

ARTICLE

Salting-in/Salting-out Mechanism of Carbon Dioxide in Aqueous Electrolyte Solutions[†]

Xia Zhang^{a‡}, Lu Zhang^{b‡}, Tan Jin^b, Zhi-jun Pan^b, Zhe-ning Chen^b, Qiang Zhang^{a*}, Wei Zhuang^{b*}*a. Department of Chemistry, Bohai University, Jinzhou 121013, China**b. State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China*

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The solvation of carbon dioxide in sea water plays an important role in the carbon circle and the world climate. The salting-out/salting-in mechanism of CO₂ in electrolyte solutions still remains elusive at molecule level. The ability of ion salting-out/salting-in CO₂ in electrolyte solution follows Hofmeister Series and the change of water mobility induced by salts can be predicted by the viscosity B-coefficients. In this work, the chemical potential of carbon dioxide and the dynamic properties of water in aqueous NaCl, KF and NaClO₄ solutions are calculated and analyzed. According to the viscosity B-coefficients, NaClO₄ (0.012) should salt out the carbon dioxide relative to in pure water, but the opposite effect is observed for it. Our simulation results suggest that the salting-in effect of NaClO₄ is due to the strongly direct anion-CO₂ interaction. The inconsistency between Hofmeister Series and the viscosity B-coefficient suggests that it is not always right to indicate whether a salt belongs to salting-in or salting-out just from these properties of the salt solution in the absence of solute.

Key words: Salting effect, Viscosity B-coefficient, Hofmeister Series, Water dynamics

I. INTRODUCTION

The oceanic storage and adsorption of CO₂ is one important step in the carbon circle leading to the greenhouse gases on the earth [1]. Solubility of CO₂ in sea water is sensitive to the concentration and composition of the co-existing salts [2, 3]. Salt-effect on the solubility of molecular solute in aqueous electrolyte solutions has been a topic of significant interest in many research fields [4–7], and different theories have been proposed for the underlying mechanism like the hydration theories, water dipole theories, and electrostatic theories [7]. None of these theories, however, is consistent with all the existing experimental observations, especially with the salting-in phenomenon [7]. The salting-effect is usually attributed to the change of solvent density, structure and dynamics induced by ions. As a consequence, the solubility of solute changes in aqueous electrolytes. It is usually right for the salting-out effect, but it seems more complex for the salting-in effect than the salting-out [7, 8]. Molecular mechanism of the salting-effect

on the solubility of carbon dioxide at molecule level, therefore, remains elusive.

The salting-effect on solubility of non-polar solute like carbon dioxide in aqueous solution is often quantified by the Setschenow equation [9]:

$$\lg\left(\frac{S_0}{S}\right) = \frac{K_S}{C_S} \quad (1)$$

where S_0 and S are the solubility of the CO₂ in pure water and in a salt solution at a finite concentration C_S , respectively. Previous studies focused on rationalizing the correlations between the CO₂ solubility and the macroscopic properties such as activity coefficient, partial molar volume and viscosity [10]. For instance, ions with positive viscosity B-coefficient, such as like F⁻ (0.107 at 25 °C) and Na⁺ (0.085 at 25 °C) [11], are the so-called water “structure makers”, while those with negative values, such as K⁺ (-0.009 at 25 °C), Cl⁻ (-0.005 at 25 °C) and ClO₄⁻ (-0.063 at 30 °C) [11], are “structure breakers”. From the thermodynamic view point, ions salt out the non-polar solute such as CO₂ in electrolyte solutions by an indirect way [12, 13]: the structure maker ions strengthen the water-water hydrogen bond network and reduce the entropy of water, then reduce the solubility of the non-polar solutes. Mostly, there is a good correlation observed between salting-out coefficient K_S and viscosity B-coefficient. However, exceptions do exist. For instance, there is a strong salt-

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[‡]These authors contributed equally in this work.

*Authors to whom correspondence should be addressed. E-mail: zhangqiang@bhu.edu.cn, wzhuang@fjirsm.ac.cn

in effect on solubility of CO₂ in NaClO₄ aqueous solutions, but NaClO₄ has a positive value of the viscosity B-coefficient (0.012) [11]. This inconsistency is not well understood due to the lack of knowledge on the molecular mechanism underlying.

Analysis of a carefully chosen molecular dynamic behavior, that is experimentally measurable (by spectroscopy *e.g.*) and can be assigned to clear structural origins, helps us understand the definitive physical factors responsible for the important phenomenon in general [5, 14, 15]. The rotational time of water and the translational diffusion constant of water, measured by ultrafast infrared or NMR techniques, are found to nicely correlate with K_S in most cases: previous work indicates that a slower water molecular dynamics usually associates with the “structure maker” ions in the solution, with a positive value of K_S [5, 6, 11].

In this work, the chemical potentials of carbon dioxide, the water rotational time and water self-diffusion constant are calculated for aqueous KF, NaCl and NaClO₄ solutions. We found a good correlation between the K_S coefficient and the molecular rotational time and the translational self diffusion constant of water in NaCl and KF aqueous solutions. On the other hand, similar to that observed in viscosity measurement, an inconsistency is observed between the salt concentration dependence of K_S coefficient and the microscopic dynamic properties of water for NaClO₄. Further analysis shows that in NaCl and KF solutions the direct association between CO₂ and cation and anion is not preferred compared to water-CO₂ pair. Mobility of water is retarded with respect to that in pure water, the solubility of carbon dioxide should therefore reduce due to the decrement of the water entropy induced by ions in an indirect way [5–7]. In the aqueous NaClO₄ solutions, a specific direct binding between anion and CO₂ exists according to the Kirkwood and Buff theory [16], which induces an increment of the solubility of carbon dioxide in aqueous NaClO₄ solutions.

II. EXPERIMENTS

A. Simulation detail

The KF, NaCl and NaClO₄ aqueous solution at 0.2, 0.5, 1.00, and 2.00 mol/L, were selected in this work. Each empty cubic box was randomly inserted with 1000 water molecules, one carbon dioxide molecule and ions according to the molar concentration (for 1 mol/L box, the ratio of salt/water=1 salt:55 water). The force fields of alkali and halide ions are taken from ion Joung-Cheatham models [17]. The famous SPC/E model [18] and EPM2 model [19] are used for solvent water and solute CO₂. The geometry and the non-bond interaction parameters of ClO₄⁻ are directly obtained from Ref.[20] and Ref.[21] respectively. In running simulations, the geometries of water and ions were kept rigid

by the LINCS Algorithm [22]. Each sample was kept at 1 atm and at 298 K weakly coupled to a bath with the Nose-Hoover thermostats [23, 24] at the interval of 0.1 ps. The equations of motion were integrated with 2 fs time step. Before the harvest simulations, a 5 ns NPT simulation was run to reach the equilibration. Then, additional 2 ns NVE simulations are carried out to get the dynamic properties of system. The long-range Coulombic interactions are calculated with the particle-mesh Ewald method [25]. The non-bonded van der Waals interactions are truncated at 12 Å using the switching functions. All simulations are performed using the GROMACS simulation package [26].

B. The chemical potential of CO₂ in electrolyte solutions

The chemical potential of carbon dioxide in electrolyte solution at salt concentration C_S was calculated with the Bennett’s acceptance ratio method (BAR) proposed by Bennett in 1976 [27(a)]. When the change from initial state A (the electrolytes solution with CO₂) to final state B (the electrolytes solution without CO₂) is large (unlike states), some intermediate states are chosen by a coupling parameter λ according to a linear relationship:

$$H(\lambda) = \lambda H_B + (1 - \lambda)H_A \quad (2)$$

H_A and H_B are the Hamiltonians at initial states A ($\lambda=0$) and final state B ($\lambda=1$). The difference of chemical potentials between two neighboring intermediate states i and j can be calculated at λ_i and λ_j as Eq.(1) with BAR method [27(a)].

$$\Delta\mu_{ij}^{\text{BAR}} = k_B T \ln \frac{\langle f(H_i - H_j + C) \rangle_j}{\langle f(H_j - H_i - C) \rangle_i} + C \quad (3)$$

where f is the Fermi function. k_B and T are the Boltzmann constant and the temperature respectively. H_i and H_j are the Hamiltonians at intermediate states i and j . The value for C is determined iteratively until to meet

$$\langle f(H_i - H_j + C) \rangle_j = \langle f(H_j - H_i - C) \rangle_i \quad (4)$$

Then,

$$\Delta\mu_{ij}^{\text{BAR}} = -k_B T \ln \left(\frac{N_j}{N_i} \right) + C \quad (5)$$

The chemical potential of CO₂ at final state B relative to initial state A is evaluated with \bar{g} .bar tool in GROMACS software [26, 27].

$$\mu = \sum_{i=1}^{n-1} \Delta\mu_{i+1,i}^{\text{BAR}} \quad (6)$$

where N_i and N_j represent the number of configurations at intermediate states i and j respectively. n is the number of intermediate states. Convergence of this iterative

process can only be reached if there is sufficient overlap between the forward and backward energy differences [27]. In order to enhance the accuracy of BAR, the coupling procedure is further divided into two stages, the discharging process and the neutral soft particle disappearing process. The coupling parameters λ were chosen at $\lambda=1.0, 0.95, 0.9, 0.8, 0.7, 0.65, 0.6, 0.55, 0.50, 0.45, 0.40, 0.35, 0.30, 0.25, 0.20, 0.15, 0.10, 0.05, 0.00$ for the discharging process. $\lambda=1.0, 0.95, 0.9, 0.85, 0.80, 0.75, 0.70, 0.65, 0.6, 0.55, 0.50, 0.45, 0.40, 0.30, 0.20, 0.10, 0.00$ are used for the neutral soft particle disappearing stage. For each value of λ , the ensemble average of chemical potential is collected within the time period of 2 ns. Simulations were carried out at the same pressure and temperatures as the dynamic properties in method part.

C. Dynamic properties

The rotational correlation functions of water along OH bond vector \mathbf{u} and are written as:

$$C_2(t) = \langle P_2[\mathbf{u}(0)\mathbf{u}(t)] \rangle \quad (7)$$

where P_2 is the second-rank Legendre polynomial. The rotational relaxation time of water (τ) is approximately obtained by fitting double exponential functions as described in previous works [28–30]. The self-diffusion coefficient D can be derived from the time-dependent mean square displacements of the mass center of water molecule in aqueous electrolyte solutions, according to the Einstein relation [31].

III. RESULTS AND DISCUSSION

A. The chemical potential of CO₂

The chemical potential of carbon dioxide in saturated CO₂ aqueous solution without salt ($\mu(S_0)$) and with a finite salt concentration C_S ($\mu(S)$):

$$\mu^g = \mu(S_0) = \mu_\infty^0 + RT \ln \left(\frac{S_0}{c_\infty} \right) \quad (8)$$

$$\mu^g = \mu(S) = \mu_\infty^1 + RT \ln \left(\frac{S}{c_\infty} \right) \quad (9)$$

μ_∞^0 and μ_∞^1 are the chemical potential of CO₂ in pure water and in electrolyte solution at salt concentration C_S , with dilute concentration of CO₂ c_∞ . They correspond to the chemical potential in Eq.(6), which is derived from the BAR method. Given CO₂ at the gas-liquid equilibrium state, $\mu(S_0)$ and $\mu(S)$ are equal to the chemical potential of CO₂ (μ^g) in gas with same vapor pressure. Setchenow equation is then expressed as:

$$\frac{\mu_\infty^1 - \mu_\infty^0}{RT} = \ln \left(\frac{S_0}{S} \right) = \ln(f) = K_S C_S \quad (10)$$

The Setchenow salting-out coefficient K_S is the slope of linear function $\ln(f)$ over the salt concentration C_S and usually can be obtained according to the linear relationship $\ln(f) \propto C_S$ [7, 32].

The calculated chemical potential of CO₂ in pure water in this work is (1.88 ± 0.22) kJ/mol. It is in agreement with the experimental value of 1.00 kJ/mol [34]. The calculated values of $\ln(f)$ in the Setchenow salting-out equation in KF, NaCl and NaClO₄ aqueous solution at 0.2, 0.5, 1.00, and 2.00 mol/L are shown in FIG. 1, which is also consistent with the tendency of the experimental $\ln(f)$ with concentration [32, 33]. $\ln(f)$ of both KF and NaCl solutions increase monotonously with concentration in FIG. 1(a), while the value of NaClO₄ decreases with concentration FIG. 1(b). This suggests that NaCl and KF both have salting-out effect on the carbon dioxide and have positive values of the Setchenow salting-out coefficient K_S . KF has the strongest ability to reduce the solubility of CO₂ at each concentration. NaClO₄ has a salting-in effect on CO₂ with concentration and negative value of the Setchenow salting-out coefficient K_S . The slight deviation from the linear relationship between $\ln(f) \propto C_S$ at high concentration is probably due to the artifact of the force field used in simulation.

B. Water dynamics induced by salts

We next calculated the rotational time and the translational self-diffusion constant of water, and discussed the correlation between the change of these dynamic behaviors of water induced by ions and the salting-effect of on the solubility of CO₂.

The rotational times and the self diffusion constants of water in KF, NaCl and NaClO₄ aqueous solution at 0.2, 0.5, 1.00, and 2.00 m are shown in FIG. 2. With adding KF and NaCl into water, the rotational time of water increases monotonously with concentration. The translational self-diffusion constant of water decreases correspondingly. Slower water dynamics is observed in KF than in NaCl solution. The dynamic properties with concentration from simulations are consistent with the predictions of Hofmeister Series as well as the viscosity B-coefficients (B-coefficients of KF and NaCl are 0.098 and 0.080, respectively). On the other hand, the rotation and the translation of water in aqueous NaClO₄ electrolyte solutions are both retarded, while a negative value of the Setchenow salting-out coefficient K_S is observed (FIG. 1). This is a controversy between the predictions by Hofmeister Series [32] and the viscosity B-coefficients for NaClO₄ [11, 12].

C. Specific and direct effect of anion

To rationalize the observed correlations between the CO₂ solubility and water molecular dynamics, we need

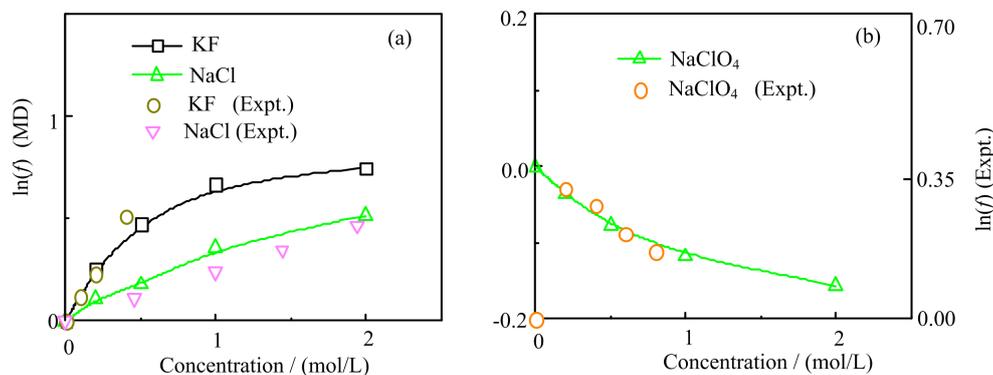


FIG. 1 The values of $\ln(f)$ in Setchenow salting-out equation calculated with Eq.(10) for the MD simulations in KF, NaCl and NaClO₄ aqueous solution at 0.02, 0.05, 1.00, and 2.00 mol/L. The corresponding experimental values are taken from Refs.[32, 33].

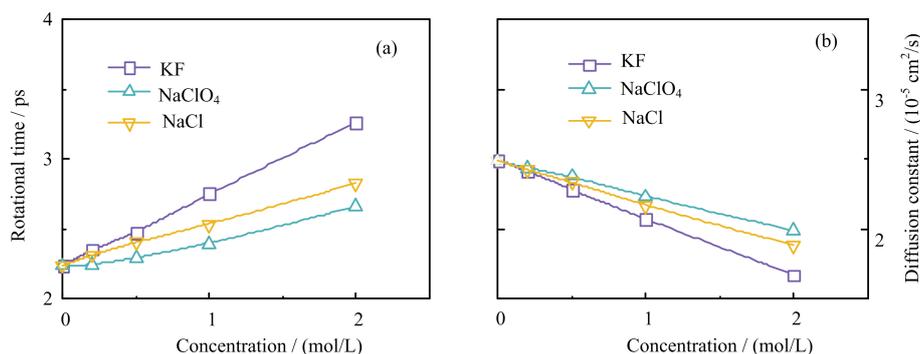


FIG. 2 (a) The rotational time of water and (b) the self diffusion constants of water in KF, NaCl and NaClO₄ aqueous solution at 0.2, 0.5, 1.00, and 2.00 mol/L.

to relate the solubility with a molecular structure factor. According to the Kirkwood-Buff theory [16, 35], the Setchenow salting-out coefficient (the slope of Setchenow equation in Eq.(10)) is proportional to the first order derivative of the chemical potential of carbon dioxide in electrolyte solution (Eq.(11)), when the concentration of carbon dioxide approaches zero and at constant pressure P and temperature T [16, 35].

$$\lim_{\rho_C \rightarrow 0} \left(\frac{\partial \mu}{\partial x_S} \right)_{T,P} = \frac{RT(\rho_W + \rho_S)}{\eta} (G_{CW} - G_{CS}) \cong K_S C_S \quad (11)$$

where x and C is the molar fraction density and the molarity of salt. ρ_W , ρ_S , and ρ_C are the number densities of water, salt, and carbon dioxide. R is the gas constant. G_{CW} and G_{CS} are the CO₂-water and CO₂-salt KB integrals (KBIs), which are defined as:

$$G_{ij} = \int_0^\infty 4\pi [g_{ij}(r) - 1] r^2 dr \quad (12)$$

$g_{ij}(r)$ is the pair radial distribution function between components i and j .

η is a positive constant at the limit of concentration

of CO₂ for ideal solution.

$$\eta = \rho_W + \rho_S + \rho_W \rho_S (G_{WW} + G_{SS} - 2G_{SW}) \quad (13)$$

where $G_{WW} + G_{SS} - 2G_{SW} = 0$ in ideal solutions. At this condition, the term $(G_{CW} - G_{CS})$ in Eq.(11) can be used to examine the salting effect on the solubility.

The radial distribution functions $g(r)$ of water-water, CO₂-water, CO₂-anion and CO₂-cation pairs, are shown in FIG. 3. There are weak changes observed for the water-water and CO₂-water radial distributions at different salt solutions. In aqueous solutions, F⁻, Cl⁻, K⁺ and Na⁺ stay far away from the carbon dioxide, which is suggested by lower first solvation peaks (<1) of their CO₂-anion and CO₂-cation radial distribution functions. There is lower possibility to directly bind to carbon dioxide for them. The salting-out effect of KF and NaCl on the solubility CO₂ is imposed by the surrounding solvent water in an indirect way. The large positive value $(G_{CW} - G_{CS})$ is observed in KF, NaCl solutions (FIG. 4). This means that the affinity between CO₂ and water is higher than that between water molecules themselves.

In the solution of NaClO₄, there is a much stronger short-range correlation, within first solvation shell, observed for the CO₂-ClO₄⁻ pair than the CO₂-water pair

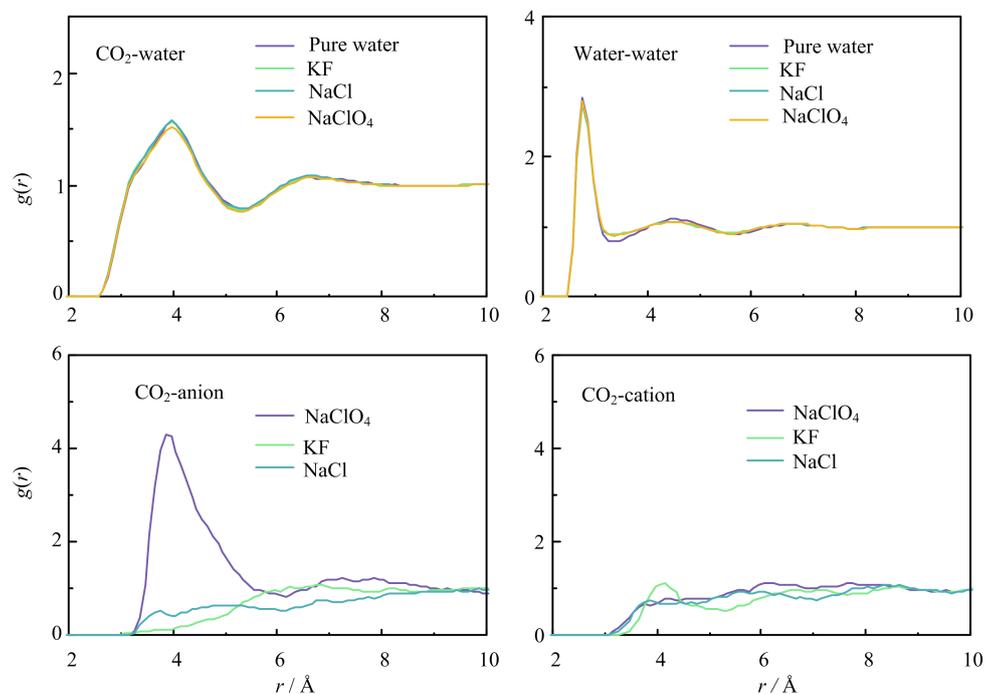


FIG. 3 The radial distribution functions of CO₂-water, water-water, CO₂-anion and CO₂-cation pairs in KF, NaCl and NaClO₄ aqueous solution at 0.5 mol/L.

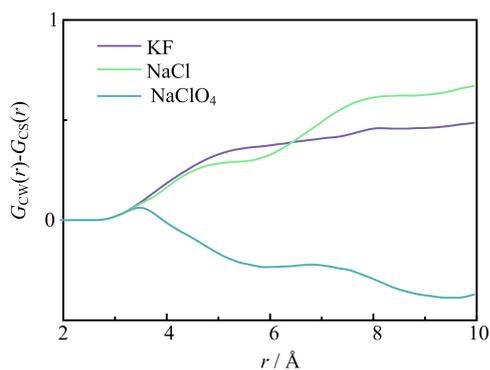


FIG. 4 The values of the Kirkwood and Buff integrations ($G_{CW}-G_{CS}$) in KF, NaCl and NaClO₄ aqueous solution at 0.5 mol/L.

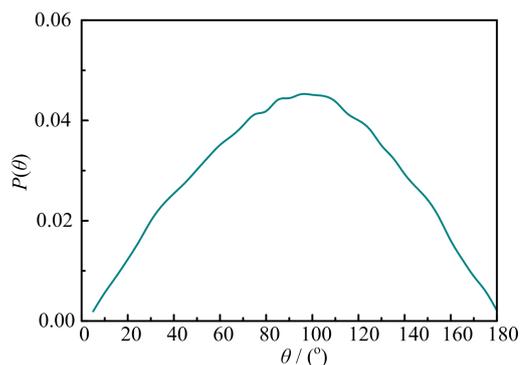


FIG. 5 The orientation of carbon dioxide around ClO₄⁻ in NaClO₄ aqueous solution at 0.5 mol/L.

in FIG. 3. Additionally, a negative value ($G_{CW}-G_{CS}$) is found for NaClO₄. Given the connection between the salting-out coefficient and the microscopic structure ($g(r)$) in Eq.(11), the direct binding is the main factor for the salting-in effect of NaClO₄ on the solubility of carbon dioxide. On the other hand, the mobility of water is retarded by NaClO₄. The structure analysis therefore suggests that the specific interaction of CO₂-ClO₄⁻ leads to the controversial expectations according to the Hofmeister Series and the ion induced water dynamics for NaClO₄.

A further analysis is made for the orientation of CO₂ within the first solvation shell of ClO₄⁻ according to

the anion-water radial distribution. The orientation is described by the angle of the vector of C=O bond (the nearest oxygen atom of CO₂ from the chloride atom) of CO₂ and the Cl-O bond vector (the nearest oxygen atom of ClO₄⁻ from the carbon atom) of ClO₄⁻ in FIG. 5. The orientation angle (θ) has the highest population around 90°. This means that CO₂ molecule prefers a perpendicular orientation to the nearest Cl-O bond around ClO₄⁻. Namely, it tends to be tangent to the surface of ClO₄⁻ sphere.

IV. CONCLUSION

In this work, the chemical potential of carbon dioxide in electrolyte solutions and pure water, the rotational

time of water and the self diffusion constant of water, as well as the microscopic structures in aqueous KF, NaCl and NaClO₄ solutions, are explored to uncover the salting-in or salting-out mechanism of different salts by molecular simulations. Hofmeister Series and the viscosity B-coefficients both can reasonably predict the salting-out ability of salt and the dynamic properties induced by salt respectively. However, it is not consistent for some salting-in salts like NaClO₄. The mechanism is due to the role of water in the solubility of carbon dioxide. The salt-out salt like NaCl and KF usually reduces the solubility of carbon dioxide by making the water more structuring than pure water, which results in the non-polar CO₂ uncomfortably in electrolyte solution relative to in pure water. The salting-out salts reduce the solubility of CO₂ by the indirect way, but the salting-in effect is more specific and complex than the salting-out effect of ions. A specific direct interaction between anion and CO₂ is the real reason for the salting-in effect like NaClO₄, according to the Kirkwood and Buff theory. This indicates that we can't predict the salting-in or salting-out effect by the viscosity B-coefficients of salts, which is valid most for salting-out salts.

V. ACKNOWLEDGMENTS

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