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CALCULATED AND EVALUATING SEVEN CUBIC EQUATIONS OF STATE IN PREDICTING GAS AND LIQUID PHASE VOLUMETRIC PROPERTIES OF NINE OZONE-SAFE REFRIGERANTS

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Abstract- The present work is devoted to evaluating seven cubic equations of state (EOS) in predicting gas and liquid phase volumetric properties of nine ozone-safe refrigerants both in super and sub-critical regions. The evaluations, in sub-critical region, show that TWU and PR EOS are capable of predicting PVT properties of refrigerants R32 within 2%, R22, R134a, R152a and R143a within 1% and R123, R124, R125, and y TWU and PR EOS's, from literature data are 0.5% for R22, R32, R152a, R143a, and R125, 1% for R123, R134a, and R141b, and 2% for R124. Moreover, SRK EOS predicts PVT properties of R22, R125, and R123 to within aforementioned errors. The remaining EOS's predicts volumetric properties of this class of fluids with higher errors than those above mentioned which are at most 8%. In general, the results are in favor of the preference of TWU and PR EOS over other remaining EOS's in predicting densities of all mentioned refrigerants in both super and sub critical regions. Typically, this refrigerant is known to offer advantages such as ozone depleting potential equal to zero, Global warming potential equal to 140, and no toxic.

Keywords-component- volumetric properties; refrigerant; super and sub-critical regions

I. INTRODUCTION

Since van der Waals (1873) proposed his well-known cubic equation of state over a century ago, numerous equations of state have been proposed to calculate the thermodynamic properties of both pure components and mixtures in vapor and liquid phases.

The ability of a CEOS to correlate the phase equilibria of mixtures depends not only on the mixing rule, but also on the alpha function. Remarkable success in the development of a generalized alpha function was shown by Soave (1972). He recognized that a prerequisite for the correlation of the phase equilibria of mixtures is the correlation of the vapor pressures of the pure components. The soave modification of the Redlich and Kwonog (1949) equation has been a major success in correlation of the phase behavior of multi-component systems containing non-polar and slightly polar components. The soave approach was subsequently used in work by peng and Robinson (1976). This also helped the PR equation to become one of the most widely used equations of state in industry for correlating the vapor – liquid equilibria (VLE) of systems containing non-polar and slightly polar components.

II. REVIEW OF EQUATIONS OF STATE VAN DER WAALS EOS

$$\left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT \quad (1)$$

Where p represents pressure, T is temperature, V_m is molar volume and R is the molar gas constant. The

parameter a is a measure of the attractive forces between the molecules and the parameter b is a measure of the size of the molecules (hard body term). Both adjustable parameters a and b can be obtained from the critical properties of the fluid. The van der Waals equation can be regarded as a “hard-sphere (repulsive) + attractive” term equation of state composed from the contribution of repulsive and attractive intermolecular interactions, respectively.

It gives a qualitative description of the vapour and liquid phases and phase transitions (Van Konynenburg and Scott, 1980), but it is rarely sufficiently accurate for critical properties and phase equilibria calculations. A simple example is that for all fluids, the critical compressibility predicted by Eq. (1) is 0.375, whereas the real value for different hydrocarbons varies from 0.24 to 0.29. The van der Waals equation has been superseded by a large number of other, more accurate equations of state.

Where a , b and R are constants that depend on the specific material. They can be calculated from the critical properties as:

$$a = \frac{R^2 T_c^2}{P_c} \quad (2)$$
$$b = 0.125 \frac{RT_c}{P_c} \quad (3)$$

In 1873, the van der Waals equation of state was one of the first to perform markedly better than the ideal gas law. In this landmark equation a is called the attraction parameter and b the repulsion parameter or the effective molecular volume. While the equation is

definitely superior to the ideal gas law and does predict the formation of a liquid phase, the agreement with experimental data is limited for conditions where the liquid forms. While the van der Waals equation is commonly referenced in text-books and papers for historical reasons, it is now obsolete. Other modern equations of only slightly greater complexity are much more accurate. Van der Waals equation may be considered as the ideal gas law, "improved" due to two independent reasons:

1. Molecules are thought as particles with volume, not material points. Thus V cannot be too little, less than some constant. So we get $(V - b)$ instead of V .
2. While ideal gas molecules do not interact, we consider molecules attracting others within a distance of several molecules' radii. It makes no effect inside material, but surface molecules attract to inside. We see this as diminishing of pressure on the outer shell (which is used in the ideal gas law), so we write $(P + \text{something})$ instead of P . To evaluate this 'something', let's examine addition force acting on an element of gas surface.

A. Redlich-Kwong EOS

Introduced in 1949 the Redlich-Kwong equation of state was a considerable improvement over other equations of the time. It is still of interest primarily due to its relatively simple form. While superior to the van der Waals equation of state, it performs poorly with respect to the liquid phase and thus cannot be used for accurately calculating vapor-liquid equilibria. However, it can be used in conjunction with separate liquid-phase correlations for this purpose.

The Redlich-Kwong equation is adequate for calculation of gas phase properties when the ratio of the pressure to the critical pressure (reduced pressure) is less than about one-half of the ratio of the temperature to the critical temperature (reduced temperature). The Redlich-Kwong EOS by Redlich and Kwong is a modification of the Van der Waals EOS it should only be used in order to demonstrate the inabilities of simple EOS, because better EOS exist. Use of this EOS only requires the input of T_c and P_c .

The parameters a and b (for each component):

$$p = \frac{RT}{v-b} - \frac{a/T^{0.5}}{v(v+b)} \quad (4)$$

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c} \quad (5)$$

$$b = \frac{0.08664R^2T_c}{P_c} \quad (6)$$

B. Peng-Robinson EOS

This equation of state is fairly similar to the Soave-Redlich-Kwong equation, but with a slightly different denominator for the second term. Again, the parameter ω has a temperature dependence, and the parameter giving its dependence ω have been found by comparing the predictions of the equation with experimental boiling points. The Peng-Robinson equation is particularly accurate for predicting the properties of hydrocarbons, including the behavior of mixtures and vapor-liquid equilibrium. It is not expected to be accurate when predicting properties of highly polar molecules, particularly those that are capable of hydrogen bonding. The Peng-Robinson EOS is the EOS most widely used in chemical engineering thermodynamics. The EOS requires three inputs per compound: T_c , P_c and the acentric factor ω .

The Peng-Robinson EOS is the EOS most widely used in chemical engineering thermodynamics. The EOS requires three inputs per compound: T_c , P_c and the acentric factor ω .

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (7)$$

Where ω is the acentric factor for the species

The Peng-Robinson equation was developed in 1976 in order to satisfy the following goals:

1. The parameters should be expressible in terms of the critical properties and the acentric factor.
2. The model should provide reasonable accuracy near the critical point, particularly for calculations of the Compressibility factor and liquid density.

III. CALCULATION

Figure 1 illustrates deviation plot of the calculated vapor density from the literature data for refrigerant R152a in super-critical ($T = 2700$ K) region.

Figure 2 demonstrates a plot of the calculated a comparison between the calculated and literature values of saturated vapor of R134a system.

III. Second virial coefficient

A close look at figures reveals that PR and SRK are in good agreement with those obtained from recent correlations obtained by Tsonopoulos and Weber and speed of sound measurements. Therefore, these two EOS stand over other EOS both in sub and super critical regions. All EOS follow two-parameter principle of corresponding states at T/T_c higher than 8 and lower than 1 except NM EOS. In the temperature range $1 < T/T_c < 8$, PR and SRK still follow above mentioned principle. The same trend has been observed for other refrigerants

1. The present work is devoted to evaluating seven cubic equations of state (EOS) in predicting gas and liquid phase thermodynamic properties of several refrigerants both in super and sub-critical regions.

2. Refrigerants include R22, R32, R123, R124, R125, R134a, R141b, R143, and R152a and equations of state, considered here, are Ihm-Song-Mason (ISM), Peng-Robinson (PR), Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK), Modified Redlich-Kwong (MRK), Nasrifar-Moshfeghian (NM), and Twu-Coon-Cunningham (TCC).

3. The evaluations, in sub-critical region, show that TCC and PR EOS are capable of predicting PVT properties of refrigerants R32 within 2%, R22, R134a, R152a and R143a within 1% and R123, R124, R125, and R141b to within 0.5%. It should be mentioned that NM EOS can also predict volumetric properties of R22, R32, R123, R152a, and R143a within aforementioned estimated accuracies. Moreover, in this region, the ISM EOS predicts these properties of R123 and R141b with above-mentioned accuracies.

4. In super-critical region, the deviations of calculated vapor densities, obtained by TCC and PR EOS's, from literature data are 0.5% for R22, R32, R152a, R143a, and R125, 1% for R123, R134a, and R141b, and 2% for R124. Moreover, SRK EOS predicts PVT properties of R22, R125, and R123 to within aforementioned errors.

IV. IN SUN

The results are in favor of the preference of TCC and PR EOS's over other remaining EOS's in predicting vapor densities of all mentioned refrigerants in both super and sub critical regions.

As a thermodynamic property, second virial coefficients of R143a have been calculated from NM

EOS.,PR EOS.,SRK EOS. TCC EOS. Our calculations are in agreement with literature values especially at high temperatures

V. NOMENCLATURE

p	pressure (bar)
T	temperature (K)
Z	compressibility factor
V	volume
V_m	molar volume
R	ideal gas constant (8.31451 J/ (mol K))
ω	acentric factor

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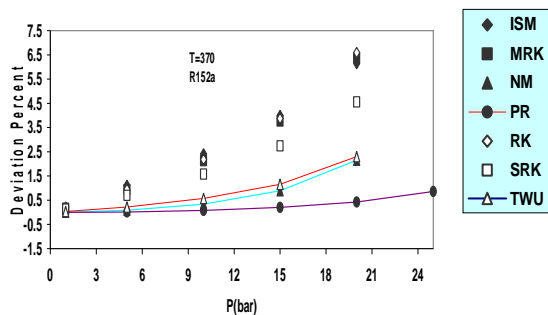


Fig. 1 Deviation plot of the calculated vapor density from the literature data for refrigerant R134a in super-critical (T= 500 K) region

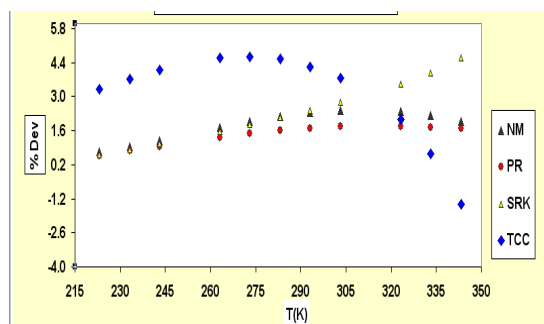


Fig.2 Comparison between the calculated and literature values of saturated vapor of R134a system.