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A Molecular Dynamics Simulation of the Diffusivity of O_2 in Supercritical Water

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Abstract Equilibrium molecular dynamics simulations were carried out to study the diffusion process of oxygen in supercritical water (SCW). Both infinite-dilution diffusion and Maxwell–Stefan (MS) mutual diffusion coefficients were calculated. The differences between the simulated Maxwell–Stefan diffusion coefficients and those predicted by the Darken equation were examined. It suggests that the velocity cross correlation function plays an important role in the oxygen–SCW mutual diffusion. The Darken equation may not be valid in predicting the Maxwell–Stefan diffusion coefficients for this mixture.

Keywords Diffusivity · Molecular dynamics simulation · Oxygen · Supercritical water

1 Introduction

Supercritical water (SCW) has received increasing attentions because of its importance in industrial applications such as supercritical power generation and SCW oxidation (SCWO) [1]. The O_2/H_2O binary mixture is one of the most important SCW mixture systems, since in the SCWO technology, oxygen or hydrogen peroxide is added as an oxidizing agent. Also, O_2 plays a particular role in the corrosion of the facilities both in SCWO and in supercritical power plants.

In considering binary reaction processes, the diffusions of solutes in SCW are particularly important. A better understanding of the diffusion process and the local structure of water around O_2 would help in the design of supercritical oxidation

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reactors as well as in corrosion protection. A number of correlations have been proposed to estimate the self-diffusion coefficients of pure liquids and the infinite-dilution diffusion coefficients in liquid mixtures [2]. Estimation of the infinite-dilution diffusion coefficient of oxygen in water often uses a correlation developed by Wilke and Chang [3], which is based on the Stokes–Einstein equation,

$$D_{O_2-H_2O} = 7.4 \times 10^{-8} \frac{T\left(\varphi_{H_2O} M_{H_2O}\right)^{1/2}}{\mu V_{O_2}^{0.6}} \tag{1}$$

where T is the absolute temperature, φ_{H_2O} is the association parameter of water (it was suggested to be 2.26 in [4], fitted from experimental data therein), M_{H_2O} is the molecular weight of water, μ is the viscosity of water, and V_{O2} is the molar volume of oxygen at the normal boiling point (the value given in [5] is $25.6\,\text{cm}^3 \cdot \text{mol}^{-1}$). However, the accuracy of the equation is limited, and its validity in the supercritical region has not been verified. A number of experiments were carried out to measure the diffusion coefficients of oxygen in water. The temperature is generally lower than 350 K, and the measured diffusion coefficients partly scatter noticeably [6–8]. The experimental data for oxygen diffusion in SCW are scarce because of the difficulties in experimental measurements under such harsh conditions.

Molecular dynamics (MD) simulations have been successfully applied to study the structures of SCW and to estimate the diffusion coefficients. Seminario et al. [9] investigated the interaction of individual O_2 and H_2O molecules by *ab initio* and non-local density functional methods. In their simulations, O_2/H_2O mixtures under both normal (300 K, 1 bar) and supercritical (850 K, 250 bar) conditions showed that O_2 expands the volume of the SCW and decreases the extent of clustering of the water molecules. Ohmori and Kimura [10] studied the local water structure around O_2 and reported a deficiency structure of water around O_2. The authors related the temperature dependence of the diffusion coefficients to the local water structure around O_2 and declared an anomalous temperature dependence of the diffusion coefficients. Their prediction for the water depletion from O_2 by means of molecular dynamics simulation was confirmed by Kazuko et al. [11] with a Raman spectroscopic study. The infinite-dilution diffusion coefficient was also calculated by Xiao et al. [12]. Despite all the successes achieved in molecular scale simulations, the study of oxygen/SCW mutual diffusion is still insufficient. In this report, we carried out equilibrium molecular dynamics simulations of the thermodynamic properties and diffusion process of the O_2/H_2O system within a wide range of oxygen concentrations. The Maxwell–Stefan diffusion coefficients were also studied.

2 Simulation Methods

2.1 Molecular Model

The empirical simple-point-charge (SPC) and simple-point-charge extension (SPCE) models have been extensively used in the molecular dynamics simulation of water including in the supercritical region. Both of them are rigid three-site models with partial charges located directly on the oxygen and hydrogen atoms. We compared the two models in calculating the self-diffusion coefficient of water under normal conditions. The results are $(2.57 \pm 0.5) \times 10^{-9}\,\mathrm{m^2 \cdot s^{-1}}$ for the SPCE model and $(3.92 \pm 0.15) \times 10^{-9}\,\mathrm{m^2 \cdot s^{-1}}$ for the SPC model at 298 K and 0.1 MPa. The values calculated by Mahoney and Jorgensen [13] using molecular dynamics simulation are $(2.49 \pm 0.5) \times 10^{-9}\,\mathrm{m^2 \cdot s^{-1}}$ for the SPCE model and $(3.85 \pm 0.09) \times 10^{-9}\,\mathrm{m^2 \cdot s^{-1}}$ for the SPC model under the same condition. The experimental value of the self-diffusion coefficient of water at 298 K and 1 atm is $2.3 \times 10^{-9}\,\mathrm{m^2 \cdot s^{-1}}$ [14]. The SPCE model predicts a better self-diffusion coefficient when compared with the experimental value. So the SPCE model was employed as the potential model of water in this report. The water–water interaction is a sum of the 12-6 Lennard–Jones interactions between the oxygen atoms in water and the Coulomb forces between the point charges;

$$u(r) = \sum_{i=1}^{3}\sum_{j=1}^{3} \frac{q_1^i q_2^j}{r_{ij}} + 4\varepsilon \left[\left(\frac{\sigma_{\mathrm{OO}}}{r_{\mathrm{OO}}} \right)^{12} - \left(\frac{\sigma_{\mathrm{OO}}}{r_{\mathrm{OO}}} \right)^{6} \right] \tag{2}$$

where q is the point charge, and σ and ε are, respectively, the diameter and energy parameter of the oxygen atom in water. The model of the oxygen molecule was taken from the CHARMM library [15], where O_2 was taken as a diatomic LJ model molecule formed by two identical LJ sites with a bond distance $L = 1.208$ Å. The parameters for oxygen and water potential models are shown in Table 1. The interactions between unlike LJ sites of two molecules are calculated using the Lorentz–Berthelot combining rule,

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \tag{3}$$

and

$$\varepsilon_{12} = \sqrt{\varepsilon_1 \cdot \varepsilon_2} \tag{4}$$

Table 1 Potential parameters

	Oxygen	SPC	SPCE
Mass ($\mathrm{g \cdot mol^{-1}}$)	$M_O = 15.9994$	$M_O = 15.9994$ $M_H = 1.008$	$M_O = 15.9994$ $M_H = 1.008$
ε ($\mathrm{kJ \cdot mol^{-1}}$)	$\varepsilon_O = 0.502$	$\varepsilon_O = 0.650$ $\varepsilon_H = 0.0$	$\varepsilon_O = 0.650$ $\varepsilon_H = 0.0$
σ (Å)	$\sigma_O = 3.029$	$\sigma_O = 3.166$ $\sigma_H = 0.0$	$\sigma_O = 3.166$ $\sigma_H = 0.0$
Partial charge (e)	$q_O = 0.0$	$q_O = -0.820$ $q_O = 0.41$	$q_O = -0.8476$ $q_O = 0.4238$
Bond length (Å)	$b_{O-O} = 1.208$	$b_{O-H} = 1.0$	$b_{O-H} = 1.0$
Angle (°)	–	$\alpha_{HOH} = 109.47$	$\alpha_{HOH} = 109.47$

2.2 Diffusion Coefficient

Mass diffusion is defined as a transport process where an initially non-uniform distribution of particles processes toward a uniform distribution. The infinite-dilution diffusion denotes the diffusion of the solute whose mole fraction is close to zero so that the solute particles are only surrounded by solvent. It can be calculated with the same method as that of self-diffusion. Mutual diffusion can be characterized by Fick's law or the Maxwell–Stefan equation. In Fickian diffusion, the concentration gradient is taken as the driving force, while in MS diffusion, the chemical potential gradient is treated as the driving force for the particles. Accordingly, the diffusion coefficient is named, respectively, the Fickian diffusion coefficient and the MS diffusion coefficient. Since MS diffusion is related to the microscopic motion of the particles, it is convenient to be calculated from molecular dynamics simulation.

Diffusion coefficients can be calculated by time-correlation function theory using the Green–Kubo integral formula or by the mean square displacement via the Einstein relation. Theoretically, the two methods will give the same result. Our simulation on the self-diffusion shows that the agreement is very good as the difference is within 1 %. Since the decay of the velocity auto-correlation function (VACF) can give more information on the motions of molecules, the Green–Kubo method is employed in this simulation. In the Green–Kubo method, the self-diffusion coefficient D_{self} is presented by the integral over the velocity auto-correlation function,

$$D_{\mathrm{self}} = \frac{1}{3}\int_0^\infty \langle \vec{u}_i(t) \cdot \vec{u}_i(0) \rangle \mathrm{d}t \tag{5}$$

where $\vec{u}_i(t)$ is the velocity vector of the mass center of molecule i at time t. For water in this work, the mass center of the oxygen atom was treated to be the center of the water molecule. $< \cdots >$ denotes the ensemble average. Equation 5 is an average over all the molecules of the species studied. In a binary mixture, the MS mutual diffusion coefficient can be calculated by the integral over the correlation function of the mass flux as

$$Đ_{12}=\frac{1}{3Nc_1c_2}\int_0^\infty \left\langle \left[c_1 \sum_{i\in 2} \vec{u}_i(t) - c_2 \sum_{j\in 1} \vec{u}_j(t) \right] \cdot \left[c_1 \sum_{i\in 2} \vec{u}_i(0) - c_2 \sum_{j\in 1} \vec{u}_j(0) \right] \right\rangle \mathrm{d}t \tag{6}$$

where c_1 and c_2 denote the mole fractions of components 1 and 2, respectively, and N is the total number of particles. $J(t) = c_1 \sum_{i\in 2} \vec{u}_i(t) - c_2 \sum_{j\in 1} \vec{u}_j(t)$ is the inter-diffusion mass flux.

2.3 Simulation Details

The systems used in this report to calculate the infinite-dilution coefficients were composed of 1 000 water molecules and 1 or 2 oxygen molecules. This concentration is low enough to be treated as an infinite-dilute solution. To test the size effect, systems with 2 000 and 4 000 water molecules were also simulated. The self-diffusion coefficients in systems of 1 000, 2 000, and 4 000 molecules agree with each other in a deviation less than 1 %. The systems with 1 000 molecules with oxygen number fractions from 0.1 to 0.9 were used to calculate the MS diffusion coefficient. The molecules were initially placed in a cubic simulation cell under periodic boundary conditions. The total momentum of the system was set to be zero. The length of the cubic cell was determined by the required density. Simulations were performed in NVT ensembles for the calculation of infinite-dilution diffusion coefficients and in NPT ensembles for the mutual diffusion. A Nose–Hoover thermostat and barostat were applied to control the temperature and the pressure. The long-range Coulomb force was treated with the particle–particle particle–mesh method. The cutoff distance for all interactions was set to be 1 nm. Water and oxygen molecules were kept rigid with the SHAKE algorithm throughout the simulation. The Newton equation was integrated by the velocity–Verlet algorithm with a timestep of 1 fs. The first 10 ps to 15 ps was used to reach equilibrium before any sampling was taken. Since in the calculation of the MS diffusion coefficient each sampling needs to sum over all the molecules to calculate the correlation function of the mass flux, the sampling number is only $1/N_\mathrm{s}$ of that of the self-diffusion coefficient if the same time origins are used (N_s is the number of molecules used to calculate the self-diffusion coefficient). The sampling number in the MS diffusion calculation is much smaller than that in the self-diffusion calculation, more time origins are needed to get better statistics. Self-diffusion coefficients were calculated by averaging over more than 100 000 independent autocorrelation functions. The time origins were taken every 1 000 time steps. For calculation of infinite-dilution diffusion and MS diffusion coefficients, the time origins were taken every 50 time steps. The time origins are much more than that in the calculation of self-diffusion diffusion. 50 000 independent autocorrelation functions were averaged. The integral time of the correlation function was truncated when the function decays to 0.5 % of its initial value to get rid of the influence of the long time tail.

3 Results and Discussion

3.1 Infinite-Dilution Diffusion Coefficient

The infinite-dilution diffusion coefficient of oxygen in water under normal conditions was first calculated with the Green–Kubo method. The results were compared with available experimental data [6–8] and that derived from Eq. 1, as shown in Fig. 1. The agreement between our simulation and averaged experimental values is reasonable. Meanwhile, our simulation results agree well with the values derived by Eq. 1.

Figure 2 shows the normalized VACFs of oxygen at various densities at 973 K as well as at standard ambient conditions. The VACF of oxygen decays exponentially at supercritical temperatures. It decays slower in dilute systems because of the less frequent collisions. In ambient water, the VACF of oxygen has a small negative part which is believed to be related to the "cage effect" [16]. The cage effect means that in condensed water, the oxygen molecule is sieged by its neighbor water molecules

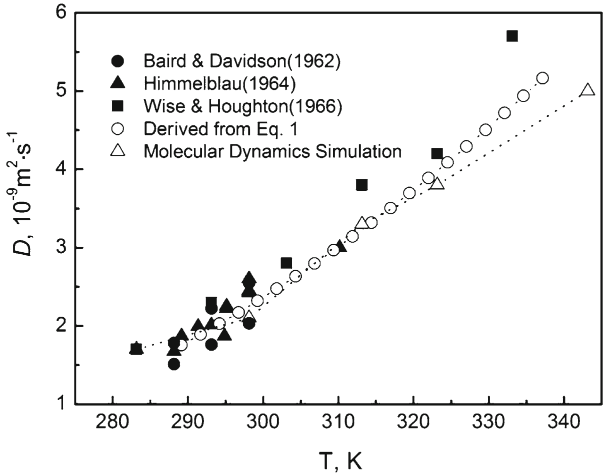

Fig. 1 Diffusion coefficient of oxygen in water (1 atm). Experimental data are from [6–8]

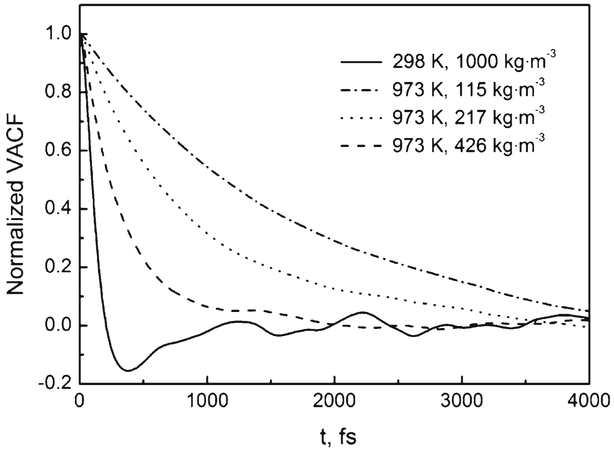

Fig. 2 Time profile of VACFs of oxygen for infinite-dilution diffusion

which form a “cage.” The oxygen molecule suffers backscattering collisions which will hinder the diffusion of oxygen. This phenomenon has not been observed in the supercritical state at smaller densities. This might also partly explain the remarkably different diffusion values under normal and supercritical states.

The temperature and density dependencies of the infinite-dilution diffusion coefficients were also calculated. The results are compared with the data in [10]. The comparison is shown in Fig. 3 and tabulated in Table 2. The statistical uncertainty of the simulation data was estimated to be within 10 %. The comparisons show a reasonable agreement at a supercritical density of $426\,\mathrm{kg \cdot m^{-3}}$, while a larger deviation occurs at a lower density of $216\,\mathrm{kg \cdot m^{-3}}$. Moreover, the D_{O_2} behaves insensitively to the temperature at a density of $426\,\mathrm{kg \cdot m^{-3}}$ which contradicts the regular

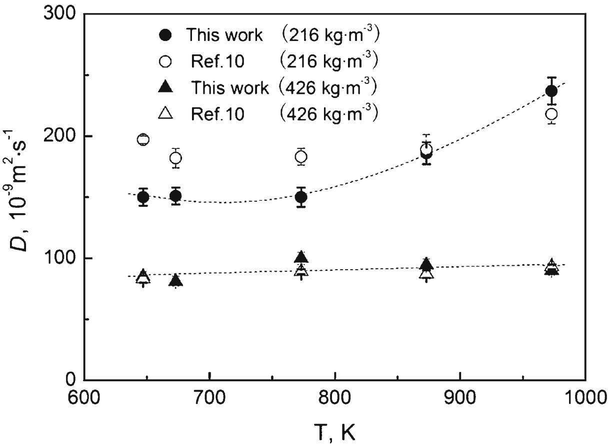

Fig. 3 Temperature dependence of D_{O_2} at various densities

Table 2 Results of infinite-dilution diffusion coefficients

T(K)	D (10^{-9} m$^2\cdot$s^{-1})			
	216 kg·m^{-3}		426 kg·m^{-3}	
	This work	Ref. [10]	This work	Ref. [10]
647	150 (7)	197 (3)	85 (4)	83 (3)
673	151 (7)	182 (8)	81 (4)	–
773	150 (8)	183 (7)	100 (5)	89 (2)
873	186 (9)	189 (12)	95 (5)	87 (3)
973	237 (11)	218 (8)	90 (4)	93 (2)

Arrhenius-type temperature dependence of diffusivity. The insensitivity was also addressed in reference [10] with the same density. However, the negative correlation between the D_{O_2} and the temperature reported in [10] with the density of 216 kg·m^{-3} was not reproduced in this simulation. This might be attributed to the influences of different oxygen potential models employed and a comparatively smaller system of 256 molecules used in [10].

The radial distribution function (RDF) of water molecules around oxygen at 216 kg·m^{-3} is shown in Fig. 4. The RDF for O_{O_2}–O_{H_2O} is less than unity at 647 K while there is a peak larger than unity at higher temperatures. The RDFs at high temperatures are less distinguishable. It can be attributed to the weak influence of temperature on the RDF in this temperature region. In addition, the limited amount of oxygen would bring uncertainty to the calculation of RDF. The differences between the RDFs indicate that the effects of the temperature near the critical region and far away from the critical region are different. The shape of the RDF at 647 K denotes that the density of neighboring water molecules around the oxygen is smaller than the average. It implies that the water molecules are repelled from oxygen. In other

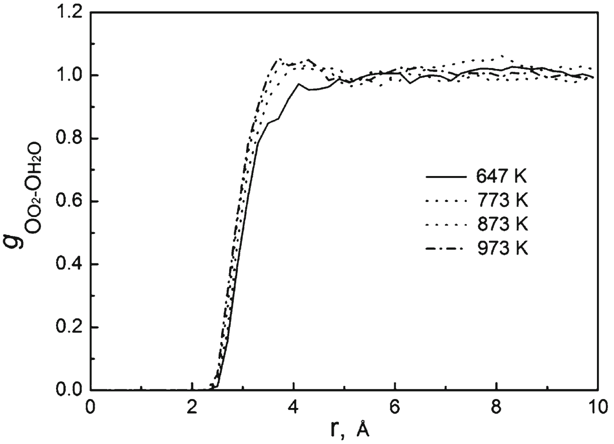

Fig. 4 Radial distribution function of O_{O_2}–O_{H_2O}

words, there might be a deficient structure of water molecules around the oxygen. This phenomenon agrees with the simulation results in [9,10], and was also verified by Kazuko et al. [11] in Raman spectroscopic experiments. With increased temperature, the deficient structure is weakened, possibly because of the enhanced thermal motion.

3.2 Maxwell–Stefan Mutual Diffusion

Both self-diffusion and MS diffusion coefficients in mixtures are concentration-dependent quantities. MS diffusion is important in characterizing the mutual diffusion. In practice, the MS coefficients are difficult to be measured via experiments. Empirical correlations are often used to predict them such as the Darken equation [17].

If the velocity cross correlation function (VCCF) $\langle \vec{u_i} \cdot \vec{u_j} \rangle (i \neq j)$ can be neglected, Eq. 6 can be simplified as

$$\mathit{Đ}_{12} = \frac{c_2}{3} \int_0^\infty \langle \vec{u_1}(t) \cdot \vec{u_1}(0) \rangle \mathrm{d}t + \frac{c_1}{3} \int_0^\infty \langle \vec{u_2}(t) \cdot \vec{u_2}(0) \rangle \mathrm{d}t \tag{7}$$

Equation 7 corresponds with the Darken equation which relates the MS diffusion with self-diffusion

$$\mathit{Đ}_{12} = c_1 D_{2,\mathrm{self}} + c_2 D_{1,\mathrm{self}} \tag{8}$$

The molecular dynamics simulation provides a way to test the Darken relation by comparing the MS diffusion coefficient from Eqs. 6 and 8. By checking whether the VCCF could be neglected, the validity of the Darken equation could be determined. The negligibility of VCCF depends on the ideality of the binary mixture.

Table 3 Results of Maxwell–Stefan diffusion coefficients

X_{O_2}	25 MPa (10^{-8} m$^2 \cdot$ s^{-1})				500 MPa (10^{-8} m$^2 \cdot$ s^{-1})			
	D_{O_2}	D_{H_2O}	D_{Darken}	D_{MS}	D_{O_2}	D_{H_2O}	D_{Darken}	D_{MS}
0	28.2	16.1	28.2	28.2 (–)	2.92	2.33	2.92	2.92 (–)
0.1	30.7	21.6	29.8	32.2 (1.5)	3.02	2.50	2.97	3.30 (0.21)
0.2	34.3	24.8	32.4	39.3 (2.0)	3.01	2.63	2.93	4.83 (0.31)
0.3	35.7	28.0	33.4	42.9 (2.0)	3.01	2.74	2.93	7.44 (0.39)
0.4	37.8	31.4	35.2	45.3 (2.1)	2.95	2.89	2.93	7.85 (0.40)
0.5	38.3	33.4	35.9	48.6 (2.5)	2.83	2.99	2.91	10.10 (0.55)
0.6	37.8	34.4	35.8	47.8 (2.2)	2.84	3.09	2.99	10.99 (0.53)
0.7	37.8	36.7	37.0	51.1 (2.8)	2.92	3.20	3.11	9.77 (0.42)
0.8	37.7	43.3	42.1	54.7 (3.0)	3.07	3.28	3.24	8.16 (0.39)
0.9	36.8	44.7	43.9	51.9 (2.0)	3.34	3.30	3.30	6.25 (0.31)
1.0	34.7	52.2	52.2	52.2 (–)	3.8	3.38	3.38	3.38 (–)

The uncertainty for self-diffusion is within 1 % and not given in this table

Simulations were carried out at 700 K under pressures of 25 MPa and 500 MPa. The mole fraction of the oxygen ranged from 0.1 to 0.9, and the results were extrapolated to 0 and 1 by a polynomial fitting method. The self-diffusion of oxygen and water can be predicted with a statistical uncertainty less than 1 %, while for MS diffusion, there is an average of 10 % in the uncertainty. The different uncertainties in calculating self-diffusion and MS diffusion is due to that the self-diffusion is a property of each single molecule, while the MS diffusion is a collective property of all the molecules in the system. The calculated self-diffusion and MS diffusion coefficients are depicted in Fig. 5a and b, and tabulated in Table 3. As shown in the figures, the concentration dependencies of the self-diffusion and MS diffusion coefficients are very different under different pressures. Under both pressures, the self-diffusion coefficients of oxygen and water mostly increase with increasing oxygen fraction, while the MS diffusion coefficient is non-monotonic. The differences between the simulated MS diffusion coefficients and those predicted by the Darken equation are significant. The MS diffusion is remarkably larger than that predicted by the Darken equation, and the difference increases with increasing pressure. It suggests that the VCCF is positive and plays an important role in the oxygen–SCW mutual diffusion. This agrees with the statement of Rogak et al. [18] that the oxygen/water mixture is highly non-ideal at supercritical conditions. The Darken equation may not be valid in predicting the MS diffusion coefficients for this mixture, and more accurate correlations for the prediction of MS diffusion coefficients are expected.

4 Conclusion

We carried out molecular dynamics simulations to study the diffusion process of oxygen in SCW. The Green–Kubo method was employed in calculating the diffusion

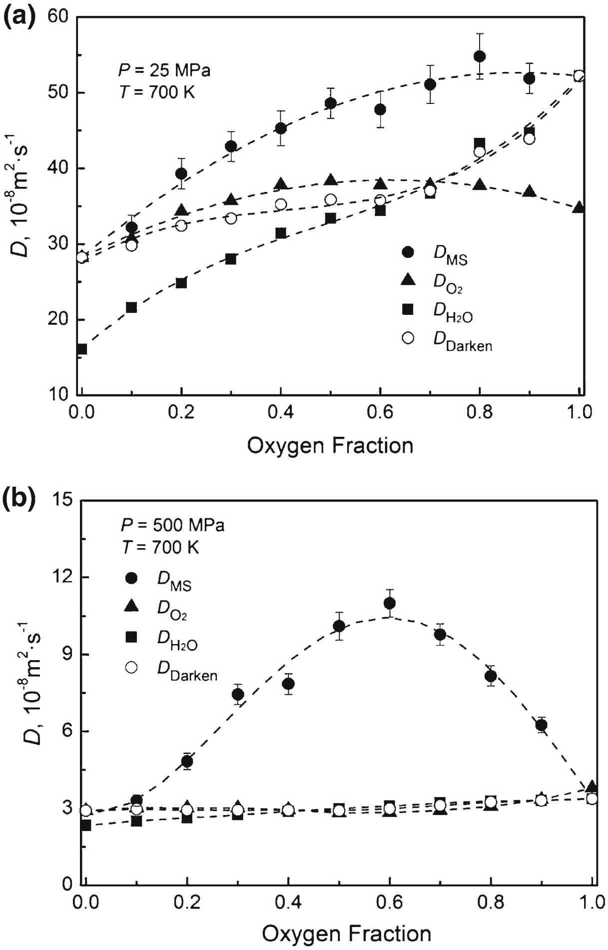

Fig. 5 Concentration dependence of diffusion coefficient (the uncertainty for the self-diffusion is about 1 %, so the *error bars* are not shown in the figure). (a) 25 MPa and (b) 500 MPa

coefficients. The infinite-dilution diffusion coefficient of oxygen in water is insensitive to the temperature at supercritical conditions. By analyzing the RDF, the deficient structure of water molecules around oxygen near the critical temperature was reconfirmed in this simulation. The self-diffusion and Maxwell–Stefan diffusion of oxygen/water system were calculated in the binary mixture with the mole fraction of oxygen varying from 0.1 to 0.9 at the same temperature but at two different pressures. The differences between the simulated MS diffusion coefficients and those predicted by the Darken equation were examined. It suggests that the velocity cross-correlation function is positive and cannot be neglected in this system. The Darken equation may not be valid in predicting the MS diffusion coefficients for this mixture. The oxygen/water system is highly non-ideal at supercritical conditions.

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References

1. M.D. Bermejo, M.J. Cocero, AIChE J. **52**, 3933 (2006)
2. H. Liu, C.M. Silva, E.A. Macedo, Chem. Eng. Sci. **53**, 2403 (1998)
3. C.R. Wilke, P. Chang, AIChE J. **1**, 264 (1955)
4. W. Hayduk, H. Laudie, AIChE J. **20**, 611 (1974)
5. J.R. Welty, C.E. Wicks, R.E. Wilson, *Fundamentals of Momentum, Heat, and Mass Transfer*, 3rd edn. (Wiley, New York, 1984), p. 495
6. M.H. Baird, J.F. Davidson, Chem. Eng. Sci. **17**, 473 (1962)
7. D.M. Himmelblau, Chem. Rev. **64**, 527 (1964)
8. D.L. Wise, G. Houghton, Chem. Eng. Sci. **21**, 999 (1966)
9. J.M. Seminario, M.C. Concha, J.S. Murray, Chem. Phys. Lett. **222**, 25 (1994)
10. T. Ohmori, Y. Kimura, J. Chem. Phys. **116**, 2680 (2002)
11. S. Kazuko, F. Hideo, K. Seiichiro, J. Supercrit. Fluids **32**, 293 (2004)
12. J. Xiao, J.F. Lu, J. Chen, Y.G. Li, Chin. Phys. Lett. **18**, 847 (2001)
13. M.W. Mahoney, W.L. Jorgensen, J. Chem. Phys. **114**, 363 (2001)
14. R. Mills, J. Phys. Chem. **77**, 685 (1973)
15. M. Schlenkirch, J. Brickmann, A.D. MacKerell, in *Biological Membranes*, ed. by K.M. Merz, B. Roux (Birkhauser, Boston, 1996), p. 31
16. C.Y. Liao, F. Sciortino, S.H. Chen, Phys. Rev. E **6**, 6776 (1999)
17. L.S. Darken, Trans. Am. Inst. Min. Metall. Eng. **175**, 184 (1948)
18. S.N. Rogak, D. Faraji, J. Heat Transf. **216**, 419 (2004)