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Accurate Modeling of Phase Equilibrium and Pressure-Volume-Temperature (*PVT*) properties of Water with Equation of State

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It is already known that a density difference of about $0.1 \text{ kg}\cdot\text{m}^{-3}$ are sufficient to develop negatively buoyant plumes on kilometer scale in weakly stratified environments (Haugan and Drange, 1992). The accurate prediction of the density changes of aqueous solutions after CO_2 is injected in the deep interior of the Earth is crucial for the modeling of CO_2 capture and storage (or sequestration). For this purpose, we must be capable of accurate prediction of both phase equilibrium and pressure-volume-temperature (*PVT*) properties of water, which has proven to be very difficult, especially in the critical region. In order to solve this problem, the International Association for the Properties of Water and Steam (IAPWS) collected and evaluated the thermophysical data of water published before 1990, where the selected high-quality data have been incorporated into a very accurate equation of state (EOS) developed by Wagner and Pruss (2002) and adopted by IAPWS in the IAPWS-95 formulation. The formulation can reproduce all thermodynamic properties of water from 273.16 to 1275 K and from 0 to 1 GPa, with experimental accuracy (or an accuracy close to it). However, it is difficult to extend this formulation to mixtures. In view of this point, we proposed a virial-type multiparameter EOS for water on the basis of some existing EOS (Kedge and Trebble, 1999, 2002, 2004). The EOS has the following form:

$$\begin{aligned} \frac{P}{RT} &= \frac{1}{V} + \frac{a_2}{V^2} + \frac{a_3}{V^3} + \frac{a_4}{V^4} + \frac{a_5}{V^5} + \frac{a_6}{V^6} + c \\ c &= \frac{a_7}{1 + f_7(V - V_C)^2} + \frac{a_8}{1 + f_8(V - V_C)^2} + a_9 \exp(-\alpha_1 V) + a_{10} \exp(-\alpha_2 V) \\ a_2 &= a_{20} + a_{21}\theta + a_{22}\theta^2 + a_{23}\theta^3 + a_{24}\theta^4 + a_{25}\theta^5 + a_{26}\theta^6 \\ a_3 &= a_{30} + a_{31}\theta + a_{32}\theta^2 + a_{33}\theta^3 + a_{34}\theta^4 \\ a_4 &= a_{40} + a_{41}\theta + a_{42}\theta^2 + a_{43}\theta^3 + a_{44}\theta^4 \\ a_5 &= a_{50} + a_{51}\theta + a_{52}\theta^2 + a_{53}\theta^3 + a_{54}\theta^4 \\ a_6 &= a_{60} + a_{61}\theta + a_{62}\theta^2 + a_{63}\theta^3 + a_{64}\theta^4 + a_{65}\theta^5 \\ a_7 &= a_{70} + a_{71}\theta + a_{72}\theta^2 \\ a_8 &= a_{80} + a_{81}\theta + a_{82}\theta^2 \\ a_9 &= a_{90} + a_{91}\theta + a_{92}\theta^2 + a_{93}\theta^3 \\ a_{10} &= a_{100} + a_{101}\theta + a_{102}\theta^2 + a_{103}\theta^3 \\ \theta &= T_r^{-1} - 1 \end{aligned}$$

where $T_r = T/T_C$, T is temperature (K), T_C is the critical temperature of water, R is the universal gas constant, P is pressure (bar), V is molar volume ($\text{cm}^3\cdot\text{mol}^{-1}$), a_{ij} , α_1 and α_2 are all empirical constants. In the expression of c , the first two terms can improve the performance of the EOS in the critical region, and the two exponential terms can improve the performance of the EOS in the gas region near T_C . The constants in the EOS are regressed with non-linear least-square fitting technique under the constraints of critical *PVT* parameters and saturation properties (vapor pressure and the volumes of saturated liquid and gas) along the whole vapor-liquid equilibrium curve.

A systematic comparison was made between the EOS and the IAPWS-95 formulation (Figs 1–3). The maximum

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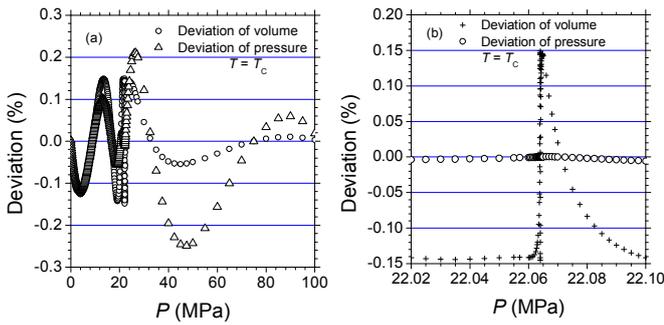


Fig. 1 Deviations of predicted pressures and molar volumes at critical temperature
(a) $P = 0\text{--}100$ MPa; (b) The part near the critical region

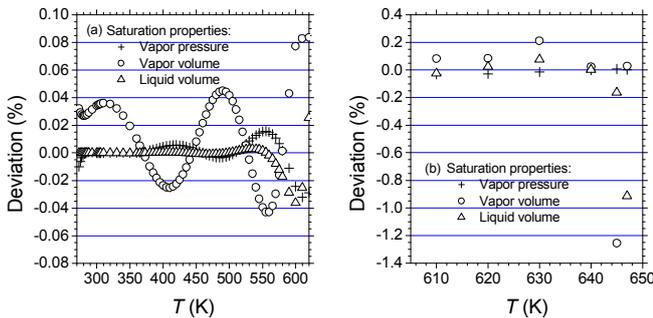


Fig. 2 Deviations of predicted saturation properties along the vapor-liquid equilibrium curve
(a) The region far from critical point; (b) The region near critical point

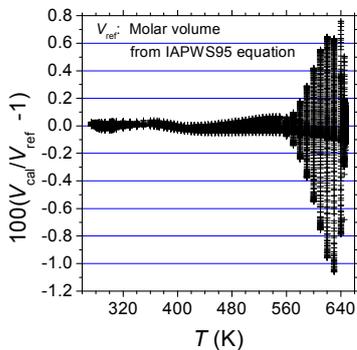


Fig. 3 Deviations of predicted molar volumes in the single-phase (gas or liquid) region

deviations of the predicted vapor pressures, saturated gas and saturated liquid volumes are 0.032%, 1.26% and 0.91%, respectively, and the average deviations are 0.005%, 0.047% and 0.019%, respectively. In the single-phase region, the maximum deviations of the predicted gas and liquid volumes are 0.76% and 1.06%, respectively (Fig. 3), and the average deviations are 0.065% and

0.052%, respectively. The overall average deviation of liquid and gas volumes is 0.058%. In the temperature interval that is most important for CO₂ capture and storage ($T < 433$ K), the maximum deviations of the predicted saturation properties and single-phase volumes of water are all less than 0.05%. When temperature increases to 520 K, the maximum deviations of volumes and phase equilibrium properties are all within 0.06%.

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Key words: water, vapor-liquid equilibrium, *PVT* properties, vapor pressure, saturated liquid, saturated gas, equation of state, critical region

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