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Viscosity of NaCl Aqueous Solution under Supercritical Conditions: A Molecular Dynamics Simulation

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ABSTRACT: Reverse nonequilibrium molecular dynamics (RNEMD) simulation has been carried out to study the concentration dependence of the viscosity of sodium chloride aqueous solution under supercritical conditions. This simulation predicts the viscosities of pure water at two supercritical conditions with deviations from experimental values within 3 %. The calculated viscosity of sodium chloride solution increases with increasing concentration. The simulated viscosities are also compared with an empirical correlation derived based on experimental values at subcritical conditions. However, with the same increment of concentration, the viscosity of sodium chloride aqueous solution increases much slower than that at subcritical conditions. For example, at a concentration of 2.886 $\text{mol}\cdot\text{kg}^{-1}$ and at conditions of 700 K, 600 $\text{kg}\cdot\text{m}^{-3}$ and 700 K, 700 $\text{kg}\cdot\text{m}^{-3}$, the viscosities of supercritical sodium chloride aqueous solution increase 8 % and 11 %, respectively, when compared with pure water, while the predicted increment of viscosities by the empirical correlation is about 50 % .

INTRODUCTION

Supercritical water (SCW) has received increasing attentions because of it importance in industrial applications. Supercritical water oxidation (SCWO) is widely accepted as an environmental-friendly technology for the treatment of industrial waste and sludge.[1] Supercritical power generation is one of the major options in high efficiency, low emissions power generation technology. Salts are formed during SCWO when acidic solution is neutralized to reduce corrosion. In supercritical power generation, a small quantity of salts remain in the feedwater, albeit strict water treatment has been done. Viscosity of salt solution is of considerable interest in light of its importance in these industrial applications. It was observed long ago that the viscosity of salt aqueous solution may differ from that of pure water. Under supercritical conditions, the situation might be more serious. In some cases, the properties of supercritical water are sensitive to the surrounding conditions. The presence of salts may shift the properties of supercritical water, which should be taken into account when designing the system or interpreting the experimental data.

Sodium chloride (NaCl) is one of the typical salts in SCWO and supercritical power generation technologies. The experimental measurement of the viscosity of NaCl solution is one of the most widely accomplished in all the salt aqueous solutions.[2] The first measurement was carried out in 1929.[3] Ozbek et al.[4] reviewed the experimental methods in measuring the viscosity of NaCl aqueous solution and the obtained values and established a databank of the published data in 1977. The highest temperature was 423.15 K, though the largest pressure reached 30 MPa. Mao and Duan[2] gave an exhaustive review on the experimental values in 2009. They collected more than 2200 data points, and the highest temperature reached was 629.49 K, still lower than the critical temperature.

Empirical equations for the prediction of the viscosity of electrolyte aqueous solution have been developed based on the experimental results. One of the most commonly used relations was given by Jones and Dole[5] in the form of

$$\eta/\eta_w = 1 + Am^{1/2} + Bm \tag{1}$$

where η_w is the viscosity of pure water and m is the molality ($\text{mol}\cdot\text{kg}^{-1}$) concentration. Kaminsky[6] modified the Jones-Dole equation by adding a quadratic term Dm^2. However, the Jones-Dole equation and its extensions cannot reproduce experimental data for concentrated systems.[7] In 2009, Mao and Duan[2] derived a simple empirical correlation by fitting a great deal of experimental values in a wide range [(273 to 573) K, (0.1 to 35) MPa, and 0 $\text{mol}\cdot\text{kg}^{-1}$ to 6 $\text{mol}\cdot\text{kg}^{-1}$] for the NaCl$-H_2$O system. The correlation is given as

$$\ln(\eta/\eta_w) = Am + Bm^2 + Cm^3 \tag{2}$$

A, B, and C are polynomial functions of temperature as

$$A = a_0 + a_1T + a_2T^2 \tag{3}$$

$$B = b_0 + b_1T + b_2T^2 \tag{4}$$

$$C = c_0 + c_1T \tag{5}$$

The constants in eqs 3 to 5 are given in Table 1.[2] The average deviation from the experimental data is within 1 % in this wide range. However, it has not been tested if this correlation could be extrapolated to supercritical conditions or not.

In the supercritical region, the viscosity data of the salt solution are scare. The effect of the tiny NaCl ions on the viscosity of supercritical water has not been reported experimentally or numerically yet. A better understanding of the transport properties of supercritical salt aqueous solution would help the system

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Table 1. Parameters for Equations 3 to 5

parameters	value[2]
a_0	0.21319213
a_1	$0.13651589 \cdot 10^{-2}$
a_2	$-0.12191756 \cdot 10^{-5}$
b_0	$0.69161945 \cdot 10^{-1}$
b_1	$-0.27292263 \cdot 10^{-3}$
b_2	$0.20852448 \cdot 10^{-6}$
c_0	$-0.25988855 \cdot 10^{-2}$
c_1	$0.77989227 \cdot 10^{-5}$

design in SCWO and supercritical power generation. In this situation, molecular dynamics simulation seems to be an effective option. A number of methods to calculate the viscosity of fluid systems in classic molecular dynamics simulation have been developed and verified.[8,9] In this paper, the reverse nonequilibrium molecular dynamics simulation method (RNEMD)[9,10] is employed to calculate the viscosity of sodium chloride aqueous solution under supercritical conditions.

SIMULATION METHOD

Reverse Nonequilibrium Molecular Dynamics. Several methods are available for calculating shear viscosity of liquid in molecular dynamics simulations. The equilibrium molecular dynamics (EMD) calculates the viscosity based on the internal pressure or momentum fluctuations. The nonequilibrium molecular dynamics (NEMD) method applies an external perturbation on the system to drive it out of equilibrium and measure the resulting flux. A comprehensive review of the equilibrium method and nonequilibrium method has been made by Hess.[8] In this paper, the reverse nonequilibrium molecular dynamics method[9] is employed. In the RNEMD, the momentum flux is imposed, and the corresponding velocity gradient is measured. The proportionality coefficient is the shear viscosity η. If the x direction component of the momentum is transported through the z direction, we have the relationship

$$j_z(p_x) = -\eta \frac{\partial v_x}{\partial z} \tag{6}$$

The simulation box is divided into N bins in the z direction. A momentum flux is imposed in this direction by exchanging the momentum between atoms with the most negative x velocity in the lowest bin ($n = 1$) and atoms in the bin of $n = N/2 + 1$ that has the most positive x velocity at a certain exchanging rate. Periodic boundary condition is applied to all three directions. The method is applicable to systems with monatomic or molecular liquid. For molecular systems with fixed bonds and angles, the method is modified slightly by exchanging the center-of-mass velocity.[11] The total momentum exchange p_{total} can be recorded exactly, and the imposed momentum flux is calculated by

$$j_z(p_x) = -\frac{p_{\text{total}}}{2tS} \tag{7}$$

where S is the cross area of the simulation box in the $x-y$ plane. A linear velocity profile is induced if proper exchange rate and box size are chosen. The slope of the velocity profile gives the velocity gradient, and thus the shear viscosity can be calculated. More details about this method refer to the references.[12,13]

Table 2. Potential Parameters (LJ Well Depth ε, LJ Size Parameter σ, and Partial Charge q) for Different Atoms

atom	$\varepsilon/\text{kJ}\cdot\text{mol}^{-1}$	σ/nm	q/e
O	0.6501	0.3166	−0.8476
H	0.0000	0.0000	+0.4238
Na	0.5442	0.2350	+1.0000
Cl	0.4186	0.4400	−1.0000

Potential Model. The SPCE water model is one of the most used models in characterizing supercritical water, which has critical values very close to experimental data. Fuller and Rowley[14] suggested that the internal flexibility would improve the accuracy of the simulated viscosity for water. Thus, the flexible SPCE water model is adopted in the present simulation. In the simulation, the velocity exchange is between atoms rather than the center-of-mass velocities of water molecules because of the employment of the flexible model. The intramolecular parts are modeled as harmonic bond and angle vibration terms as

$$\varphi(r_{ij}) = \sum_{\text{bonds}} \frac{1}{2}k_{\text{b}}(r - r_0)^2 + \sum_{\text{angles}} \frac{1}{2}k_{\theta}(\theta - \theta_0)^2 \tag{8}$$

The spring constants of the bond and the angle are the same as in the work of Fuller and Rowley.[14] r_0 and θ_0 are 0.1 nm and 109.47°, and k_{b} and k_θ are $4.637 \cdot 10^5$ $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{nm}^{-2}$ and 383 $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{rad}^{-2}$, respectively. The ions are modeled as charged Lennard-Jones particles.[15] All the intermolecular interactions are expressed as sums of electrostatic and Lennard-Jones (12-6) potentials

$$\varphi(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} \tag{9}$$

The potential parameters for unlike pairs are expressed by the Lorentz−Berthelot mixing rule. The potential parameters used are given in Table 2.

COMPUTATIONAL DETAILS

The classic molecular dynamics simulation package LAMMPS[16] is used in this study. For the flexible model, a relatively small time step is needed because of the existence of high-frequency intramolecular vibration. A multiple time step algorithm (*r-RESPA*)[17] is used with the inner/outer timesteps being 0.2 fs/1 fs in the simulation to improve calculative efficiency. All the simulations are carried out in canonical ensembles with the same density. The system size is calculated by the desired density. The initial configuration of water molecules in the cubic simulation box is optimized by using the open source package "Packmol".[18] Periodic boundary conditions are applied to all the directions. A cutoff radius of 1 nm is used for all the interactions. The electrostatic interaction is handled by the particle−particle particle−mesh method. The temperature is controlled by the Berendsen thermostat for its simplicity and robustness.[12] The coupling time is 1 ps.

The box length in the z direction should be properly set to get a reasonable linear velocity profile. The existence of shear rate will cause an inhomogeneous temperature distribution, and the density is inversely coupled to the temperature. Thus, the length should not be too large for keeping a uniform temperature and density distribution or too small to reduce the boundary effect.

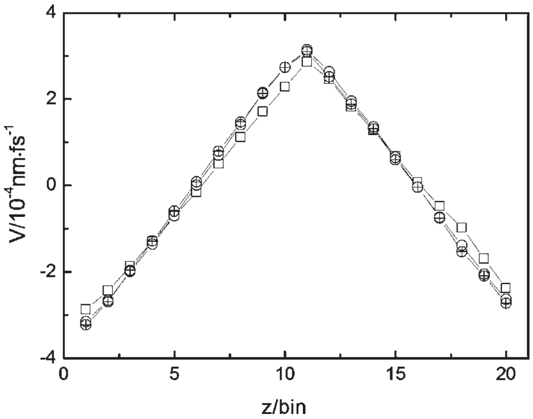

Figure 1. Typical velocity profile (□, averaged from (100 to 200) ps; ○, averaged from (200 to 300) ps; ⊕, averaged from (300 to 400) ps).

An aspect ratio of 2 ($L_z/L_x = L_z/L_y = 2.0$) is suitable in this simulation. In addition, care should be taken to select the exchange rate. The momentum exchange rate determines the scale of heat flux. Too large a heat flux will draw the system away from the linear response region, and if too small, the noise will be comparable to the signal. The box is divided into 20 bins to determine the velocity profile. The velocity gradient is calculated by linear fitting using the least-squares method. In this study, an exchange periodicity of 100 time steps is applicable. The temperature and density deviate from their average values by less than 5 %.

The first 100 ps simulation without momentum exchange allows the system to equilibrate, and another 200 ps of simulation with momentum exchange is used to let the system reach a steady state. The velocity distribution and momentum flux data are collected in the following 800 ps. The velocities are calculated every 5 time steps, averaged over 8000 times, and outputted every 50 000 time steps. Sixteen time blocks are obtained for each run. Averaging the velocity gradient over the blocks, we can determine the mean value and uncertainty. The uncertainty of the calculated viscosity is evaluated by[12]

$$\Delta\eta = \eta\left(\frac{\Delta j}{j} + \frac{\Delta G}{G}\right) \qquad (10)$$

where j is the momentum flux and G is the slope of the velocity profile.

■ RESULTS AND DISCUSSION

A typical velocity profile in the RNEMD method is shown in Figure 1. In determining the velocity gradients, good linearities are obtained with correlation factors larger than 0.998 for all the linear fittings. We compared the results with sampling times of 800 and 1200 ps, respectively. The results with the two sampling time lengths are consistent considering the statistical error. All the systems consist of 4000 water molecules with ion pairs from zero (pure water) to 250. The maximum concentration of the solution is 2.886 mol·kg^{-1}. Two other systems with 1600 and 8000 water molecules are also calculated to test the size effects. The calculated viscosities of the former system are systematically 10 % larger than those of the 4000 molecules systems. The results in the latter system are consistent within the simulated uncertainty with those of the 4000 molecules' system. Accordingly, the size effects in our simulation are thought to be negligible.

Table 3. Simulated Viscosities of Pure Water at Supercritical Conditions

	η/μPa·s		
state point	MD	ref 23	deviation/%
700 K, 600 kg·m^{-3}	70.2(0.9)	72.2	2.77
700 K, 700 kg·m^{-3}	84.2(1.4)	86.8	3.00

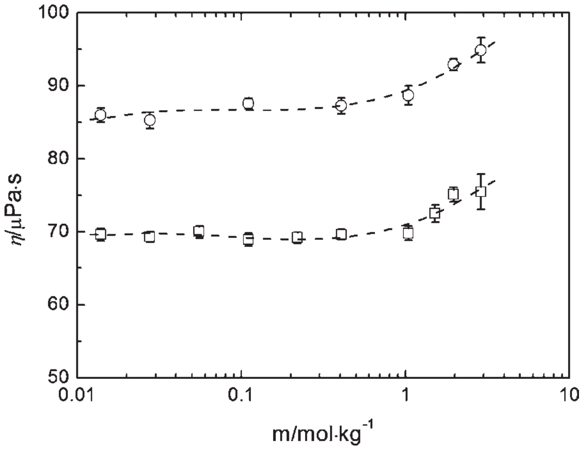

Figure 2. Concentration dependence of viscosity (□, 700 K, 600 kg·m^{-3}; ○, 700 K, 700 kg·m^{-3}).

The solubility of NaCl near the critical region is very low and increases with increasing pressure and decreasing temperature. To investigate the concentration dependence of the viscosity of NaCl aqueous solution, two state points (700 K, 600 kg·m^{-3} and 700 K, 700 kg·m^{-3}) with relatively higher solubility are chosen to guarantee that the simulated solution is within the solubility limit.

Viscosity of Pure Water. Molecular dynamics simulation has long been used to calculate the viscosity of liquids. For simple LJ liquids, which have only short-range interactions, the EMD, the NEMD, and the RNEMD methods all give reasonable results.[8,9] However, when the fluid has complex molecular structure, though theoretically all methods should give the same answer for the same force field, the differences in efficiency and accuracy disperse the results.[8] The viscosity of water at ambient condition has been calculated by many researchers with EMD and/or NEMD simulations.[19−22] The calculated viscosities disperse and deviate remarkably from the experimental values.[10] On the contrary, the RNEMD method predicts viscosity of water at ambient condition with considerable accuracy. Bordat and Müller[10] calculated a viscosity of (0.86 ± 0.06) mPa·s at 300 K using the RNEMD method with a flexible SPCE model, while the experimental value is 0.851 mPa·s. Müller et al.[12] also calculated the viscosity of water and found their results agree well with that of Bordat and Müller.[10] In this study, the viscosities of pure water at two supercritical conditions are computed and compared with the IAPWS recommended values,[23] and the results are shown in Table 3. The calculated viscosities are 2.77 % and 2.99 % smaller than the reference values, respectively. The agreement is quite reasonable, which verifies the validity of the RNEMD method in calculating the viscosities of water at supercritical conditions.

Table 4. Viscosities at Different Concentrations

	$\eta/\mu\text{Pa}\cdot\text{s}$	
concentration/$\text{mol}\cdot\text{kg}^{-1}$	600 $\text{kg}\cdot\text{m}^{-3}$	700 $\text{kg}\cdot\text{m}^{-3}$
0.000	70.2(0.9)	84.2(1.4)
0.014	69.6(0.9)	86.0(1.0)
0.028	69.3(0.7)	85.3(1.1)
0.055	70.0(0.8)	—
0.1100	68.9(0.9)	87.6(0.7)
0.219	69.2(0.7)	—
0.407	69.6(0.7)	87.3(1.1)
1.043	69.8(1.0)	88.7(1.3)
1.519	72.5(1.1)	—
1.967	75.1(1.0)	92.9(0.8)
2.886	75.5(2.4)	94.9(1.7)

Viscosity of NaCl Aqueous Solution. The simulated concentration dependence of the viscosity is shown in Figure 2 and tabulated in Table 4. The ratios of the viscosities between NaCl aqueous solution and pure water are shown in Figure 3. The values predicted by eqs 2 to 5 at (700 and 330) K are also shown. The coefficients in eq 2 are calculated by the corresponding temperatures and the constants in eqs 3 to 5 given by Mao and Duan.[2] The solid line represents the ratios between viscosities of salt solution and pure water at 330 K. The dashed line presents the ratios between viscosities of salt solution and pure water at 700 K when assuming eq 2 is applicable in the supercritical region. The viscosity increases with concentration at 330 K, and the viscosity increases faster at 700 K predicted by eq 2. The calculated ratios between the viscosities of NaCl solution and pure water by MD reasonably agree with that predicted by eq 2 at low concentrations (lower than 0.5 $\text{mol}\cdot\text{kg}^{-1}$). However, the deviation grows with further increasing concentration. As shown in Figure 2 and Figure 3, though the simulated viscosity in molecular simulations increases with increasing ions concentration at 700 K, the concentration dependence is much weaker than that predicted by eq 2 at 700 K and even weaker than that at 330 K.

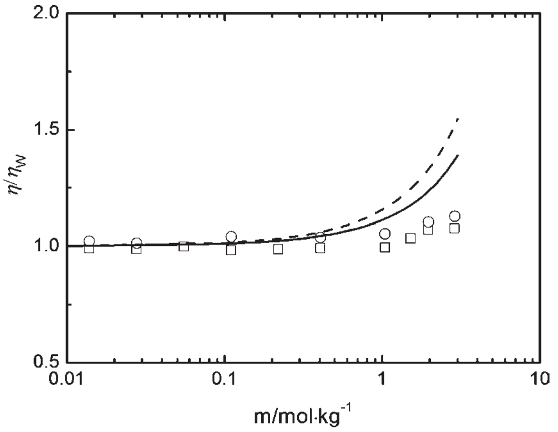

Figure 3. Ratio between the viscosities of NaCl solution and pure water (□, 700 K, 600 $\text{kg}\cdot\text{m}^{-3}$; ○, 700 K, 700 $\text{kg}\cdot\text{m}^{-3}$; —, derived by eq 2 at 330 K; ---, derived by eq 2 at 700 K).

Bernal and Fowler[24] analyzed the effects of added ions on the viscosity. It can be attributed to three mechanisms: Brown motion, Debye—Hückel interaction, and structure effect. The first two mechanisms are always positive and will increase the viscosity. The structure effect means that the addition of ions changes the structure of water, which would be positive or negative depending on the salt type. The viscosity would be larger with more ordered structure. According to Bernal and Fowler's analysis, the structure effect is often the principal term even in relatively low concentrations. A state-of-the-art review about the effect of ions on the structure of water was given by Marcus recently.[25] The structure of water is affected by the presence of solutes, and the ions in water can be classified to be *kosmotrope* or *chaotrope* type which means "structure-making" and "structure-breaking", respectively. If the salt ions weaken the water structure (*chaotrope*), the viscosity will decrease with increasing concentration, while the viscosity will increase with increasing concentration when the ions strengthen the structure (*kosmotrope*). The experimental measurements revealed that at temperatures below the critical point the viscosity of NaCl solution increased with increasing concentration. The present simulation demonstrates the same trend at supercritical conditions. Since the viscosity always increases with increasing ion concentration, and the experimental and computational data cover a quite wide range of conditions, it is most likely that NaCl is *kosmotrope* at both subcritical and supercritical conditions because the *chaotrope* salt ions will finally overcome the contribution of Brown motion and Debye—Hückel interaction and make the viscosity show opposite trend if the NaCl is *chaotrope*. In the case of CsCl aqueous solution, the *chaotrope* salt ions overwhelm the contribution of Brown motion and Debye—Hückel interaction, and the viscosity decreases with increasing concentration even at very low concentration.[24] Bondarenko et al.[26] carried out comprehensive experimental and molecular dynamics studies concerning the effect of NaCl on the structure of water at temperatures ranging from (20 to 500) °C and a constant pressure of 100 MPa. They measured the pair correlation functions of both NaCl solution and pure water. The results showed that the short-range ordering of the hydrogen-bonded structure of the bulk water was improved by the addition of ions. It further confirms the structure-making effect of the NaCl ions.

At the two state points of 700 K, 600 $\text{kg}\cdot\text{m}^{-3}$ and 700 K, 700 $\text{kg}\cdot\text{m}^{-3}$, the viscosities of the NaCl solution at a concentration of 2.886 $\text{mol}\cdot\text{kg}^{-1}$ increase 8 % and 11 %, respectively, when compared with those of the pure water at the same states. The viscosity increments predicted by the Mao and Duan empirical correlation at (700 and 330) K with the same concentration of 2.886 $\text{mol}\cdot\text{kg}^{-1}$ are about 50 % and 35 % higher when compared to those of the pure water. The empirical correlation derived from the experimental values at subcritical conditions seems to be invalid in the supercritical region at concentrations larger than 0.5 $\text{mol}\cdot\text{kg}^{-1}$. Also, the viscosity of supercritical NaCl solution is noticeably less sensitive to concentration than under subcritical conditions. It has been proven in both experiments and molecular dynamics simulations that in supercritical water the hydrogen bond structure is greatly reduced compared to normal conditions.[27] Water at supercritical conditions behaves almost as a nonpolar solvent rather than a polar one, which has a considerably high solubility with gas and organics but extremely low solubility with inorganic salt.[1] This might reduce the ability for the polar ions to strengthen the water structure. The structure-making effect of the added ions on the viscosity, which means the NaCl ions increase the viscosity by strengthening the short-range ordering of water, becomes weaker.

Electrolytes dissolved in water dissociate into cations and anions that could be hydrated. In relatively dilute solution, the

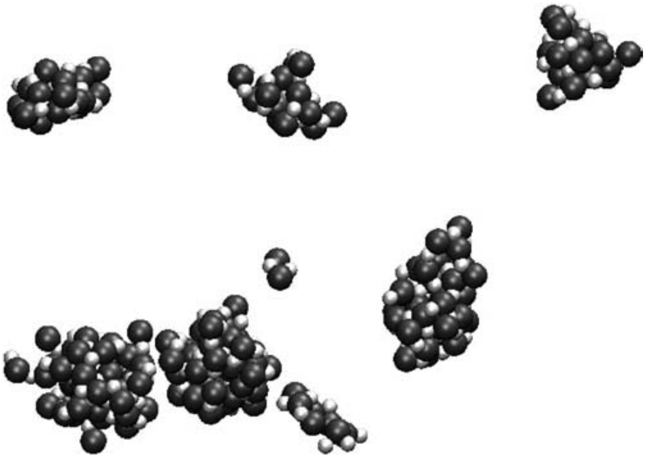

Figure 4. Cluster structure of sodium chloride (black for Cl ions; white for Na ions).

electric field forces a part of the polar water molecules to be adsorbed in the hydration shells around the ions which are separated by solvent. With increasing concentration, the ion pairing begins to occur, and cluster structures are formed. The forming process and kinetics have been studied by molecular dynamics simulations in the literature at both ambient and supercritical conditions.[28,29] The viscosities for concentrations larger than 2.886 $\text{mol}\cdot\text{kg}^{-1}$ are not carried out in this study because the NaCl ions tend to deposit from water and form clusters. The system is no longer uniform, and the viscosity calculation method is not applicable anymore. Figure 4 shows a snapshot of the clustered ions in an ion concentration of 4.193 $\text{mol}\cdot\text{kg}^{-1}$.

CONCLUSION

The reverse nonequilibrium molecular dynamics has been used to calculate the viscosity of sodium chloride aqueous solution with different concentrations under supercritical conditions. The flexible SPCE water model and charged LJ model for ions are employed. The predicted viscosities of pure water at two studied supercritical state points reasonably agree with the IAPWS recommended values. The calculated viscosity increases with increasing NaCl concentration. The dependence is identical to that under subcritical conditions.

The results are also compared with an empirical correlation derived from the experimental data at subcritical conditions. At two state points of 700 K, 600 $\text{kg}\cdot\text{m}^{-3}$ and 700 K, 700 $\text{kg}\cdot\text{m}^{-3}$, the viscosities of sodium chloride aqueous solution with an ion concentration of 2.886 $\text{mol}\cdot\text{kg}^{-1}$ increase 8 % and 11 %, respectively, when compared with those of the pure water at the same states, while the viscosity increments predicted by the empirical correlation at (700 and 330) K are about 50 % and 35 % higher than the viscosity of the pure water. Comparisons show that this empirical correlation is not valid in the supercritical region with concentrations larger than 0.5 $\text{mol}\cdot\text{kg}^{-1}$. Also, the viscosity of supercritical NaCl solution is noticeably less sensitive to concentration than under subcritical conditions. The possible reason is that the structure-making effect of the added ions on the viscosity becomes weaker under supercritical conditions.

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