are plotted against x for the polar fluids investigated. The statistical test revealed that the coefficients of Equation (12) are significant. For normal fluids, Equation (12) with $x = 0$ was found to give results at least as good as Equation (10).

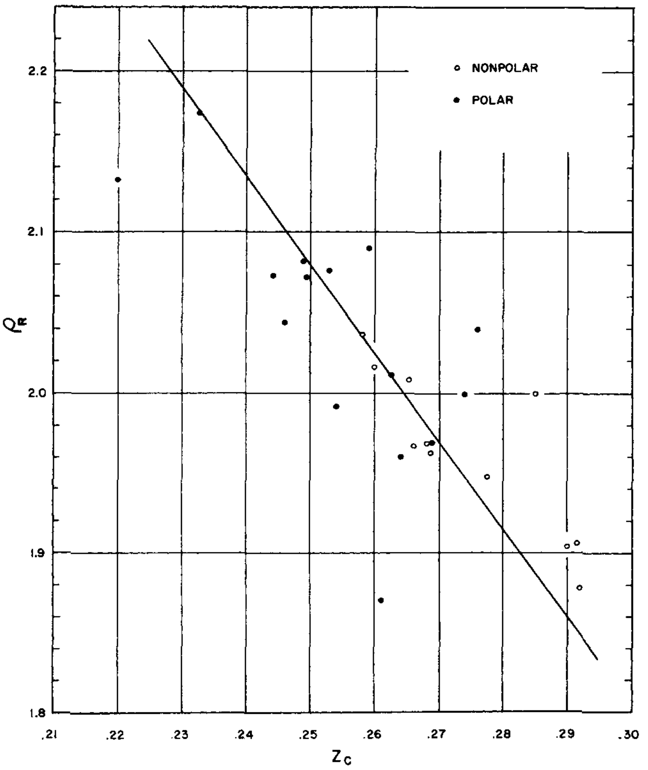

Fig. 3. Relationship between reduced density and critical compressibility factor at $T_R = 0.9$ for nonpolar and polar fluids.

In Table 3 values of v^* for *n*-butanol obtained from the data of Ambrose and Townsend (*1*) are compared with the values calculated from Equation (12). The per cent errors in volume resulting from equation (10) of Lyckman, Eckert, and Prausnitz (*18*) are also included. The average deviation for Equation (12) is 0.69% and 6.38% for Equation (10). Also, for methyl fluoride at $T_R = 0.923$ (*21*), the per cent error in v is 1.22% for Equation (12) and 4.48% for Equation (10).

THE COMPRESSIBILITY FACTOR OF SATURATED VAPORS

For saturated nonpolar vapors, Pitzer, et al. (*25*) have

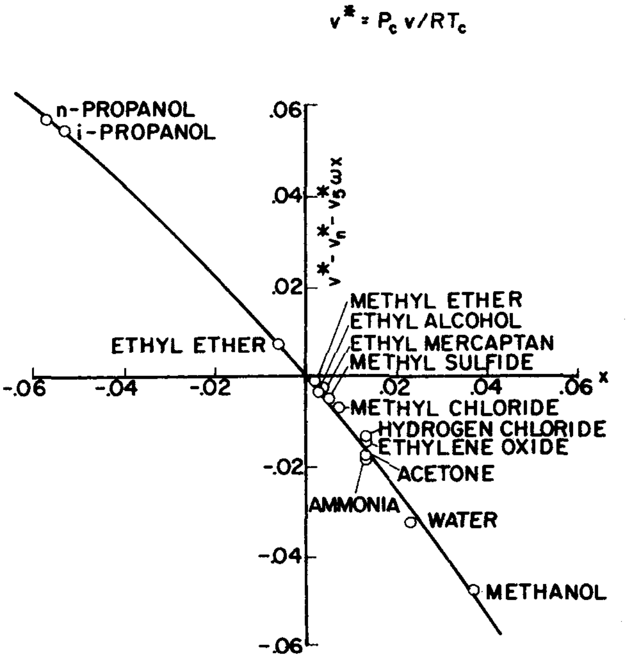

Fig. 4. Correlation for v* for saturated liquids at $T_R = 0.7$.

Table 2. Values of Normal and Polar Fluid Functions for Density of Saturated Liquids[†]

T_R	$v^{*(0)}$	$v^{*(1)}$	$v^{*(2)}$	$v^{*(3)}$	$v^{*(4)}$	$v^{*(5)}$
0.56	0.1102	—0.081	—1.02	0.069	—2.41	1.39
0.60	0.1129	—0.079	—1.06	0.064	—2.44	1.45
0.64	0.1159	—0.078	—1.10	0.059	—2.58	1.49
0.68	0.1195	—0.078	—1.13	0.057	—2.76	1.53
0.72	0.1235	—0.079	—1.16	0.057	—2.95	1.56
0.76	0.1281	—0.081	—1.18	0.057	—3.15	1.58
0.80	0.1335	—0.082	—1.21	0.056	—3.35	1.58
0.84	0.1401	—0.086	—1.23	0.057	—3.61	1.59
0.88	0.1490	—0.092	—1.27	0.062	—3.99	1.61
0.90	0.1547	—0.096	—1.29	0.066	—4.25	1.62
0.92	0.1614	—0.100	—1.31	0.071	—4.58	1.64
0.94	0.1696	—0.105	—1.33	0.076	—5.01	1.65
0.96	0.1799	—0.109	—1.36	0.079	—5.54	1.65
0.98	0.1968	—0.112	—1.39	0.078	—6.22	1.61
1.00	0.291	—0.114	—1.42	0.069	—7.05	1.51

[†] A more complete table for $0.56 < T_R < 0.88$ has been deposited as document 00567 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for $1.00 for microfiche or $3.00 for photocopies.

presented values of $z^{(0)}$ and $z^{(1)}$ for $T_R = 0.56$ to 1.00. Lydersen, Greenkorn, and Hougen (*19*), Barile and Thodos (*3*), and Hobson and Weber (*14*) developed correlations for the compressibility factor of saturated vapors with z_c and the third parameter.

For saturated polar vapors there are only meager experimental data for the larger polar molecules such as *n*-propanol and *n*-butanol which are required for the establishment of the quadratic terms in the Taylor series expansion for the compressibility factor. Therefore, only linear terms were employed for this property, and experimental density data for normal fluids and for water, ammonia, methyl ether, ethyl ether, hydrogen chloride, methyl chloride, ethylene oxide, methyl alcohol, and ethyl alcohol were used to establish the normal and polar fluid functions of the relationship

$$z = z^{(0)} + \omega z^{(1)} + xz^{(2)} \qquad (13)$$

The sources of the density data for the polar fluids are included in Table 1. The references for the vapor pressure used to establish the compressibility factors are given by Halm and Stiel (*13*). The use of Equation (13) is restricted to polar fluids with positive values of x.

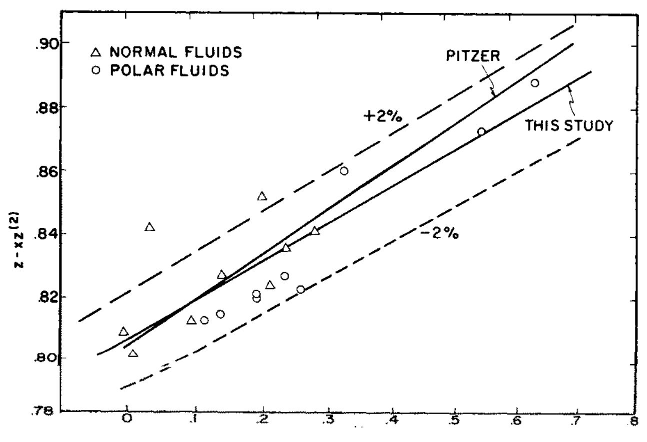

Fig. 5. Relationship between $z - xz^{(2)}$ and ω for normal and polar saturated vapors at $T_R = 0.80$.

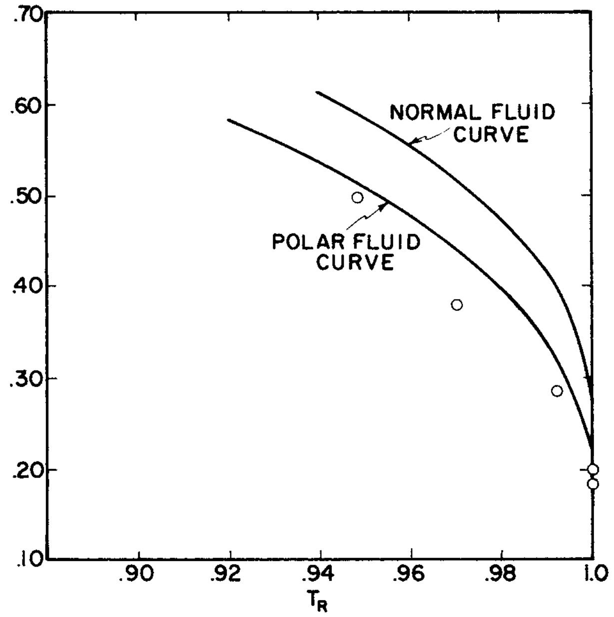

Fig. 6. Comparison of data for hydrogen cyanide ($\omega = 0.409$, $x = 0.080$).

In Table 4 the values of $z^{(0)}$, $z^{(1)}$, and $z^{(2)}$ obtained are presented for $T_R = 0.70$ to $T_R = 0.98$. The normal fluid functions agree well with those of Pitzer et al. Below $T_R = 0.70$ the available experimental data did not permit the establishment of $z^{(2)}$, but the polar correction is very small for this region. In Figure 5 values of $z - xz^{(2)}$ for the normal and polar fluids at $T_R = 0.8$ are plotted against ω. This figure indicates that with the values of $z^{(2)}$ developed in this study, Equation (13) gives about as good agreement for polar fluids as do Pitzer's functions applied to normal fluids. In Figure 6 experimental values of the compressibility factor of hydrogen cyanide (*16*, *32*) are compared with the curves resulting from Equation (13) and from the normal fluid relationship. There is some scatter in the data but the use of the polar correction term results in considerable improvement. A similar plot is presented in Figure 7 for acetone. The data from the International Critical Tables (*16*) are seen to deviate excessively at low reduced temperatures, but the values of z calculated from the second-virial coefficient data presented by O'Connell and Prausnitz (*24*) conform closely to the polar fluid curve.

THE ENTROPY OF VAPORIZATION OF POLAR FLUIDS

The entropy of vaporization is related to the difference between the compressibility factors of the saturated liquid and vapor and the slope of the vapor pressure curve through the Clapeyron equation,

Table 3. Comparison of Data of Ambrose and Townsend (*1*) with Values Calculated from Equations (10) and (12)

T_R	v^*	% Error, Equation (12)	% Error, Equation (10)
0.78	0.1037	+0.83	+7.45
0.82	0.1088	+0.73	+6.89
0.86	0.1154	+0.35	+6.85
0.90	0.1239	—0.48	+6.05
0.94	0.1370	—1.97	+4.60

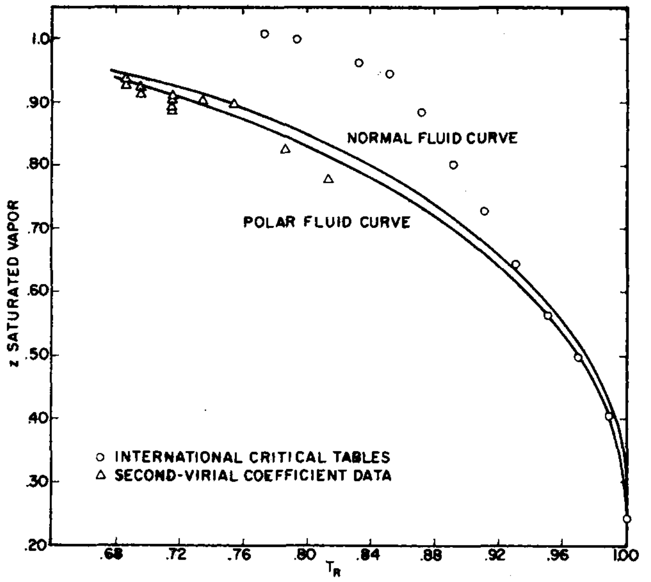

Fig. 7. Comparison of data for acetone.

$$\Delta S = \frac{R\,\Delta z}{T_R}\frac{\partial \log P_R}{\partial\left(\dfrac{1}{T_R}\right)} \tag{14}$$

Since Equation (3) for $\log P_R$ is linear in x for $T_R < 0.7$, Equation (5) for the entropy of vaporization of polar fluids is consistent with the Clapeyron equation for this region with the assumption (which is good at low reduced temperatures) that $\Delta z = 1.0$. For $T_R > 0.7$, since the polar correction for the reduced vapor pressure is zero, the following relationship results from Equation (14) for the entropy of vaporization of polar fluids:

$$\Delta S_p = \Delta S_n \frac{\Delta z_p}{\Delta z_n},\ T_R > 0.7 \tag{15}$$

The relationships developed in this study for the saturated-liquid and vapor densities of normal and polar fluids can be used in conjunction with the functions for ΔS_n tabulated by Pitzer, et al. (*25*) to calculate values of the entropy of vaporization of polar fluids from Equation (15). The exact functional dependence of ΔS_p on ω and x will be quite complicated, particularly because of the form of the relationship for the saturated liquid density. However, the ratio $\Delta z_p/\Delta z_n \simeq 1.0$, so that ΔS_p can be taken equal to ΔS_n for this region. Halm and Stiel (*13*) found that the linear relationship for ΔS_p, Equation (5), is not satisfactory for $T_R > 0.72$, but that the polar correction is very small for this region. At $T_R = 0.802$, the experimental entropy of vaporization of water is 14.37 (*17*), while the value calculated from the normal fluid relationship [Equation (5) with $x = 0$] is 14.43, a difference of only 0.4%.

DISCUSSION OF RESULTS

The results of this study confirm the validity of the fourth parameter x defined by Halm and Stiel (*13*) for the calculation of the thermodynamic properties of polar fluids. In order to develop correlations suitable for a wide group of substances including large polar molecules, higher order terms may be required in the Taylor series expansions for the properties. Thus for polar fluids the requirements for accurate data and the problems in smoothing the values of the correction functions are more severe than for normal fluids.

TABLE 4. VALUES OF NORMAL AND POLAR FLUID FUNCTIONS FOR COMPRESSIBILITY FACTOR OF SATURATED VAPORS

T_R	$z^{(0)}$	$z^{(1)}$	$z^{(2)}$
0.70	0.904	0.094	−0.79
0.72	0.887	0.099	−0.80
0.74	0.868	0.105	−0.84
0.76	0.849	0.110	−0.91
0.78	0.828	0.114	−1.00
0.80	0.806	0.118	−1.13
0.82	0.783	0.116	−1.13
0.84	0.758	0.110	−1.10
0.86	0.731	0.105	−1.07
0.88	0.700	0.097	−1.02
0.90	0.665	0.086	−0.96
0.92	0.627	0.071	−0.93
0.94	0.589	0.042	−0.88
0.96	0.541	0.009	−0.86
0.98	0.478	−0.029	−0.86

In the defining equations for ω and x in terms of the vapor pressure only linear terms are retained and dispersion and polarity effects are not segregated for large polar molecules. If a new third parameter ω' is postulated which characterizes the group a/ρ_0 of Equation (1) and a fourth parameter x' is defined which characterizes $\mu^2/\epsilon\rho_0{}^3$, the reduced vapor pressure can be expressed as

$$\log P_R = f_4(T_R, \omega', x') \tag{16}$$

Therefore, since $\omega = -\log P_R|_{T_R=0.7} - 1.00$

$$\omega = f_5(\omega', x') \tag{17}$$

Strictly, the acentric factor is a measure of the dimensionless shape group resulting from a three-parameter intermolecular potential such as the Kihara potential, but as indicated by Equation (17) ω for a polar fluid includes both shape and polarity effects. The exact functional form of Equation (16) is not known and thus it is not possible

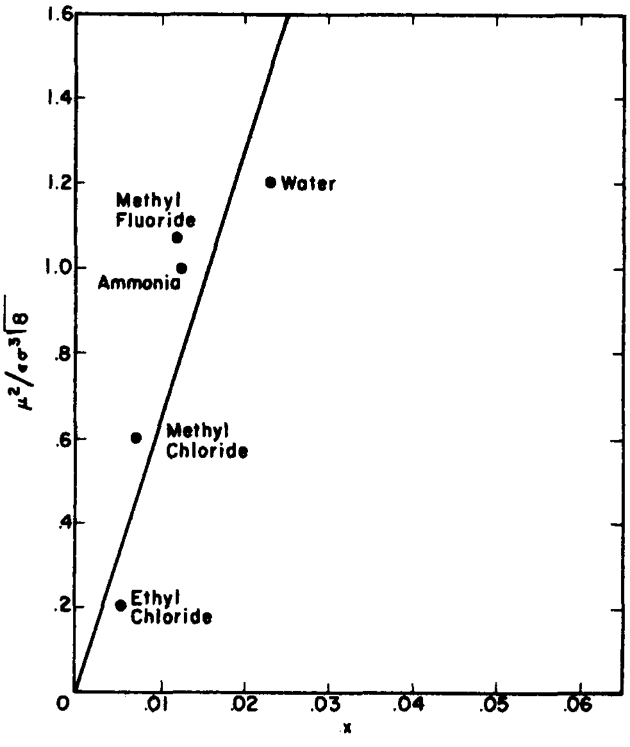

Fig. 8. Relationship between $\mu^2/\epsilon\sigma^3\sqrt{8}$ and x for the Stockmayer potential.

through the vapor pressure to separate shape and polarity effects in the definitions of the third and fourth parameters. Because of this difficulty, several investigators (*11*, *24*) have defined ω' for a polar fluid as that of the acentric factor of an appropriate homomorph, a nonpolar substance having the same size and shape. However, the determination of a suitable homomorph for a polar fluid is usually somewhat arbitrary. The present approach enables both shape and polarity effects to be accounted for by the direct use of vapor pressure data, accurate values of which are usually available.

From Equations (4) and (17),

$$x = f_6(\omega', x') \tag{18}$$

For a small polar molecule such as hydrogen chloride, $\omega' \simeq 0$, so that x (as well as ω) does represent primarily the polarity of the molecule. In Figure 8 the group $\mu^2/\epsilon\sigma^3 \sqrt{8}$ for the Stockmayer potential is plotted against x for small polar molecules. For larger molecules x will include shape effects, as indicated by Equation (18). The negative values of x for large polar molecules such as n-propanol and n-butanol are due to the influence of shape effects and the use of only linear terms in the definitions of ω and x. Because of the relationships of Equations (17) and (18), the parameters ω and x can be used in place of ω' and x' for the extension of this approach to other reduced thermodynamic properties of polar fluids, as confirmed by the results of this study.

ACKNOWLEDGMENT

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NOTATION

a = radius of spherical core
$g(\theta)$ = angle dependent term of dipole-dipole interaction
P_c = critical pressure, atm.
P_R = reduced pressure
r = distance between molecular centers
R = gas constant, 1.987 cal./g. mole °K.
ΔS = entropy of vaporization, cal./g. mole °K.
T = temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
v = volume, cc./g. mole
v^* = liquid volume group, $P_c v/RT_c$
v_R = reduced volume
x = fourth parameter
x' = fourth parameter characteristic solely of polarity effects
z = compressibility factor
z_c = critical compressibility factor

Greek Letters

α_c = Riedel parameter
ϵ = maximum energy of attraction, erg.
κ = Boltzmann constant, 1.3805×10^{-6} erg./°K.
μ = dipole moment of molecule, debyes
ρ = density, g. mole/cc.
ρ_c = critical density, g. mole/cc.
ρ_0 = shortest distance between molecular cores at the potential minimum
ρ_R = reduced density, ρ/ρ_c
σ = force constant for Stockmayer potential, A
$\psi(r)$ = intermolecular potential function
ω = acentric factor
ω' = third parameter characteristic solely of shape effects

Subscripts and Superscripts

n = normal fluid
p = polar fluid
(0) = simple fluid function
(1) = normal fluid linear correction term
(2) = polar fluid linear correction term
(3) = normal fluid quadratic correction term
(4) = polar fluid quadratic correction term
(5) = cross coefficient correction term

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