

Tuning Cubic Equations of State for Supercritical Water Applications

Shyh-Ming Chern

Abstract—Cubic equations of state (EoS), popular due to their simple mathematical form, ease of use, semi-theoretical nature and reasonable accuracy, are normally fitted to vapor-liquid equilibrium P - v - T data. As a result, they often show poor accuracy in the region near and above the critical point. In this study, the performance of the renowned Peng-Robinson (PR) and Patel-Teja (PT) EoS's around the critical area has been examined against the P - v - T data of water. Both of them display large deviations at critical point. For instance, PR-EoS exhibits discrepancies as high as 47% for the specific volume, 28% for the enthalpy departure and 43% for the entropy departure at critical point. It is shown that incorporating P - v - T data of the supercritical region into the retuning of a cubic EoS can improve its performance at and above the critical point dramatically. Adopting a retuned acentric factor of 0.5491 instead of its genuine value of 0.344 for water in PR-EoS and a new F of 0.8854 instead of its original value of 0.6898 for water in PT-EoS reduces the discrepancies to about one third or less.

Keywords—Equation of state, EoS, supercritical water, SCW.

I. INTRODUCTION

MANY organic substances have undergone reactions in supercritical water, e.g. alkanes [1], organic solvents [2], organic wastes [3], glucose, lignin, biomass, etc. Recently, Tang and Kitagawa [4] modeled the gasification of biomass based on the assumption of thermodynamic equilibrium and the method of free energy minimization with the help of Peng-Robinson equation of state (PR-EoS) [5]. Since an EoS capable of predicting the state of water and the associated thermodynamic properties with good enough accuracy is the key to the success of modeling supercritical water processes, it is desirable to evaluate its performance prior to being implemented in a simulation. In the present study, the performance of the well-known Peng-Robinson and Patel-Teja (PT) EoS [6] has been examined in terms of their ability to predict the behavior of water both for the saturated region from 273.16 K to critical point and for the superheated region (10-60 MPa, 673-873 K). The properties compared include the specific volume, the enthalpy departure and the entropy departure. Based on the results of the examination, the parameters of the PR-EoS and PT-EoS are adjusted to improve their performance for water around the critical point and in the supercritical region.

II. CUBIC EQUATIONS OF STATE

Countless equations of state have been developed over the years and new ones are continuously being proposed. The performance of these models in terms of the accuracy of predicting the state of matter has improved over time. Nevertheless, no perfect model has been found that is exactly accurate under all circumstances. The application of an EoS always involves a compromise between applicability and accuracy. More often than not, cubic equations of state, especially with three parameters, are chosen due to their simple mathematical form, ease of use, semi-theoretical nature and reasonable accuracy. Since the appearance of van der Waals EoS in 1873,

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (1)$$

numerous modifications have been proposed, and their performance has improved ever since. Since all these modified van der Waals EoS's can be transformed into third-order polynomial equations, they are called cubic EoS. The first significant modification was presented by Redlich and Kwong [7] by treating the adjustable parameter of the second term on the right-hand-side of (1) as a function of temperature

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v^2} \quad (2)$$

Since then, modifications have been focused on the second term of (1), including those of PR-EoS and PT-EoS, which are examined in this study. No comprehensive review on the cubic EoS's is attempted here.

The PR-EoS [5] takes the following form

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (3)$$

where

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T, \omega) \quad (4)$$

$$\sqrt{\alpha} = 1 + \kappa \left(1 - \sqrt{T/T_c}\right) \quad (5)$$

and

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (6)$$

S. M. Chern is with the Department of Chemical Engineering, I-Shou University, Kaohsiung, 84001 Taiwan (phone: 886-7-6577711ext3419; fax: 886-7-6578945; e-mail: smchern@isu.edu.tw).

which was originally proposed for nonpolar species and has been further developed for a wide variety of pure components and mixtures. The PT-EoS [6]

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

is very similar to the PR-EoS in form, although the rationale behind the development is quite different, with

$$a(T) = \Omega_a \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (8)$$

$$\sqrt{\alpha} = 1 + F \left(1 - \sqrt{T/T_c} \right) \quad (9)$$

$$b = \Omega_b R T_c / P_c \quad (10)$$

and

$$c = \Omega_c R T_c / P_c \quad (11)$$

where, for water, $\Omega_a = 0.50455$, $\Omega_b = 0.065103$, $\Omega_c = 0.1930$ and $F = 0.689803$. The PT-EoS was proposed for both nonpolar and polar components, and hence is expected to do better than the PR-EoS for water. Both PR-EoS and PT-EoS determined their parameters by fitting the equation to data along the saturation curve from low pressure to the critical point, resulting in a poor performance around and above the critical point, as can be seen later. The formulation for the evaluation of common thermodynamic properties is well documented for both PR-EoS [5] and PT-EoS [6].

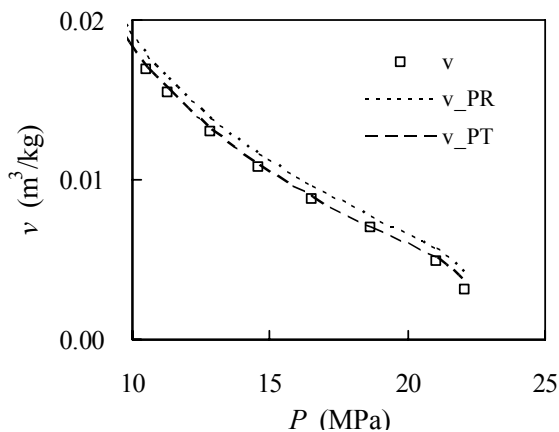


Fig. 1 Comparison of specific volumes along the water saturation curve

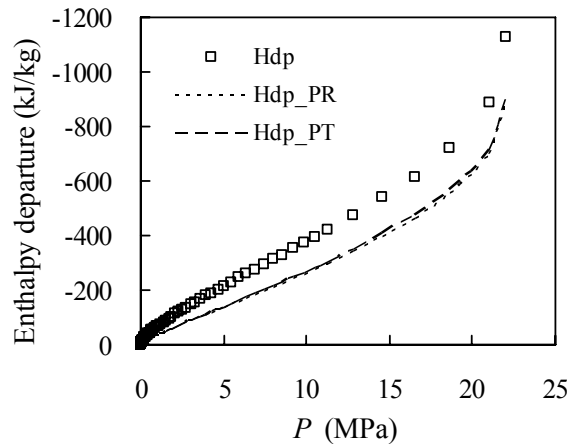


Fig. 2 Comparison of enthalpy departures along the water saturation curve

III. EVALUATION OF EQUATIONS OF STATE

Data from saturated and superheated steam stable were employed to evaluate the performance of PR-EoS and PT-EoS for water. For each data from steam table, the experimental enthalpy departure and the entropy departure of the gaseous phase can be easily determined by subtracting values calculated for ideal gas from respective experimental values. At the same T and P of the data point, compressibility factors were determined for PR-EoS and for PT-EoS and the specific volume, the enthalpy departure and the entropy departure of the gaseous phase were then calculated and compared to the experimental ones. The comparisons for the specific volume, the enthalpy departure and the entropy departure along the water saturation curve are presented on Figs. 1 through 3, respectively. The counterparts for a typical supercritical region, represented by the area enveloped in 673-873 K and 10-60 MPa, are presented on Figs. 4 through 6. The experimental data from the steam table and their derived values are denoted by solid lines.

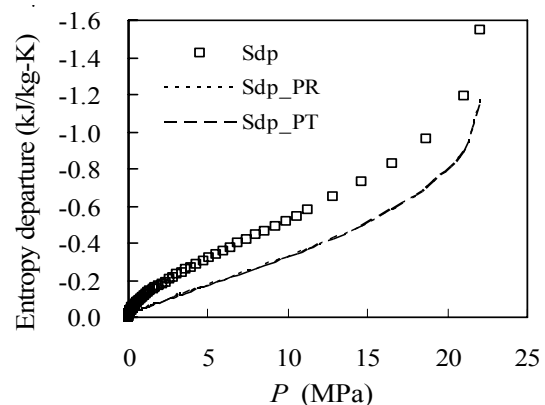


Fig. 3 Comparison of entropy departures along the water saturation curve

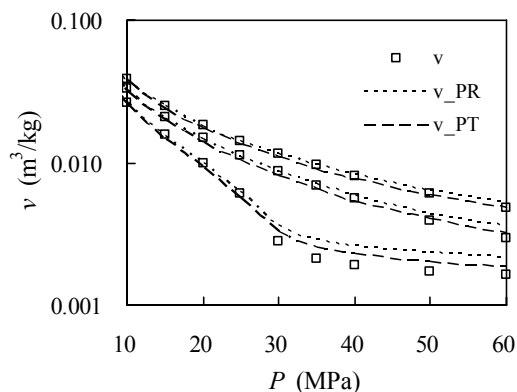


Fig. 4 Comparison of specific volumes for the superheated vapor region

As can be seen from Fig. 1, where low pressure portion of the water saturation curve is not shown for better clarity, the PT-EoS constantly predicts the specific volume better than the PR-EoS with tiny discrepancies, except for the vicinity of the critical point. This is understandable since the PR-EoS adopted a fixed Z_C , the compressibility factor at the critical point, of 0.3074 for all substances and the PT-EoS has a Z_C of 0.269 for water, whose genuine Z_C is 0.230. In other words, the performance of the two EoS's at the critical point is sacrificed for the overall performance of the EoS. The performance of PT-EoS is only slightly better in predicting the enthalpy departures and no better at all in predicting the entropy departures than PR-EoS along the saturation curve, as seen from Figs. 2 and 3. Sizable amount of discrepancies exist even in the low pressure region with an average of about -150 kJ/kg for enthalpy departure and -0.2 kJ/kg-K for entropy departure. For the supercritical region, the discrepancies for all three measures begin to shoot up as the pressure increases above 25 MPa and the temperature is relatively low, about 673 K, as seen from Figs. 4 through 6. At higher temperature, the discrepancies seem relatively small. The performance of PT-EoS seems to be better in the high pressure and low temperature region but not clearly superior when the temperature is above 773 K, and is even inferior in predicting the enthalpy departure when the temperature is near 873 K.

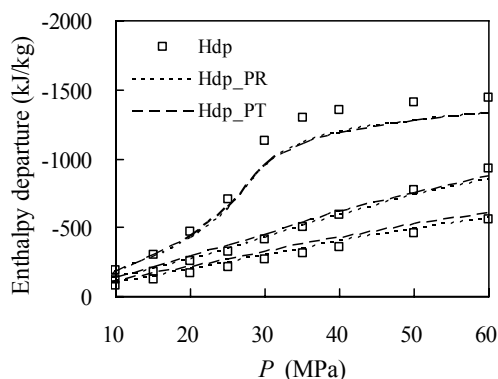


Fig. 5 Comparison of enthalpy departures for the superheated vapor region

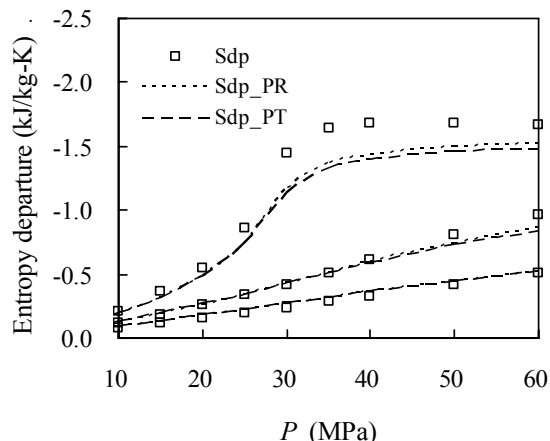


Fig. 6 Comparison of entropy departures for the superheated vapor region

Both PR-EoS and PT-EoS do reasonably well in predicting the specific volume with PT-EoS being clearly the better of the two. However, they are much more matched in predicting the enthalpy and entropy departures. The highest discrepancy observed always occurs at the critical point, about 47% for the specific volume, 28% for the enthalpy departure and 43% for the entropy departure. Given the magnitude of the discrepancy observed, one can only expect the simulation results of supercritical water processes to possess sizable discrepancies if one of the two EoS's is employed. Therefore, an EoS better tuned for supercritical water is desired for better simulation results.

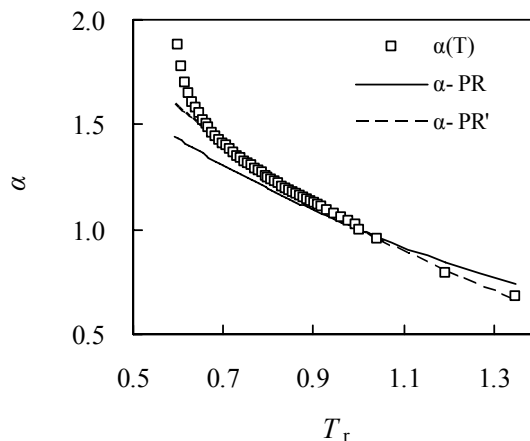
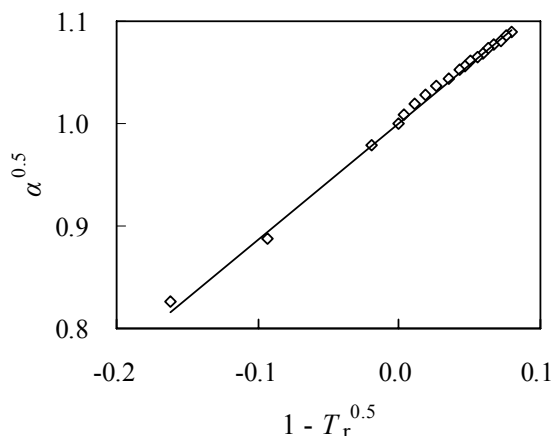


Fig. 7 Comparison of α for PR-EoS

Fig. 8 Fitting of α for PR-EoS

IV. TUNING PR-EoS AND PT-EoS

For PR-EoS [5], the fugacity of a pure component can be evaluated from

$$\ln \frac{f}{P} = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln \left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \quad (12)$$

where f denotes fugacity, Z , compressibility factor,

$$A = aP / R^2 T^2 \quad (13)$$

and

$$B = bP / RT \quad (14)$$

and for PT-EoS [6], from

$$\ln \frac{f}{P} = Z - 1 - \ln(Z - B) - \frac{a}{2RTN} \ln \left(\frac{Z + M}{Z + Q} \right) \quad (15)$$

where

$$N = \left[bc + \frac{(b+c)^2}{2} \right]^{1/2} \quad (16)$$

$$M = \left(\frac{b+c}{2} - N \right) P / RT \quad (17)$$

and

$$Q = \left(\frac{b+c}{2} + N \right) P / RT \quad (18)$$

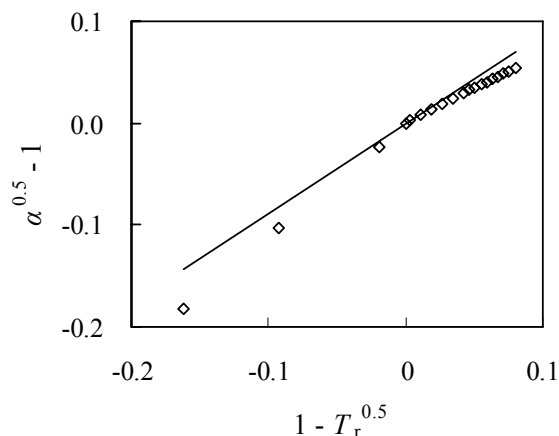
For each experimental data along the saturation line, applying the phase equilibrium condition for PR-EoS

$$f^V = f^L \quad (19)$$

gives, from (12)

$$\begin{aligned} Z^V - \ln(Z^V - B) - \frac{A}{2\sqrt{2}B} \ln \left(\frac{Z^V + (1 + \sqrt{2})B}{Z^V + (1 - \sqrt{2})B} \right) \\ = Z^L - \ln(Z^L - B) - \frac{A}{2\sqrt{2}B} \ln \left(\frac{Z^L + (1 + \sqrt{2})B}{Z^L + (1 - \sqrt{2})B} \right) \end{aligned} \quad (20)$$

Hence a single value of A can be determined for the data point, and a value of α can be obtained through (4) and (13). Similarly, a value of α can be calculated for PT-EoS using (8), (15) and (19) for each saturated data point.

Fig. 9 Fitting of α for PT-EoS

For supercritical region or where a single vapor phase exists, fugacity for experimental data can be evaluated by

$$RT \ln \frac{f}{f^0} = (h - h^0) - T(s - s^0) \quad (21)$$

where h and s denote specific enthalpy and entropy, respectively, of the vapor at T and P , and the superscripts symbolize the thermodynamic property of a vapor at the same T and a low pressure, low enough for the vapor to be regarded as ideal gas. Then a value of α for PR-EoS can be obtained from (4), (12) and (13) for each experimental data point. By the same way, a value of α for PT-EoS can be determined for each experimental data with (8), (13), (15) and (21).

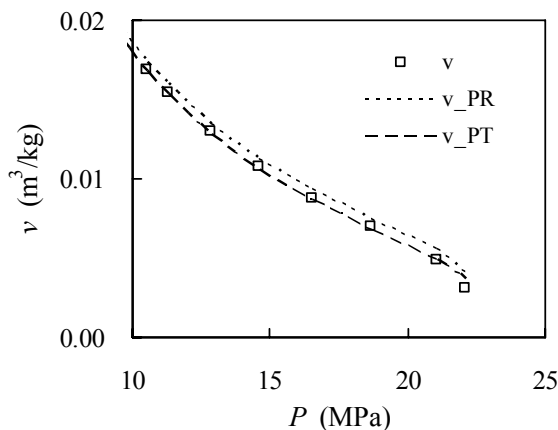


Fig. 10 Specific volumes along the water saturation curve: retuned PR-EoS and PT-EoS

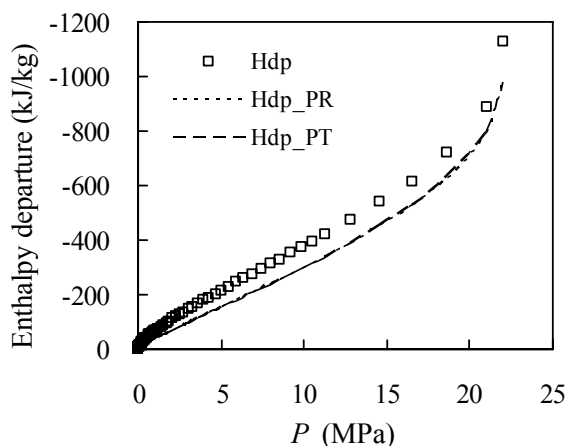


Fig. 11 Enthalpy departures along the water saturation curve: retuned PR-EoS and PT-EoS

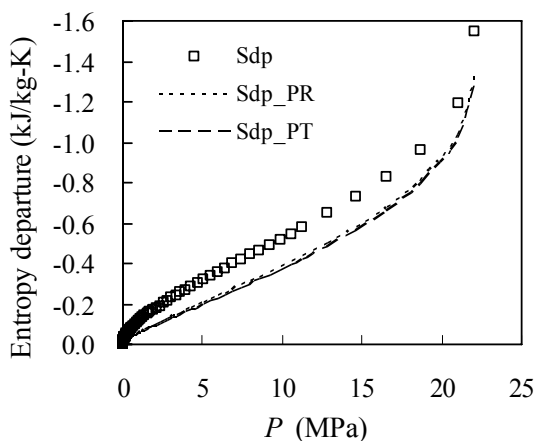


Fig. 12 Entropy departures along the water saturation curve: retuned PR-EoS and PT-EoS

The value of α from experimental data for PR-EoS is plotted as symbols against T_r , the reduced temperature, in Fig. 7. For $T_r < 1$, saturated vapor data were used, and for $T_r > 1$, superheated

vapor at 673, 773 and 873 K under 30 MPa were employed. Also shown in Fig. 7 are values of α calculated from (5) and (6), using the real value of acentric factor, $\omega = 0.344$, as a solid line, and using a refitted $\omega = 0.5491$, as a dashed line. As can be seen, the dashed line fits the experimental data much better, especially for $T_r = 0.7$ to 1.3. Consequently, a better performance is expected from PR-EoS with $\omega = 0.5491$. The procedure of obtaining the new fitting is delineated as follows.

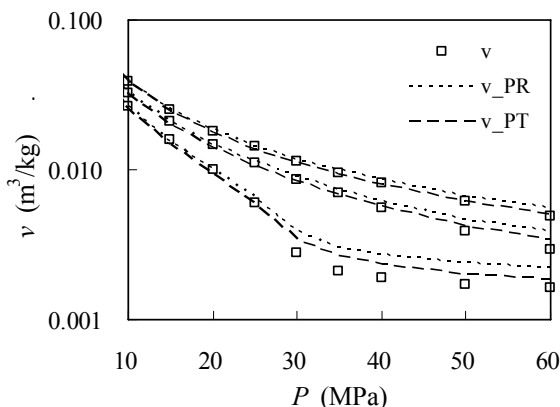


Fig. 13 Specific volumes for the superheated vapor region: retuned PR-EoS and PT-EoS

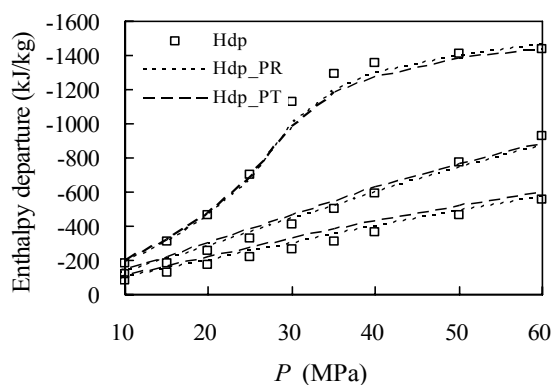


Fig. 14 Enthalpy departures for the superheated vapor region: retuned PR-EoS and PT-EoS

The values of $\alpha^{0.5}$ are plotted against $1 - T_r^{0.5}$, as shown in Fig. 8, for T_r between 0.85 and 1.35, a typical subcritical and supercritical region. The data exhibit a trend of straight line and are fitted via means of least square by the following

$$\sqrt{\alpha} = 1 + 1.1401(1 - \sqrt{T_r}) \quad (22)$$

Comparing (22) with (5) gives $\kappa = 1.1401$, which is then plugged into (6) to obtain a fitting value of $\omega = 0.5491$.

Similarly, the values of α for PT-EoS from experimental data are displayed in Fig. 9 against the reduced temperature. Although there is a change in slope at the critical point, a linear regression is still attempted, which is later proven to be effective. The regression

$$\sqrt{\alpha} = 1 + 0.8854(1 - \sqrt{T_r}) \quad (23)$$

is forced to go through the point ($\alpha = 1$ at $T_r = 1$) to make it compatible with the original PT-EoS formulation. As a result, the value of F for water is changed from the original value of 0.6898 to a new value of 0.8854.

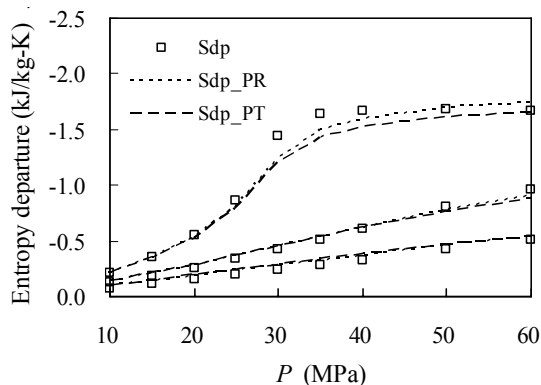


Fig. 15 Entropy departures for the superheated vapor region: retuned PR-EoS and PT-EoS

The specific volumes, enthalpy departures and entropy departures are recalculated using PR-EoS with the new fitting value of $\omega = 0.5491$ and using PT-EoS with the new F value of 0.8854, and presented in Figs. 10 through 12 for the saturation curve, and in Figs. 13 through 15 for the typical supercritical region. For the saturated region, though the discrepancies for the specific volumes are not greatly reduced, the prediction of the enthalpy departures and the entropy departures has improved significantly, especially near the critical area. Similarly, for the supercritical region, the prediction of enthalpy departures and entropy departures is better improved than that of specific volumes. The improvement is better achieved near the critical area, e.g., at 673K where the discrepancies are the greatest, than further away from the critical area, like at 773 and 873K where the original deviations are small. As a whole, the performance of the retuned PR-EoS and PT-EoS generally exceeds that of untuned PR-EoS and PT-EoS, respectively, around and above the critical point, except for the specific volume.

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