International Journal of Thermophysics, Vol. 17, No. 3, 1996

Improvements of the Patel–Teja Equation of State[1]

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The Patel–Teja equation of state has been improved by modifying the temperature dependence of the attractive term to give simultaneous representation of vapor pressure, liquid density, and liquid heat capacity data for polar and nonpolar compounds. For many high-boiling industrially important compounds, the combination of available heat capacity and vapor pressure data provides a thermodynamically sound method of establishing the temperature dependence of the attractive term in the most practical range of 273–523 K. The performance of the equation of state is greatly improved if the critical pressure is used as the adjustable parameter to correlate the thermodynamic properties under the conditions of interest.

KEY WORDS: cubic equation of state; heat capacity; liquid density; mixing rules; Patel–Teja equation; thermodynamic properties; vapor–liquid equilibrium; vapor pressure.

1. INTRODUCTION

Over the last two decades, cubic equations of state have become very popular in process design. These equations are commonly used to represent phase equilibria in the form of vapor–liquid equilibrium, liquid–liquid–vapor equilibrium, and solubility of gases in liquids. Their use has been extended from simple nonpolar and slightly polar components to highly polar components previously handled by the use of activity coefficient models. Two fundamental improvements have helped to increase the correlative and predictive power of simple cubic equations of state. First, the improvement in the temperature dependent term, often called the "alpha (α)" term, has led to better matching of the pure component vapor pressure curve along the saturation line and, second, the improvement in

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[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

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0195-928X/96/0500-0673$09.50/0

the representation of mixtures through better and more versatile mixing rules has led to correlation of vapor–liquid equilibrium data with the same quality usually found with the activity coefficient approach. Both of these topics have received significant attention in the last few years [1–3].

The main purpose of this work is to provide a more flexible α term which can be used to improve the correlation of experimental data for a variety of industrially important compounds. For this purpose a previously developed cubic equation of state is used [4]. This equation, which is often referred to as the Patel–Teja equation or the P-T equation, has several advantages over other popular equations of state [5–8]. It is possible to reduce the P-T equation to some of the most popular equations of state, e.g., the Soave–Redlich–Kwong (S-R-K) [9], the Peng–Robinson (P-R) [10], and the Redlich–Kwong (R-K) [11]. The P-T equation also provides reasonably accurate values for liquid-phase properties including density and enthalpies, and this is done without violating the two classical constraints, which require the first and second derivatives of pressure with respect to volume to be zero at the critical point. The new temperature function introduced in this work is intended to improve vapor pressure and related quantities such as enthalpies, entropies, and Gibbs free energies. Heat of vaporization is also improved as a direct consequence of the Clausius–Clapeyron relationship [12]. With the new temperature function, it is now possible to include low-temperature liquid heat capacity data with vapor pressure and liquid density data to regress equation-of-state parameters. It is also possible to extend the use of the equation of state to calculate vapor pressure in the temperature range where experimental measurement of vapor pressure is difficult but the heat capacity data can be easily measured, e.g., high-boiling compounds at or near room temperature. The use of liquid heat capacity data is not new; Ambrose and Davies [13] and King and Al-Najjar [14] have used low-temperature heat capacity data to extend vapor pressure equations, and recently Twu et al. [2] recommended the use of heat capacity data to improve the temperature dependence of the S-R-K equation of state.

2. A NEW α FUNCTION

Over the last decade, several functional forms have been proposed for the α term in the cubic equation of state (see Appendix). Many of these forms have been shown to give the correct asymptotic behavior for the α vs temperature curve to overcome the deficiency present in the original form used by the S-R-K, P-R, P-T, and other popular equations of state. As mentioned elsewhere [1–3, 15], the original functional form containing only one adjustable parameter is good for the reduced temperature range of 0.7 and higher but gives large errors at lower reduced temperatures. To improve the accuracy of the vapor pressure representation, two or more adjustable parameters are required to describe the α vs temperature relationship. A real advantage of using cubic equation of state to represent the vapor pressure curve lies in the fact that other thermodynamic properties can be calculated without additional parameters, e.g., heat of vaporization, liquid enthalpy, liquid heat capacity, etc.

In Fig. 1, three α equations are plotted for hydrogen. For Twu et al. and Melhem et al., the function behaves correctly at higher temperatures. For Gibbons and Laughton, the function approaches zero and becomes negative at higher temperature. This is not a desired behavior and needs to be fixed to avoid calculation of physically impossible negative values for α. As shown, the extrapolation is different for all three equations. To improve the overall accuracy of the Gibbons and Laughton function and to allow difficult compounds to be handled, the following function is proposed for the α term.

$$\alpha(T) = 1 + c_1(T_r - 1) + c_2(\sqrt{T_r} - 1) + c_3(T_r^N - 1) \qquad (1)$$

Here c_1, c_2, c_3, and N are pure component constants and $T_r = T/T_c$ is a reduced temperature.

The last term in Eq. (1) is intended to improve the accuracy in vapor pressure and heat capacity data. It can also be used to give proper

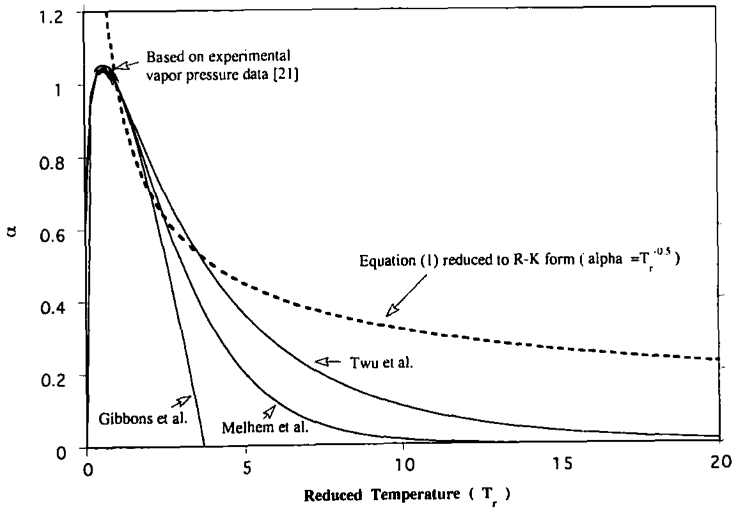

Fig. 1. Plot of α vs reduced temperature for hydrogen.

asymptotic behavior at higher temperatures for supercritical components. For example, setting $c_1 = c_2 = 0$, $c_3 = 1$, and $N = -\frac{1}{2}$, the function is reduced to the original R-K form, which is asymptotically correct and works well for the supercritical region (see Fig. 1). For most compounds, α and $d\alpha/dT$ approach zero at a temperature outside the range of interest for process design and it is not necessary to fix the asymptotic behavior. However, for supercritical components such as hydrogen, the asymptotic behavior should be fixed so that realistic values for α and $d\alpha/dT$ can be obtained as shown in Fig. 1. This can be done either by fitting Eq. (1) to the α values obtained from the saturation curve by equating fugacities of vapor and liquid phases and combining with the values of α generated from the R-K form ($\alpha = T_r^{-0.5}$) at the higher reduced temperatures ($T_r = 10$, 15, 20, etc.) or by simply using the R-K form as shown in Fig. 1.

When the new α term [Eq. (1)] is combined with the P-T equation of state, typical results indicate a deviation of 1% or less in the vapor pressure curve, 2% or less in the liquid density curve up to the reduced temperature of 0.85, 2% or less in the heat of vaporization up to the reduced temperature of 0.90, and 3% or less in the liquid heat capacity curve below the normal boiling point. The actual results are highly dependent on the quality of the experimental data and the critical parameters used. For illustrative purpose, parameters c_1, c_2, c_3, N, and ζ_c are listed in

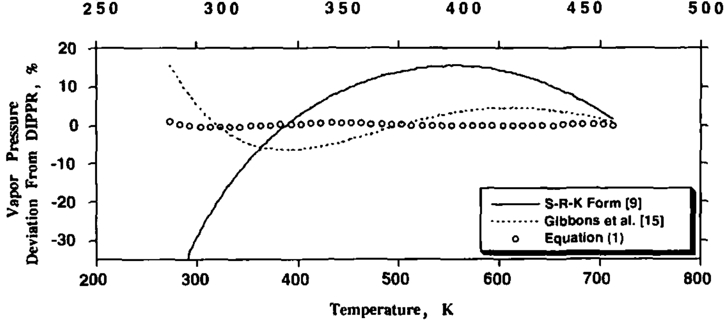

Fig. 2. Vapor pressure and liquid heat capacity of ethylene glycol. Comparisons of three forms of α using the Patel–Teja equation of state.

Table I. Parameters for the Modified Patel–Teja Equation of State[a]

Component	T_c (K)	P_c (bar)	Ref. No.	c_1	c_2	c_3	N	ζ_c	ΔP^S	ΔV^l	ΔC_p
Ethylene glycol	719.70	77.000	21	−1.11765	−1.81779	0.47892	3	0.2768	0.27	0.8	1.2
Ethylene oxide	469.15	71.900	21	0.82082	−2.80514	—	—	0.2967	0.36	1.0	1.4
Water	647.13	220.55	21	0.60462	−2.56713	—	—	0.2695	0.22	1.4	1.2
Ethylene	282.34	50.400	21	1.94572	−3.59956	−0.37410	2	0.3228	0.12	0.8	2.0
Carbon dioxide	304.21	73.830	21	0.63199	−2.69935	—	—	0.3133	0.20	0.9	3.0
Hydrogen sulfide	373.53	89.629	21	0.66433	−2.39792	−0.00669	10	0.3226	0.12	1.1	1.6
Methane	190.56	45.988	21	0.32274	−1.47606	−0.02025	6	0.3283	0.08	1.6	1.2
Acetone	508.20	47.217	21	0.19454	−1.45357	0.32485	−0.5	0.2817	0.15	1.4	1.5
Nitrogen	126.20	34.000	21	0.09339	−1.26573	—	—	0.3300	0.35	1.4	3.0
Hydrogen[b]	33.19	13.130	21	0.0	0.0	1.0	−0.5	0.3333	—	—	—
Hydrogen	33.19	13.130	21	−0.72258	1.08363	−1.4928E−06	−8	0.3333	0.16	—	—
Sensitivity of critical parameters											
Acetic anhydride	606.00	40.000	19	1.48337	−4.64181	—	—	0.2826	0.10	1.3	13.0
	569.00	46.812	20	−4.34964	4.14485	—	—	0.3296	4.80	1.2	57.0
Diethanolamine	736.60	32.70[c]	21	2.90751	−7.59778	—	—	0.2250	2.90	1.4	1.5
	736.60	42.700	21	1.52351	−5.98673	—	—	0.2708	0.12	1.2	11.0

[a] ΔP^S = deviation in vapor pressure; ΔV^l = deviation in liquid molar volumes; ΔC_p = deviation in liquid molar heat capacity. DIPPR equations were used as a substitute for experimental data. For ΔP^S, data compared up to the critical point. For ΔV^l, data compared up to the reduced temperature of 0.85. For ΔC_p, data compared up to the normal boiling point. Deviation is absolute average percentage deviation defined as follows: $\Delta P^S(\%) = (1/n) \sum_i^n \mathrm{Abs}[(P^S_{i,\mathrm{exp}} - P^S_{i,\mathrm{calc}})/P^S_{i,\mathrm{exp}}] \times 100$.

[b] Parameters constrained to R-K form for extrapolation to higher temperature.

[c] Critical pressure from Ref. 28.

Table I for selected components. Note that the last term in Eq. (1) is not required for many components. Deviations in vapor pressure, liquid volumes, and liquid heat capacity are also shown. DIPPR [21] equations were used as a substitute for actual experimental data. Details of DIPPR correlations and experimental data can be found in the DIPPR databank [21]. To show the effectiveness of Eq. (1) against other forms of the α term, results are plotted in Fig. 2 for vapor pressure and liquid heat capacity. As can be seen, Eq. (1) gives excellent results for both vapor pressure and liquid heat capacity of ethylene glycol. The P-T equation of state was used in all three cases with the same value of ζ_c.

Results are also presented in Table II in the form of deviations for the three properties used in the regression. As can be seen, the use of the last term in Eq. (1) does not always result in the best overall fit, however, the use of the last term always improve the fit of the vapor pressure data. This shows the danger of overfitting the vapor pressure curve when liquid heat capacity data are not used in the regression. The α forms suggested by Melhem et al. and Twu et al. are not shown in Table II because they were not implemented in the computer program written for the P-T equation of state. Instead, these two forms are compared with the other forms in Table III. Results are given for the sum of squared deviation in the representation of the α vs temperature relationship for ethylene glycol, water, and acetone. The experimental value of α was obtained at every

Table II. Absolute Average Percentage Deviations in Vapor Pressure (ΔP^S), Liquid Molar Volumes (ΔV^l), and Liquid Molar Heat Capacity (ΔC_p) for Three Forms of α Equations

	Soave [9]			Gibbons et al. [15]			Equation (1)			
Component	ΔP^S	ΔV^l	ΔC_p	ΔP^S	ΔV^l	ΔC_p	ΔP^S	ΔV^l	ΔC_p	N^a
Ethylene glycol	12.8	0.9	4.7	4.0	0.7	1.6	0.27	0.8	1.2	3
Ethylene oxide	1.9	1.0	8.8	0.4	1.0	1.4	0.05	1.0	7.3	2
Water	0.7	1.4	2.2	0.2	1.4	1.2	0.1	1.4	2.3	2
Ethylene	1.1	0.8	3.1	0.9	0.9	3.5	0.12	0.8	2.0	2
Carbon dioxide	0.2	0.9	1.7	0.2	0.9	3.0	0.08	0.9	21.0	2
Hydrogen sulfide	0.5	1.1	7.4	0.3	1.1	4.4	0.12	1.1	1.6	10
Methane	1.1	1.7	4.7	0.3	1.6	5.4	0.08	1.6	1.2	6
Acetone	1.3	1.4	6.2	0.3	1.4	3.6	0.2	1.4	1.5	−0.5
Nitrogen	0.7	1.4	2.2	0.4	1.4	3.0	0.05	1.3	4.1	2

[a] Values for N in Eq. (1). Except for ethylene, the value of $N = 2$ is used only for comparison purposes (it is not the optimum value).

Table III. Comparison of Different α Forms for Water, Ethylene Glycol, and Acetone[a]

α form	SSD × 10^6		
	Ethylene glycol ($\zeta_c = 0.2768$)	Water ($\zeta_c = 0.2695$)	Acetone ($\zeta_c = 0.2817$)
Soave [9]	25365	24.37	622.4
Gibbons et al. [15]	1448	4.18	46.14
Equation (1)	3.5	1.79	13.73
Melhem et al. [1]	2904.8	2.52	55.99
Twu et al. [2]	3156.1	2.09	24.32

[a] SSD, sum of squared deviation. It is given by the equation $\mathrm{SSD} = \sum_{i=1}^{n}(\alpha_{i\,\mathrm{exp}} - \alpha_{i\,\mathrm{calc}})^2$. SSD is the actual least-squares measure of the curve fitting. Experimental values of α were derived from experimental vapor pressure data by equating fugacity of vapor and liquid phases along the saturation curve with a fixed value of ζ_c. Experimental vapor pressure data were taken from DIPPR (only the "accepted" data in the DIPPR file were used). In Eq. (1), $N = 3$ was used for ethylene glycol, $N = 2$ for water, and $N = -0.5$ for acetone.

temperature using experimental vapor pressure data from DIPPR. The value of α was iterated until the fugacities of the vapor and liquid phases were equal. Once the α vs temperature curve was established, different forms of the α equations were tested using nonlinear regression program. Results shown in Tables II and III show that Eq. (1) is more flexible than the other forms of the α equations. This is not surprising since it contains four adjustable parameters and it is not constrained to give proper asymptotic behavior, which is important for supercritical components. For water and acetone, good results are obtained by all α forms, however, for ethylene glycol which is a high-boiling liquid with some uncertainty in the critical parameters, Eq. (1) is better than the other forms.

3. SENSITIVITY OF THE CRITICAL PARAMETERS

Critical parameters such as the critical pressure (P_c) and the critical temperature (T_c) play an important role in defining the predictive and the correlative capability of a given equation of state. Since classical constraints require the first and the second derivative of pressure with respect to volume to be zero at the critical point, we need to have a knowledge of the critical point or T_c and P_c. Unfortunately, many industrially important compounds tend to decompose at or near their normal boiling points. The critical parameters are often estimated by one of the available group contribution methods, e.g., Lydersen [16], Joback [17], and Ambrose [18]. The uncertainty in the critical parameters may be the main cause of poor calculation of derived thermodynamic properties such as heat capacity, enthalpy, and fugacity coefficient. For simultaneous correlation of several thermodynamic properties, it is often useful to treat one of the critical parameters as an adjustable variable. If all properties are improved in the practical range of operation, the derived critical parameter can be considered to be consistent with the measured data and deemed useful for process design. Experience has shown that the critical pressure is a better choice than the critical temperature, especially since the available estimation methods for the critical temperature are better than those for the critical pressure [22].

In Table I, results of using two sets of critical parameters are shown for diethanolamine and acetic anhydride. As can be seen, better results are obtained, depending on the choice of the critical parameters used. As shown in Table I, the values of P_c and T_c given by Ambrose and Ghiassee [19] for acetic anhydride are much more consistent than the ones reported by Vespignani [20] when compared with the vapor pressure data measured for this compound. Similarly, the criticals reported by DIPPR [21] for diethanolamine appear to be inconsistent, since large deviations are obtained in the calculated liquid heat capacity.

4. CONCLUSIONS

A new temperature dependence has been proposed for the α term of the Patel–Teja equation of state. The new model is capable of simultaneously representing vapor pressure, liquid density, and liquid heat capacity data for polar and nonpolar compounds. For most compounds, data are correlated with sufficient accuracy for process design.

For compounds with unreliable critical parameters, the performance of the equation of state is improved by using the critical pressure as an adjustable parameter. In this way, it is also possible to detect any inconsistency in the critical parameters.

APPENDIX

The Modified Patel–Teja Equation of State

$$P=\frac{RT}{V-b}-\frac{a[T]}{V(V+b)+c(V-b)}$$

$$a=\Omega_a\frac{R^2T_c^2}{P_c}\alpha[T], \qquad b=\Omega_b\frac{RT_c}{P_c}, \qquad c=\Omega_c\frac{RT_c}{P_c} \qquad \text{(A1)}$$

where, Ω_a, Ω_b, and Ω_c are functions of the predicted critical compressibility factor denoted ζ_c. The following constraints at the critical point are applied to the equation of state, Eq. (A1).

$$\left(\frac{\partial P}{\partial V}\right)_{T_c}=0, \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c}=0, \qquad \frac{P_c V_c}{RT_c}=\zeta_c$$

With the critical constraints, the following relationships are established among the three dimensionless parameters Ω_a, Ω_b, and Ω_c and the predicted critical compressibility factor ζ_c.

$$\Omega_c = 1 - 3\zeta_c$$

$$\Omega_a = 3\zeta_c^2 + 3(1-2\zeta_c)\,\Omega_b + \Omega_b^2 + 1 - 3\zeta_c$$

Ω_b is obtained by solving for the smallest positive root of the following cubic equation:

$$\Omega_b^3 + (2-3\zeta_c)\,\Omega_b^2 + 3\zeta_c^2\Omega_b - \zeta_c^3 = 0$$

For $\alpha[T]$, the following function of reduced temperature is proposed:

$$\alpha[T] = 1 + c_1(T_r - 1) + c_2(\sqrt{T_r} - 1) + c_3(T_r^N - 1) \qquad \text{(A2)}$$

Equation (A2) without the last term was originally proposed by Gibbons and Laughton [15]. Equation (A2) was used with the equation of state, Eq. (A1), to correlate experimental data for vapor pressure, liquid density, and liquid heat capacity. Constants c_1, c_2, c_3, N, and ζ_c are given in Table I for selected components. Other forms for $\alpha[T]$ suggested by Soave [9], Melhem et al. [1], and Twu et al. [2] are given below.

Soave [9]: $\alpha[T] = [1 + c_1(1 - T_r^{0.5})]^2$
Melhem et al. [1]: $\alpha[T] = \exp[c_1(1 - T_r) + c_2(1 - \sqrt{T_r})^2]$
Twu et al. [2]: $\alpha[T] = T_r^{c_3(c_2-1)} \exp[c_1(1 - T_r^{c_2 c_3})]$

The form suggested by Soave was used in the original P-T equation of state.

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