

A CUBIC EQUATION OF STATE FOR PHASE EQUILIBRIUM CALCULATIONS

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ABSTRACT

A cubic equation of state for phase equilibrium calculations is proposed and tested for a number of pure compounds over the temperature range $0.5 T_C < T < T_H$ of interest in phase equilibria. Satisfactory numerical results were obtained for molecules of various shapes and dipole moments through the introduction of simple acentric factor-dependent dimensionless scaling factors. Deviations of calculated compressibility factors from results of well known correlations indicated superiority of the present equation over the Soave-Redlich-Kwong and showed performance comparable to the Peng-Robinson equation. Pure component fugacity coefficients based on the calculated compressibility factors were in good agreement with the widely accepted Soave-Redlich Kwong results, thus establishing utility of the equation in reproducing pure substance saturation conditions. The extension of the relation to mixtures with appropriate combining rules is the subject of subsequent studies.

Introduction

The importance of the predictive capacity offered by multi-component vapor-liquid equilibrium (VLE) calculations cannot be over emphasized in the chemical system among the co-existing vapor and liquid phases at given temperature and pressure conditions allows the process engineer to make necessary adjustments in the system to meet whatever requirements the process entails. An approach to the solution of such phase equilibrium problems utilizes information on the volumetric behavior of the system in the form of an analytical relation. This method of calculation has the advantage of avoiding activity coefficients and their associated standard states, which in some cases are hypothetical. Cubic equations of state applicable to mixtures and satisfactory at both gas and liquid densities are best suited for this purpose.

One of the best known cubic equations was the Redlich-Kwong (1949), the earliest successful applications of which to VLE were given by Wilson (1964) and by Zudkevitch and Joffe (1970). In both these works, it was necessary to

improve on the original equation by assuming temperature dependent parameters established by equalizing fugacities along the vapor-pressure curve. Soave (1972) further generalized this technique of applying the Redlich-Kwong (RK): a more general temperature dependent parameter replaced altogether the $T^{-0.5}$ dependence in the attractive pressure term of the original equation. The modified form obtained, popularly known as the Soave-Redlich-Kwong (SRK) equation, has gained wide acceptance within the hydrocarbon industry because of its capability for generating reasonably accurate equilibrium ratios in VLE calculations. In a further development, Peng and Robinson (1976) pointed out that the SRK, as well as the original RK equation, still suffers from the incapability of generating satisfactory liquid density values despite the general acceptability of the corresponding vapor results. A Peng-Robinson (PR) cubic equation was thereby forwarded, claimed to yield equilibrium ratios as good as the SRK and more accurate liquid densities for a plus.

This paper presents an equation comparable in utility with the Soave-Redlich-Kwong and Peng-Robinson equations for phase equilibrium calculations. The equation was originally formulated to meet some deficiencies in many cubic equations in the spirit of the discussion given by Abbott (1973) where characteristics and behavior of cubic equations were analyzed. The original formulation, which is omitted in the foregoing equation in VLE calculations; in fact, it was done without any prior knowledge of the existence of the SRK and PR equations. The equation was only really then intended to provide good estimates of the volumetric properties of gases. Later encounters with the SRK provided the motivation for investigating the possibility that the earlier formulated equation might show similar performance in predicting VLE.

This paper is the first of two parts and deals only with the application of the proposed equation in generating compressibility factors and fugacity coefficients for pure substances. By initially ensuring that the equation satisfactorily reproduces saturation conditions for pure substances, extension to mixtures as done in the second part will only then require the search for appropriate combining rules.

The Proposed Cubic Equation and Some Thermodynamic Derivation

Generally, the best known cubic equations are of the Van der Waals type which expresses the pressure as the sum of contributions from repulsive and attractive forces. In most instances the repulsive part is represented by

$$P_{\text{repulsive}} = RT/(v-b)$$

where v is the molar volume and b a temperature independent measure of the excluded volume, roughly the size of hard spherical molecules. The expression for attractive pressure component is what differentiates one cubic equation from another but still, it can be generalized as a function of some molecular interaction parameter, a , and of the molar volume, i.e.,

$$P_{\text{attractive}} = -a/g(v) \quad (1b)$$

The function $g(v)$ may be taken to be of the form

$$g(v) = v^2 + r*bv + s*b^2 \quad (2)$$

Table 1. Four well known cubic equations

Equation	r	s	b	a
Van der Waals	0	0	$RT_c/8P_c$	$27R^2T_c^2/64P_c$
Redlich-Kwong	1	0	$0.08664RT_c/P_c$	$0.42748R^2T_c^2/P_cT_r^{0.5}$
Soave	1	0	$0.08664RT_c/P_c$	$0.42748R^2T_c^2/P_c * \{1+m(1-T_r^{0.5})\}^2$
Peng-Robinson	2	-1	$0.0778RT_c/P_c$	$0.45724R^2T_c^2/P_c * \{1+m(1-T_r^{0.5})\}^2$

where $m = m(w)$, a quadratic function.

Table 1 lists four well known cubic equations and their corresponding values for r and s . The parameters a and b , likewise shown in Table 1, are obtained by evaluating a given cubic equation at the critical point where the first and second derivatives of the pressure with respect to the volume vanish.

The choice of the temperature dependence for the attractive pressure term is an important factor to consider as it has been the focus of attention in the improvements introduced by Soave (1972) over the Redlich Kwong equation. This temperature dependence may be viewed as a dimensionless scaling factor, a function of the reduced temperature T_r , in the interaction parameter a . As evident from Table 1, the SRK and PR equations show the same temperature dependence in a . The quantity m in their scaling factor is a function of the acentric factor w defined by Pitzer and co-workers (1955) as a measure of the deviation of the intermolecular potential from that of simple spherical molecules of "normal" fluids. Such incorporation of the acentric factor leads in part to the superiority of the SRK and PR equations over the Redlich-Kwong since the molecular interaction parameter is in effect corrected for the non-central character of the force of interaction of molecules of varying shapes and dipole moments. Note that for normal fluids $w = 0$.

The equation of state presently proposed is as follows:

$$P = RT/(v-b) - a/(v + 2b/3)^2 \quad (3)$$

where $a = 27 R^2 T_c^2 / 64 P_c T_r^{2/3}$ and $b = 3 R T_c / 40 P_c$, as evaluated at the critical point. The temperature dependence in the parameter a may to a first approximation be taken as sufficient for other temperatures as well, although as seen in later developments, significant improvements and interesting observations are achieved by introducing an additional acentric factor dependent dimensionless scaling factor. In terms of equation 2, $r = 4/3$ and $s = 4/9$.

To generate compressibility factors for the coexisting liquid and vapor phases from the proposed relation, equation 3 is written in the form

$$Z^3 + Z^2 (B/r - 1) + Z (A - 4B/3 - 8B^2/9) - AB - 4B^2(1 + B)/9 = 0$$

where Z = compressibility factor, $B = bP/RT = 3 P_r / 40 T_r$, $A = aP/R^2 T^2 = 27 P_r / 64 T_r^{8/3}$, P_r = reduced pressure. This is then solved for its largest and smallest positive root under the coexistence curve, the roots being equal respectively to the vapor and liquid phase compressibility factors.

The basic condition for vapor-liquid equilibria is the equality of the vapor and liquid phase fugacities, f_i^v and f_i^l , of each component i when distributed between the two phases in equilibrium:

$$f_i^v = f_i^l$$

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Because the fugacities of a component in a mixture are proportional to the composition according to the thermodynamic relation

$$f_i^v = \phi_i^v y_i P \quad \& \quad f_i^l = \phi_i^l x_i P$$

ϕ being the fugacity coefficient, the equilibrium ratio

$$K_i = y_i / x_i \tag{6}$$

is then expressible in terms of the fugacity coefficients, i.e.

$$K_i = \phi_i^v / \phi_i^l$$

With the utilization of an equation of state to provide fugacity coefficients, the solution of the phase equilibrium problem is simply reduced to one of a problem of solving simultaneously a system of equations consisting of equations 6 and mass balance equations.

The fugacity coefficients of a component in a mixture are obtained from an equation of state through the general thermodynamic relation

$$RT \ln \phi_i = \int_V^\infty \left\{ (\partial P / \partial n_i)_{T, V, n_j} - RT/V \right\} dV - RT \ln Z_i \quad (7)$$

applied to both phases. In this paper, only pure component-fugacity coefficients are of concern. Equation 7 for a pure substance is

$$RT \ln \phi = \int_V^\infty \left\{ P/n_i - RT/V \right\} dV - RT \ln Z + RT(Z - 1) \quad ,$$

for which the proposed equation (3) yields

$$\ln \phi = -\ln(Z - B) - A / (Z + 2B/3) + Z - 1 \quad (8)$$

Equation 8 should give the same value whether one substitutes compressibility factors for the vapor phase or for the liquid phase obtained from equation 6 using vapor pressure data for pure substances.

Numerical Results

Compressibility factors for 12 substances were calculated using literature experimental data for the reduced temperature range of interest in many phase equilibrium investigations, $0.56 < T_r < 1.0$. Calculations were carried for approximately 25-30 data points for each compound, totalling roughly to around 340 data points. The accuracy of some data points used were quite uncertain due to low local availability of more recent literature vapor pressure data employing Newton's root searching technique, convergence towards a solution was easily achieved with 2 to 3 iterations, except at near critical temperatures where not even 10 iterations were sufficient. Subsequent use of the calculated liquid and gas compressibility factors yielded fugacity coefficients for both phases.

Table 2 shows the average results for each of the 12 substances examined at the specified temperature ranges. The presently proposed equation is compared with the SRK and PR equations in its ability to reproduce highly accurate gas and liquid compressibility factors predicted by well known correlations. Of course, the best test of performance is to compare the calculated results with experimental values. Because of the local unavailability of experimental literature data, such an approach is virtually impossible.

Accurate prediction of gas phase compressibility factors is not as much a problem as those for the liquid phase. Pitzer's corresponding state correlation (1955) involving the acentric factor as a third parameter still quite sufficiently represents gas phase compressibility factors despite the numerous correlations that have appeared since its conception. In this correlation, the compressibility factor is expressed as a first order expansion in the acentric factor,

$$Z = Z^{(0)} + W Z^{(1)}$$

Table 2. (a) Comparison between the proposed equation, SRK, & PR equations with respect to compressibility factor Z_1 & Z_v predictions,
 (b) Absolute differences: $\ln \phi^v - \ln \phi^l$

Substance	T_r range	Vapor Pressure Data Reference	Compressibility Factors Liquid Phase ^(a)			Ave. Absolute % deviation Gas phase ^(b)			$\ln \phi^v$ $\ln \phi^l$ (range)
			Present	SRK	PR	Present	SRK	PR	
nitrogen	0.5638– 0.9996	Reid <i>et al.</i> (1986)	9.9258	7.6458	8.4691	1.2839	1.7201	1.6760	0– 0.8841
ethane	0.6143– 0.9428	Timmermans (1950)	9.8218	7.0265	5.9532	0.9856	1.4996	1.0078	0.0001– 0.3809
CCl ₄	0.5629– 0.9998	Timmermans Boublik (1984)	11.9619	12.7256	4.7317	2.1711	2.2938	1.0149	0.0000– 0.1449
neopentane	0.5921– 0.9871	Boublik, <i>et al.</i> (1984)	11.0548	9.7665	6.0990	2.0889	2.0705	1.1447	0.0005– 0.0682
2,3 dimethyl butane	0.5657– 0.9953	Timmermans	13.3971	13.8262	5.3566	2.7705	2.4442	1.9579	0.0000– 0.1449
benzene	0.5641– 0.9982	Timmermans	12.1505	13.8463	4.8634	2.5908	2.4326	1.1243	0.0021– 0.0848
toluene	0.5629– 0.9997	Reid <i>et al.</i>	17.0129	20.3132	7.0188	3.5402	3.2517	1.1611	0.0000– 0.2040
diethylether	0.5636– 0.9983	Timmermans	14.1813	22.7584	8.9466	3.5226	2.6938	1.5306	0.0000– 0.2631
n-heptane	0.5609– 0.9948	Timmermans	10.3694	17.4767	4.0523	3.8120	2.2964	1.4791	0.0016– 0.5839
nonane	0.5771– 0.9992	Reid <i>et al.</i>	19.8013	23.1770	10.0110	4.4040	3.5812	2.5003	0.0004– 0.9978
decane	0.5879– 0.9991	Reid <i>et al.</i>	21.2598	25.1848	11.0226	4.5583	3.3028	1.6231	0.0003– 1.1430
CO ₂	0.5694– 0.9995	Reid <i>et al.</i>	8.8411	15.0164	6.6919	2.7047	2.2526	1.0832	0.0009– 0.1034

(a) compared against Rackett correlation (1970, 1972) predictions

(b) compared against Pitzer's correlation (1958) predictions

The expansion coefficients $Z^{(0)}$ and $Z^{(1)}$ are functions of T_r and P_r and are numerically tabulated at regularly spaced temperature intervals. The acentric factor at each temperature is readily evaluated for any substance from the vapor pressure data through the relation

$$\log P_r = (\log P_r)^{(0)} + w (\partial \log P_r / \partial w)_{T_r}$$

where $(\log P_r)^{(0)}$ and $(\partial \log P_r / \partial w)_{T_r}$ are likewise expansion coefficients dependent only on the temperature and also tabulated numerically.

On the other hand, of the several liquid compressibility factor correlations examined (Francis, 1957, 1959; Lyckman, *et al.*, 1965; Rackett, 1970; Bhirud, 1978), the method of Rackett (1970) as modified by Spencer and Danner (1972) and as recommended by Reid and co-workers (1986) was found most satisfactory. The liquid compressibility factor takes the form

$$Z_l = (P_r / T_r) Z_{RA} [1 + (1 - T_r)^{2/7}]$$

where Z_{RA} is a unique constant for each compound. This correlation also compared well with the more recent method of Hankinson and Thomson (1979) though slightly more convenient to use.

From Table 2, all three equations exhibit nearly the same performance in predicting gas phase values. On the other hand as consistent with Peng and Robinson's claim, their liquid compressibility factors are much more accurate than the Soave-Redlich-Kwong results. Note that the deviations reported here are relatively larger than those reported by Soave and Peng-Robinson for their equations since their predictions were compared in this paper against a certain correlation which naturally also deviates, though little, from experimental results. The liquid phase predictive capability of the presently proposed equation does not differ significantly from that of the SRK, although this is already a welcome result considering that the SRK includes the acentric factor as a third parameter.

As earlier mentioned, convergence problems in root searching appear at near critical temperatures for the proposed equation. It has been observed that the SRK and PR equations likewise suffer the same dilemma, although to a much lesser extent. Of course, other root searching techniques may be able to handle the situation. At any rate, unconverged results were not included in calculating the average percent deviations reported in Table 2.

The gas and liquid phase fugacity coefficients, determined from the compressibility factors predicted by the proposed equation, are seen to exhibit appreciable differences (Table 2). This clearly is a violation of the equilibrium condition and indicates further the necessity of introducing improvements in the original equation.

An Improvement on the Originally Proposed Equation

The unimpressive results obtained from the original equation does not come at all as a surprise because the constant quantities in the interaction parameter as evaluated at the critical point need not necessarily be the same for all substances and over all temperatures. Although a temperature dependence has already been initially taken and imposed, it is not quite safe to assume that such dependence is sufficient to correct for the difference in temperature between the critical point and any other state. Following Soave (1972), a dimensionless scaling factor α (T_r, w) may be introduced at temperatures other than the critical:

$$a(T) = a(T_c) * \alpha(T_r, w) \quad (9)$$

with α , which is a function of the reduced temperature and the acentric factor, naturally satisfying the boundary condition $\alpha = 1$ at $T_r = 1$. The introduction of this scaling factor will in effect change the temperature dependence at temperature other than the critical and will simultaneously correct for the variation in the shape and polarity of molecules as reflected in the molecular interaction potential. The cubic compressibility equation (4) and the fugacity coefficient equation (8) becomes modified by multiplying A with α .

The thermodynamic necessity of equal vapor and liquid phase fugacities at saturation conditions for pure substances provides the means of determining α . Since for pure substances one may equivalently write equation 5 purely in terms of the fugacity coefficients, one obtains for α .

$$\alpha = (64 T_r^{8/3} / 27 P_r) \ln [(Z_1 - B) / (Z_v - B)] + Z_1 - Z_v \\ (Z_1 - Z_v) / [(Z_v + 2B/3) (Z_1 + 2B/3)] \quad (10)$$

An initial estimates of $\alpha = 1$ provides the same values for Z_1 and Z_v as those reported in the previous section. Using these Z results, an improved value for α is obtained through equation 10. The calculation is repeated iteratively thereafter until a converged value for α is hit. The first iteration is usually sufficient.

Table 3 shows the average results for each of the substances examined. Clearly, significant improvement of the compressibility factor predictions are achieved (compare with Table 2). The Peng-Robinson predictions are just slightly superior over the present results. Convergence problems in root searching at near critical temperatures occurred but very seldom, just as with the SRK and PR equations. It is observed that large contributions to the average deviations obtained come from the near critical region despite the convergence. The fugacity coefficients show very good agreement with the SRK predicted values in Table 3. Incidentally, the difference between the predicted gas and liquid phase fugacity coefficients, $\ln \phi_v - \ln \phi^l$, was of the order 10^{-16} thus satisfying the equilibrium condition. It is to be noted that all these results were achieved with α values

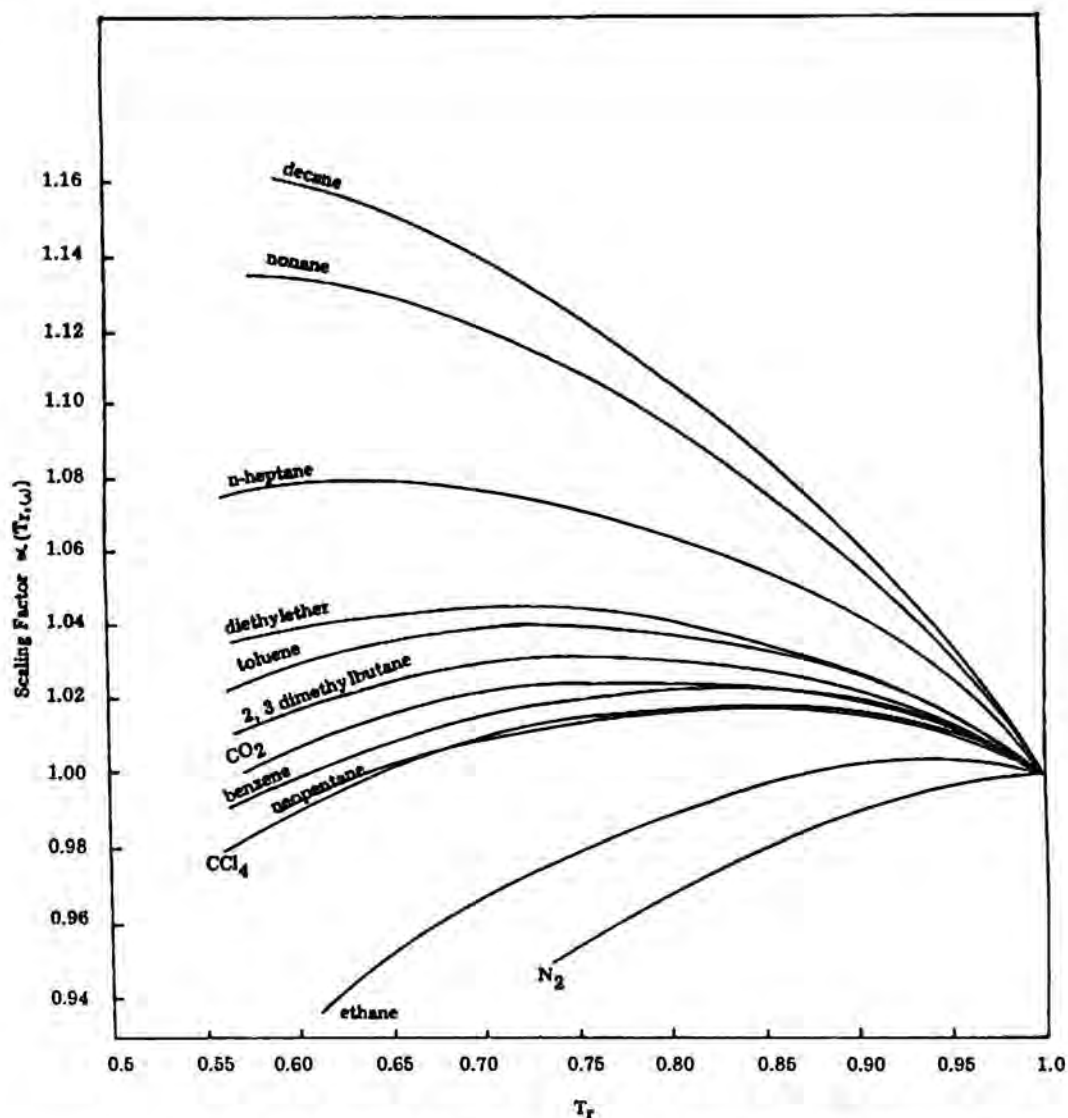


Figure 1: PLOT of SCALING FACTOR $\alpha(T_r, \omega)$ vs. REDUCED TEMPERATURE T_r

where $m(1-T_r)$ is the temperature varying slope of the $\alpha - w$ curve and $U(T_r)$ is a function only of the reduced temperature. The form (11) is consistent with the observations that the slope of the $q-w$ curve decreases with the reduced temperature and that the slopes of the $T_r = 0.7$ and 0.905 plots were nearly the same factors of $1-T_r$. In addition, with this $1-T_r$ factor the disappearance of the acentric factor dependence at the critical point easily guarantees though not exclusively, the covergency of all $\alpha-T_r$ curves at $\alpha=1$. The function $U(T_r)$ must now naturally satisfy the condition $U(1)=1$. Further support for the form (11) is finally provided by plotting U (calculated from 11 using an m value as discussed in the succeeding paragraph) vs T_r (Figure 3 includes only 3 substances). All points fell nearly on the same curve.

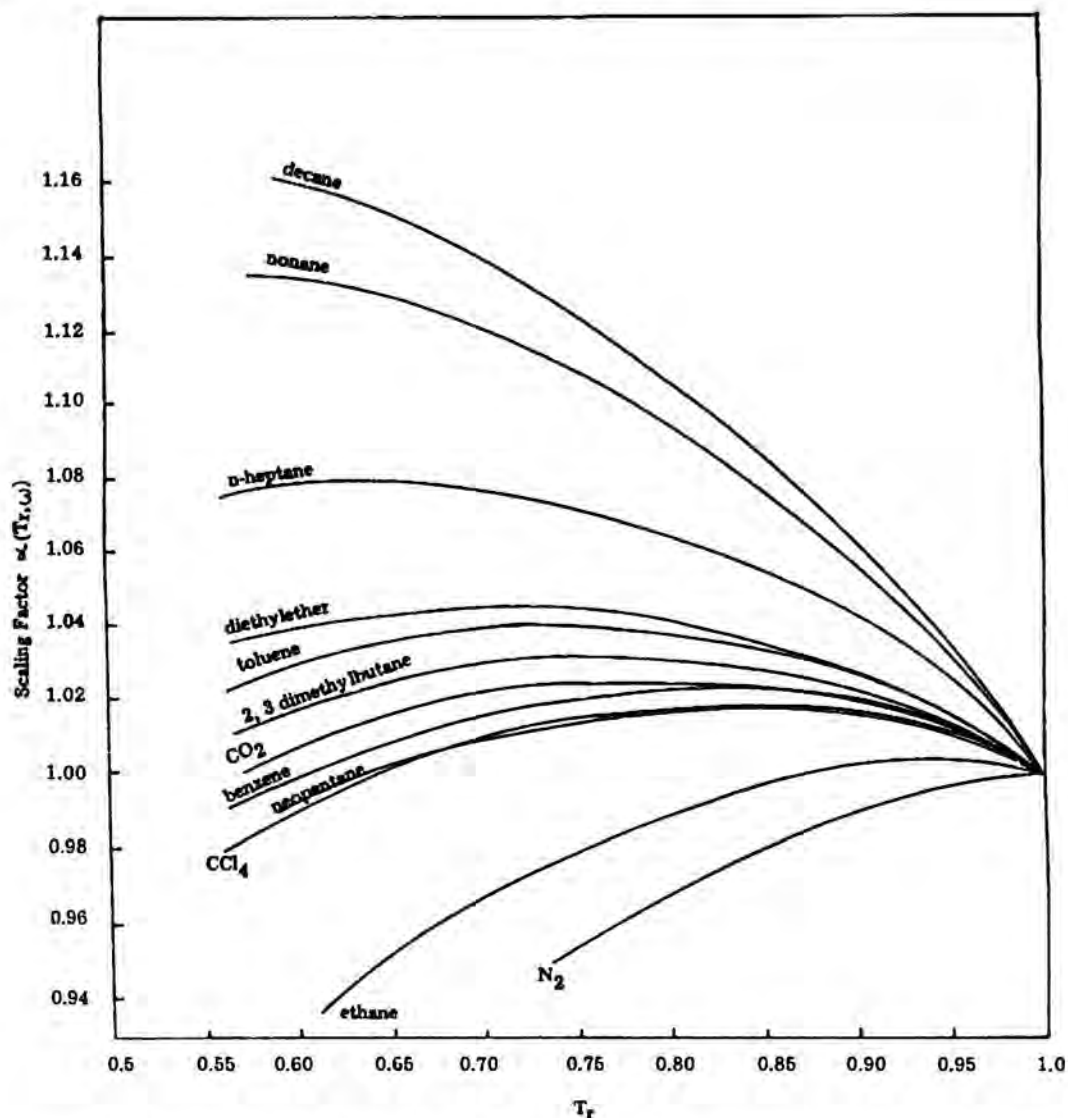


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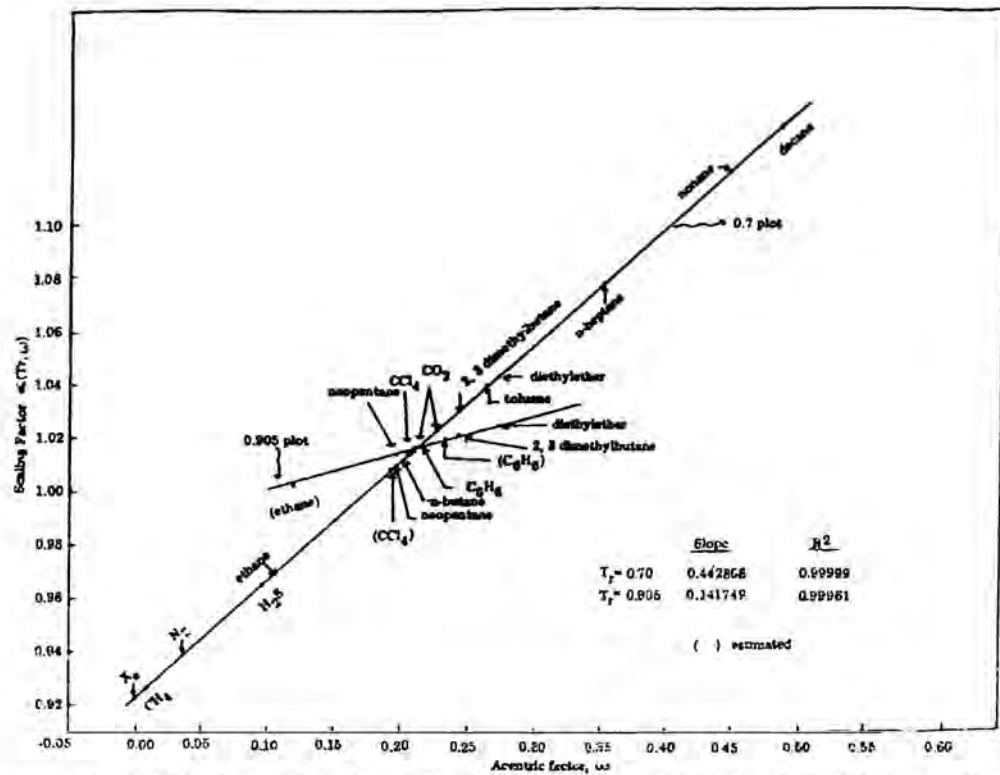


Figure 2: PLOT of the SCALING FACTOR $\alpha(T_r, \omega)$ vs. ACENTRIC FACTOR for $T_r = 0.7$ and 0.905

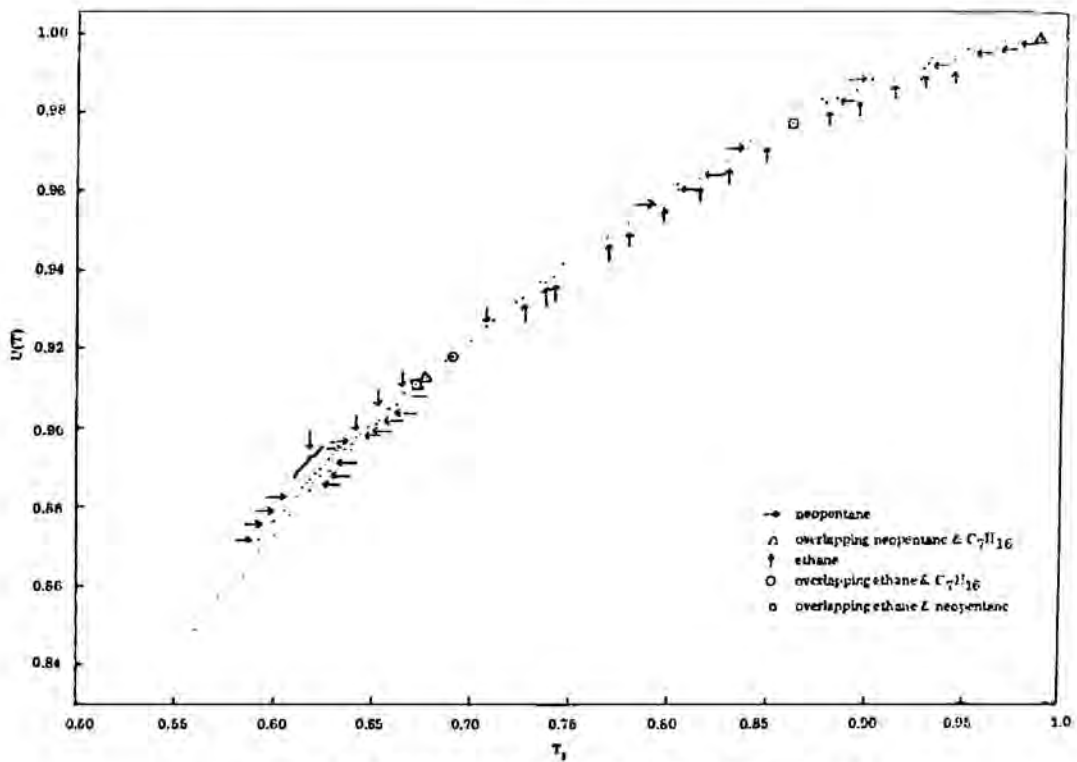


Figure 3: PLOT OF $U(T_r)$ vs. REDUCED TEMPERATURE T_r

The value of m in the acentric factor dependence is obtained from the slope of the α - w curve for $T_r = 0.7$ and is equal to 1.4921. This is in good agreement with that obtained from the 0.905 plot, equal to 1.4762. More substances were included in the regression of the α - w 0.7 plot so as to make the calculated m value more general and widely applicable to other substances as well that were not examined in this paper. Anyway, any limitations in the chosen m value can always be taken care of by $U(T_r)$. The choice of regressing data at $T_r = 0.7$ was really completely arbitrary and was perhaps only motivated by the desire to be consistent with Pitzer's original definition for w and by the fact that the existing data around that temperature was most abundant.

The function $U(T_r)$ was most satisfactorily and conveniently represented by the hyperbolic relation

$$U(T_r) = T_r / (h T_r + k) \quad (12)$$

This may be rewritten in a linear form and then T_r/U vs T_r may be plotted so as to verify that equation 12 validly represents the remaining-temperature dependence. For each data point, U was easily calculated since $U = \alpha - m w (1 - T_r)$. Whether one uses a constant value for w over all temperatures for a particular substance or a calculated value (as described in the previous section) at each temperature, the regression for T_r/U vs T_r yields nearly the same results. The regression line shown in Figure 4 gave a good correlation coefficient of 0.9992; the experimental plot (for 3 substances only in Figure 4) exhibits a slight curvature which is difficult to account for.

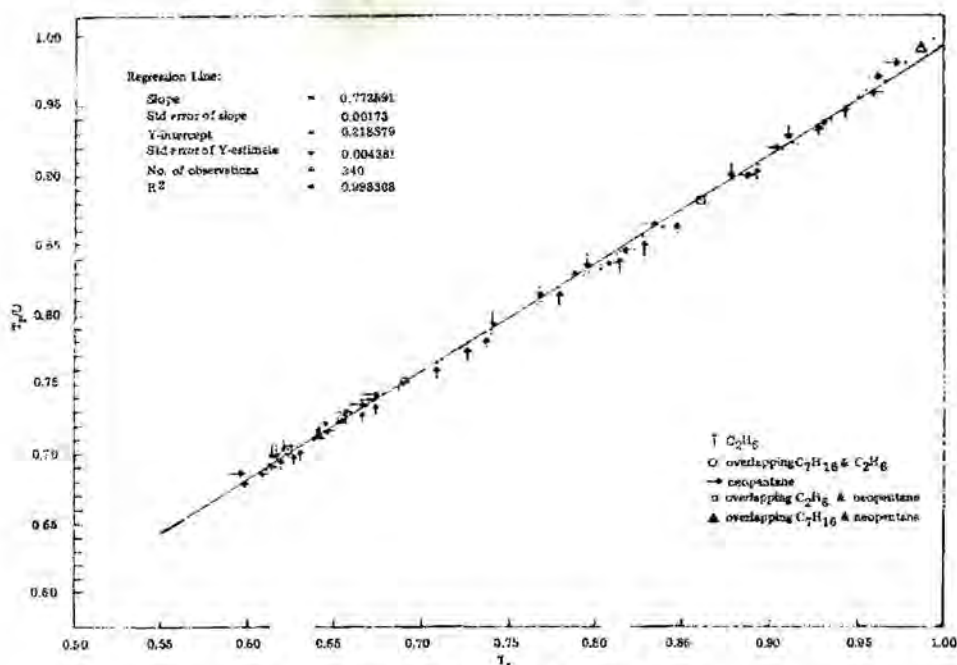


Figure 4: PLOT of T_r/U vs. T_r

All in all then, the final form of the proposed equation is as follows.

$$P = RT / (v-b) - a(T) / (v + 2b/3)^2 \quad (13)$$

where

$$a(T) = a(T_c) * 1.4921 w (1 - T_r) + T_r / (0.7729 T_r + 0.2189)$$

Conclusion and Recommendations

The proposed equation 13 has been developed and shown to provide significant predictive capability in reproducing pure substance saturation conditions. The extension of the equation to mixtures should then be forthcoming. The values of quantities m , h , and k in equation 13 may further be improved and made more general by including more substances in the regression analysis. This involves further testing of the equation to probably at least 20 more substances. Finally, it is interesting to investigate whether $U(T_r)$ is indeed the limiting curve for the plots of α vs T_r . This can be established by testing normal fluids or compounds with acentric factors close to zero. Perhaps some theoretical investigations on the significance of this limiting curve may be pursued.

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