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PREDICTION OF MOLAR VOLUME FOR PURE COMPOUNDS USINGPENG-ROBINSON EQUATION OF STATE

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ABSTRACT

The Peng Robinson equation of state (PREOS) is the semiempirical van der Waals equation in which the attractive pressure term was modified. PREOS has shown wide and reliable applicability to the calculation of vapor-liquid equilibria (VLE) for systems containing light hydrocarbons, permanent gases, carbon dioxide, and hydrogen sulfide. The principal objective of this paper is to predict the molar volume of single pure compounds in different pressure and temperature on the basis of the PREOS combining Newton's method. In the calculation, the Visual-Basic language will be used for design program and a consistent correction will be applied to improve the gas-phase volume estimation. The calculation results give a good agreement with experimental data. It is shown that PREOS combining Newton's method can reasonably predict the molar volume of single pure compounds. Also, it shows its greatest advantage, ie, simplicity and accuracy, using in the prediction of single pure compounds.

Keywords: Chemical simulation, Peng Robinson equation of state, Vapor-liquid equilibria, Molar volume, Newton's method.

1. INTRODUCTION

The equation of state [1] is widely used in petrochemical and chemical industry. Study of volumetric behavior, vapor/liquid equilibria (VLE), thermal properties of both pure compounds and mixtures (in vapor or liquid phases) have been one of the most elusive thing for thermodynamics. And the accuracy of parameters calculation is dependent largely on the choice of an equation of state or mixing rules. Therefore, a series of equation of state have been explored for an analytical and more accurate expression relating the pressure to the volume and temperature. [2-5]

There are equations for thermodynamics calculation proposed for centuries which could be sorted into four kind: ideal gas equation; virial equation; cubic equation and multiple parameter equation. [6-8] And cubic equation of state are used widely in the industry for their high precision and simple form.In 1987, Van der Waals [9] took intermolecular forces into consideration and proposed the first practical cubic equation of state. The Van der Waals equation of state (VD-WEOS) was consist of molecular attraction and intermolecular repulsion. Since that time, numerous EOS's on the modification of molecular attraction have been proposed. Redlich-Kwong [10] considered the impact of temperature on intermolecular forces and proposed a new equation (RK-EOS). In the days which followed, a review of some of the modified RK equations has been presented. One of the more recent modifications of the RK equation is that proposed by Soave [11]. The Soave-Redlich-Kwong [12] (SRK) equation has rapidly gained acceptance by the hydrocarbon processing industry for its relative simplicity and reasonably accurate equilibrium rations in vapor-liquid equilibrium (VLE) calculations. Then Peng and Ronbison [1] proposed a cubic equation with more accurate in calculation of fluid molar volume. It can used for calculation of gas phase and liquid phase [13-16].

The objective of this work is to evaluate the accuracy of using PR-EOS and Newton's predictive methods for calculation typical compounds. In the calculation, the Visual-Basic language will be used for design program and a consistent correction will be applied to improve the gas-phase volume estimation. And the molar volume of light hydrocarbons, benzene, n-butane, R134a, and water vapor will be predicted in different pressure and temperature. The calculation results will be compared with the experiment data to verify the reasonability and accuracy.

2. EQUATION OF STATE AND COMPUTATIONAL METHOD

2.1 PR equation

The PREOS is perhaps the most popular and widely used EOS in petroleum and chemical industry. With the advent of analytical expressions in computers to interpolate, extrapolate and even predict thermodynamic information has gained increasing importance for process design and for modeling of process operation [17]. This paper makes a model on the basis of PR equation to calculate the vapor molar volume of pure compounds.

The general form of that cubic EOS is as follows:

$$P = \frac{R_g T}{v-b} - \frac{a(T)}{v(v+b)+b(v\text{-}b)} \tag{1}$$

In equation (1),

$$a(T) = \left(0.45724 R_g{}^2 T_c{}^2 / P_c\right)\left[1 + f_\omega\left(1 - T_r{}^{0.5}\right)\right]^2 ;$$

$$f_\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$b = 0.0778\, R_g T_c / P_c \, ;$$

$$T_r = T/T_c \, .$$

Where P is pressure, Pa; T is temperature, K; The subscripts c and r indicate critical value and reduced value, respectively; R=8.314471J.mol-1•K-1, a universal gas constant; v is molar volume, m3•mol-1; ω is acentric factor; the parameters a and b show effects of the intermolecular forces and molecules volume, respectively [1, 17, 18].

2.2 Newton's method

There are difficulties to calculate implicit molar volume directly using PR equition, then take Newton's Iterative Method into consideration.

In numerical analysis, Newton's method (also knows as the Newton-Raphson method) [19-21] is a method for finding successively better approximations to the roots (or zeroes) of a real-valued function with the form of formulation for

$$f(v) = a_0 + a_1 v + a_2 v^2 + \cdots + a_n v^n \tag{2}$$

In this paper, the Newton's method with one variable of v is implemented as follows:

Choose a function $f(v)$ defined over the reals v, and its derivative $f\,'(v)$. Then give a initial value v0 and calculate it by iterative method with the following formula:

$$v_{k+1} = v_k - \frac{f(v_k)}{f\,'(v_k)} \tag{3}$$

Until a convergence criterion of $|v_{k+1}\text{-}v_k| < \varepsilon$ were obtained, Where ε is a sufficiently small value depending on the accurate requirement [1]. If the process is not convergence then give a maximum iteration numbers. Treat the process as being convergence when the practical calculation numbers exceeded the maximum.

Considering the lots of work of Newton's method, hand calculation is time-consuming and not accurate enough. This paper uses computer to improve calculation efficiency.

Take a series pure compounds for example, predict the molar volume of gas phase by PR-EOS. Basic parameters are taken from Ref. [22], as shown in Table 1. The experimental data of thermodynamic properties are taken from Ref. [23].

Table 1. Molar mass and critical parameters of some common gas

Substance	Formula	M	R_g	T_{cr}	P_{cr}	v_{cr}	Z_{cr}	ω
		g/mol	J/(kg.K)	K	MPa	m³/kg		
Methane	CH_4	16.043	518.30	190.4	4.60	0.00615	0.287	0.011
Ethane	C_2H_6	30.070	276.50	305.4	4.88	0.00493	0.285	0.099
Propane	C_3H_8	44.094	188.60	369.8	4.25	0.00454	0.276	0.152
n-butane	C_4H_{10}	58.124	143.00	425.2	3.80	0.00439	0.274	0.186
Benzene	C_6H_6	78.114	106.40	562.2	4.89	0.00332	0.271	0.210
Water-vapor	H_2O	18.015	461.50	647.3	22.12	0.00317	0.235	0.344
R134a	CF_3CH_2F	102.030	81.49	374.2	4.06	0.00197	0.263	0.326

Design program by Visual-Basic language to improve computational accuracy. Volume gotten from ideal gas equation of state is used as the initial v0. The main program as an appendix lies in the end of this paper.

3. RESULTS AND DISCUSSION

Figs.1-3 show running results of VB program. They are used to analyze the accuracy of PR-EOS when calculate thermodynamic properties of fluid.

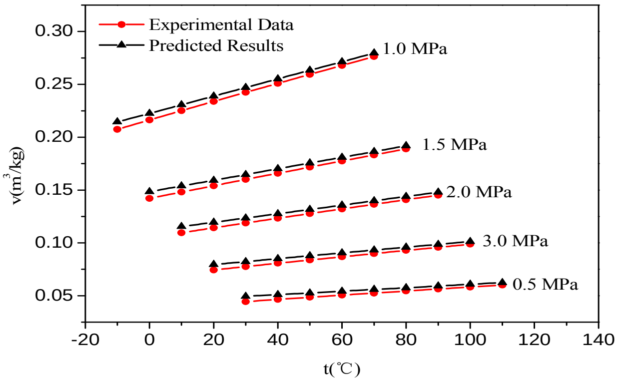

Figure 1. Comparison of prediction and experimental data [23] of R134a gas-phase thermodynamic properties

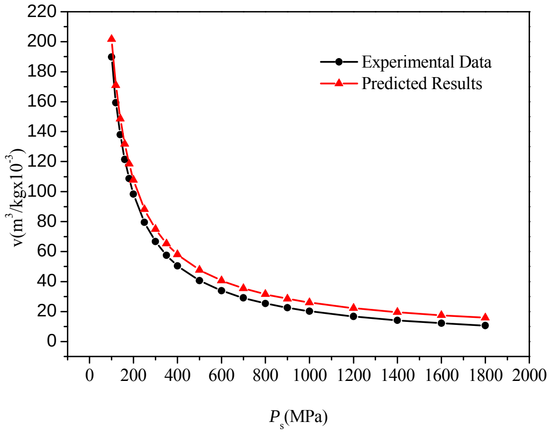

Figure 2. Comparison of prediction and experimental data [23] of R134a gas-phase molar volume in its saturated states (pressure benchmark)

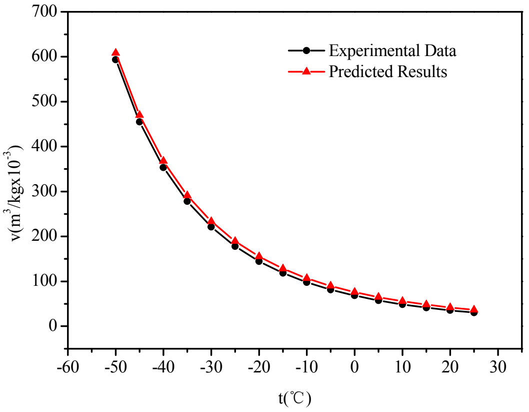

Figure 3. Comparison of prediction and experimental data [23] of R134a gas-phase molar volume in its saturated states (temperature benchmark)

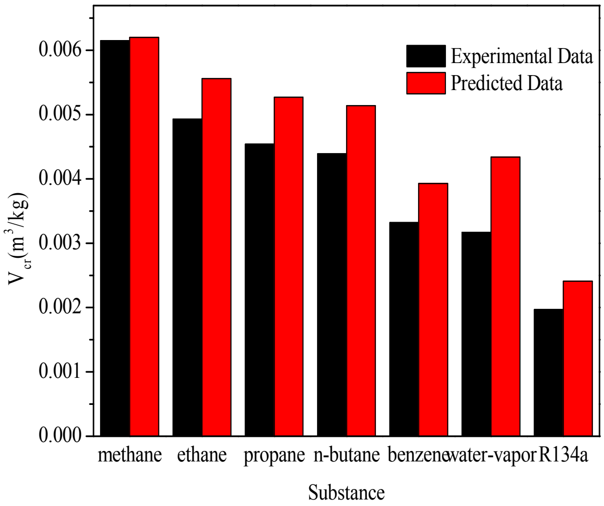

Figure 4. Comparison of prediction and experimental data [22] of molar volume of typical compounds in its critical states

As observed by Fig.1, the PR equation always predicts molar volumes for the R134a at different pressure and temperature which is slightly greater than the literature values [23].The results also shows that the bias decreases with the increase of temperature and the decrease of pressure.

The equation of state predicts saturated R134a-vapor molar volume which are also higher than the experimental data, as Fig.2-3 shown. From Fig.2, at pressure benchmark the higher is the pressure, the larger is the deviation between predicted results and experimental data [23]. And it will be 71% at 2800KPa pressure. And at temperature benchmark, Fig.3 shows the deviation increases as the temperature increases, increases from about 2% to about 20% with temperature increased from -50°C to 25°C.

In order to illustrate the prediction accuracy of molar volume at critical point, experimental values for seven pure substances have been used to compare with the values calculated from the PR equation of state.The results are presented in Fig.4. For hydrocarbon, it is fair to say that the higher the molecular-weight, the greater the deviation is. As an example, with molecular weight being 78.114 g/mol, differences for benzene between predicted and experimental values is 18.4%. However, the deviation for methane with 16.043 g/mol molecular weight is only 0.8%. And for vapor and R134a, the deviation is about 25%. Generally, the PR-EOS prediction has appropriate consistence with experimental data in its critical states. The literature values used for the comparison were taken from Ref. [22].

The black curve in Fig.3 represents the stoichiometric ratio of the mixture fraction being defined. Flame height depends on the stoichiometric mixture fraction location in flame center-line, and the location will be down slightly with the decreasing of gravity level. It should be noted is that peak temperature is in this position in three conditions.

4. CONCLUSIONS

By modifying the attraction pressure term of the semiempirical van der waals equation, PR equation of state has been obtained. PREOS has shown wide and reliable applicability to the calculation of vapor-liquid equilibria (VLE) for systems containing light hydrocarbons, permanent gases, carbon dioxide, and hydrogen sulfide.

In this paper, PREOS combining Newton's method was applied to predict the molar volume of light hydrocarbons, benzene, n-butane, R134a, and water vapor will be predicted in different pressure and temperature. In calculation, the Visual-Basic language was be used for design program and a consistent correction was applied to improve the gas-phase volume estimation. The calculation results give a good agreement compared with the experimental data. It is shown that PREOS combining Newton's method can accurately calculate gas-phase molar volume of pure substance, saturation pressure and saturation temperature. And in low pressure and low temperature, the predicted results are consistent with experimental data better. Generally speaking, the deviation can meet the requirements of engineering design. So, it shows its greatest advantage, ie, simplicity and accuracy, using in the prediction of single pure compounds.

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APPENDIX

Main program

(Take R134a at p=0.05MPa for example, Tc=374.18K; Pc=4.056MPa; ω=0.326; M=102.03 g/mol [1].)

```
Tc = 374.18
Pc = 4.056 * 10 ^ 6
w = 0.326
M = 102.03 * 10 ^ (-3)
Rg = 8.31451 / M      ‘given parameters
Dim fv#, derfv#, k#, vk#
Dim i%
For i = 5 to 16    ‘Calculation of molar volume for each data in excel
v0 = 0.01          ‘initial data of molar volume
G = v0
v = Sheet1.Cells (i, 2).Value
T = Sheet1.Cells (i, 1).Value + 273.15
P = 0.05 * 10 ^ 6       ‘P=0.05MPa
fw = 0.3746 4+ 1.54226 * w - 0.26992 * w ^ 2
Tr = T / Tc
r = (1 + fw * (1 - Tr ^ 0.5)) ^ 2
aTc = 0.45724 * Rg ^ 2 * Tc ^ 2 / Pc
aT = aTc * r
b = 0.07780 * Rg * Tc / Pc
   For k = 0 To 100       ‘Newton’s method combined with PR-EOS
      fv = P - Rg * T / (G - b) + aT / (G * (G - b) + b * (G - b))
      derfv = Rg * T / (G - b) ^ 2 - (2 * (G - b) * aT) / (G * (G + b) + b * (G - b)) ^ 2
      vk = G - fv / derfv
        If (vk - G) / G < 0.0001 Then
        Exit For
        End If
      G = vk
   Next k
   Sheet1.Cells(i, 3).Value = Format(vk, "0.00000")      ‘final result
   Sheet1.Cells(i, 4).Value = Abs((v - vk) / v)     ‘bias between predicted results and experimental data
Next i
The end
```