

# Study on the Structure of Potassium Chloride Aqueous Solution by Molecular Dynamics and Raman Spectroscopy Methods

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Study of aqueous solution micro structure is conducive to the development of water treatment materials. In this paper, molecular dynamics simulation of structure of dilute KCl aqueous solutions at 298 K was systematically carried out using the COMPASS force field. Based on simulation results, when the concentrations of KCl are 0.01 M, 0.05 M, 0.10 M, 0.50 M, 0.75 M, 1.00 M and 2.00 M, the coordination numbers of K<sup>+</sup> are 6.43, 6.41, 6.41, 6.36, 6.27, 6.24, and 5.73. Raman spectrum has been performed on this series of solutions. It revealed that the hydrogen bonds between water molecules were almost the same as that in pure water when the concentrations were below 0.10M. While at 0.50 M, 0.75 M, 1.00 M, and 2.00 M, the hydrogen bonds were obviously disturbed. The results obtained by Raman spectrum can directly support the simulation results. In general, it was speculated that the structure tends to be steady in dilute KCl solutions when the concentration is lower than 0.10 M.

## 1. Introduction

There are various water treatment materials. Such as Nanoporous Electrodes (Sechi et al., 2016) and Bimetallic Nanoparticles (Muradova et al., 2016). Interactions between waters and ions in aqueous solution system can direct the development of those water treatment materials. The aim of this paper is to get the KCl aqueous solution structure, which is conducive to effectively extract potassium from the aqueous solution. Coordination numbers for K<sup>+</sup> in aqueous solution, which obtained by Monte Carlo–Metropolis statistical thermodynamic computer simulation were  $6.27 \pm 0.25$  (Li et al., 2015). Those resulting from MD simulations were 6.1 (Zhou et al., 2002). Results received from X-ray and Neutron diffraction were 5.3 (Lawrence and Kruh, 1967) and 8 (Fishkis and Soboleva, 1974). These results exhibited a rather diversified picture.

Nowadays, progress in computer resources allows more scientists performing simulations for more sophisticated method, such as QM/MM (Azam et al., 2009), CPMD (Liu et al., 2010) etc. Azam et al. (2009) used quantum mechanical charge field (QMCF) approach to resolve the problem of constructing potential functions between the particles in the QM region and molecules in the MM zone. The coordination numbers of potassium (in KCl aqueous solution) obtained from “classical” QM/MM and QMCF assisting QM/MM were 6.2 and 6.8.

Sun et al. (2010) have recorded the Raman spectrum of NaCl-H<sub>2</sub>O, KCl-H<sub>2</sub>O, CaCl<sub>2</sub>-H<sub>2</sub>O, MgCl<sub>2</sub>-H<sub>2</sub>O and NaCl-KCl-CaCl<sub>2</sub>-H<sub>2</sub>O, and they found there is an equilibrium phenomenon between various structural species, and the equilibrium constant was obtained. Chumaevskii et al. (2001) has received the Raman spectrum of H<sub>2</sub>O and aqueous solutions of LiCl, NaCl, KCl, RbCl and CsCl, and a model of five-molecule unit was raised. The structure of hydrated K<sup>+</sup> still escape consistent experimental results for different scientists, which is caused by the fact that the ion-water distance of K-O<sub>water</sub> is very close to the O-O distance in bulk water. Molecular dynamics simulation, which can model a real experiment, could provide quantitative information of KCl aqueous solution. Simulation study of dilute aqueous KCl solutions is not comprehensive in the literature. The authors carried out a structural investigation of aqueous KCl solutions with the concentrations ranging from 0.01 M to 2.00 M by means of MD simulation and Raman spectrum. The results received from simulation was compatible with the experimental data (Soper and Weckström, 2006).

## 2. Simulation and experiment

### 2.1 Simulation details

The essential methods of molecular dynamics study are same as our previous works (Zhou et al., 2011). They are described briefly for the reader's convenience.

Molecular dynamics simulations were performed on an individual workstation (HP, xw8600). NVT ensemble was performed at an average temperature of 298 K. KCl solutions were ranging from 0.01 M to 2.00 M in the simulations. The concentrations of the KCl solutions were adjusted by the numbers of water molecules and ions. A cubic box of 5,536 waters and 1 KCl was constructed for the 0.01 M solution. Periodic boundary condition was applied. The cubic boxes were energy minimized using 10,000 steps of Newton minimization. The ion-ion and ion-water interactions were represented by Lenard-Jones potentials. Van der Waals interactions and electrostatic interactions were calculated by Atom-based method and Ewald summation method. Nose-Hoover thermostat was used to control the temperature. The total time of the simulation was 300 ps with a time step of 1fs. Atomic properties, such as energies, atomic coordinates and velocities were recorded every 100 time steps (0.1ps). The first 100 ps was used to equilibrate the system, while the last 200 ps was used to record various properties, which is used for later analysis.

### 2.2 Raman spectral measurements

In this work, deionized water was produced by a UP water purification system (UPHW-I90T), and its electric resistivity was 18.25 MΩ·cm. Aqueous KCl solutions were prepared with the same concentrations as the simulation systems. The solute was guarantee grade reagent. Raman spectra of KCl solutions and pure water were measured at ambient condition ( $T \approx 298$  K,  $p \approx 1$  bar).

The DXR Raman Microscope (Themo Fisher Company, America) was used to determine the solutions. The laser wavelength was 532 nm. The spectral resolution was less than  $1 \text{ cm}^{-1}$ . The exposure time was five seconds for thirty times. O-H stretching spectrum was recorded from  $2,800 \text{ cm}^{-1}$  to  $3,800 \text{ cm}^{-1}$ .

## 3. Results and discussion

### 3.1 Simulation results

#### 3.1.1. Model design and energy optimization

The initial velocities of the atoms in the model were random velocities from Boltzmann distribution. The optimized model is shown in Figure1. Cubic box representing microscopic structure of KCl solution was obtained (Red, white, purple and green balls denote O, H,  $\text{K}^+$  and  $\text{Cl}^-$ ). The numbers of ions and water molecules are determined by the concentrations of KCl solutions.

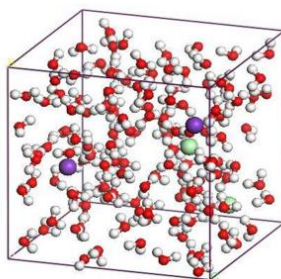


Figure 1: Structure model of the KCl solution at 298 K

#### 3.1.2. Pair distribution functions and coordination numbers

Figure 2(a) - (b) displays the pair distribution functions  $g_{ij}(r)$  of K-O, Cl-H in KCl solutions at different concentrations. The coordination numbers are defined by Eq(1) (Megyes et al., 2006).

$$n_{ij}(r) = 4\pi\rho_j \int_0^r r^2 g_{ij}(r) dr \quad (1)$$

$\rho_j$  is the atomic number density of the j atom. The characteristic properties of these PDFs, such as first peak positions, coordination numbers and corresponding data from literatures are listed in Table 1. As it shown in Figure 2, the K-O PDFs indicate clear first shells with their maximum located at 2.65 Å. Integration up to the valley point (3.45 Å) following the first shell yields the first shell coordination number of 6.43, 6.41, and 6.41 for  $\text{K}^+$  in the KCl aqueous solutions at the concentrations of 0.01 M, 0.05 M, and 0.10 M.

For the concentration of 0.50 M, 0.75 M, 1.00 M, and 2.00 M, the coordination numbers are 6.36, 6.27, 6.24, and 5.73. The increasing concentration obviously influenced the height of the first peak. That is the higher concentration the lower peak height. When the concentration rose from 0.01 M to 0.10 M, there was no apparent decline of the peak height. The remarkable reduction of the peak height for the 2.00 M KCl aqueous solution compared with the lower concentrations indicates a loose structuration of this solution. As it mentioned in Obst and Bradaczek's (1996) research, for  $K^+$ , only two distinct hydration shells were observed. The lower height of the second peaks of K-O PDFs with the increasing concentration shows less pronounced second hydration shells. The changes of PDFs for Cl-H were similar with that in K-O PDFs. The first shell coordination numbers for Cl<sup>-</sup> in 0.01 M to 2.00 M KCl aqueous solutions were 6.53, 6.50, 6.49, 6.45, 6.43, 6.42, and 5.90. Similarly, clear variation is visible for the KCl aqueous solution at the concentration of 2.00 M.

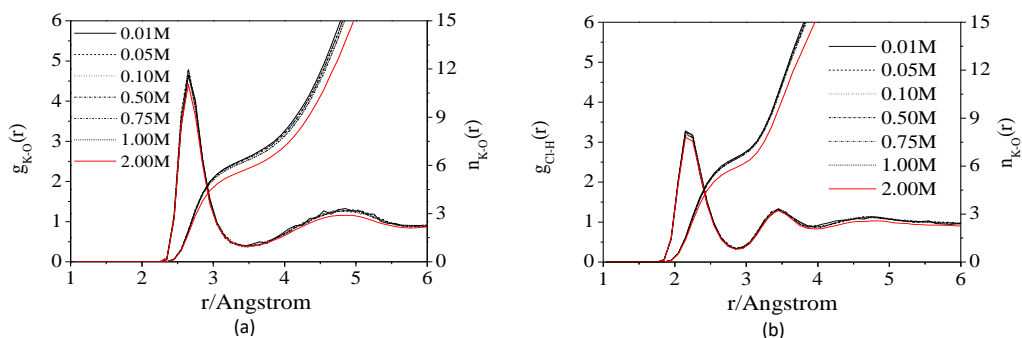


Figure 2: Pair distribution functions and corresponding  $n_{ij}(r)$  of KCl solution system at different concentrations, (a): K-O (b): Cl-H

It is necessary to notice the variation of O-O pair distribution function  $g_{O-O}(r)$  between two water molecules (Figure 3). It implied the structure changes of bulk water caused by increased concentration. If the structure of the first coordination shell is measured by the sharpness of the first peak of PDF, it can be concluded that the increase of the concentration from 0.50 M to 2.00 M leads to an obvious decrease in the structure of bulk water molecules. No apparent change is seen from 0.01 M to 0.10 M. There exists consensus among researchers that water is highly structured liquid due to an extensive network of hydrogen bonds. (Marcus, 2009) It is deduced that hydrogen bonds in KCl aqueous solution, with the concentrations from 0.01 M to 0.10 M, were identical with each other. Hydrogen bonds in 2.00 M solution were disturbed markedly comparing with those in dilute aqueous KCl solutions (0.01 M–0.10 M).

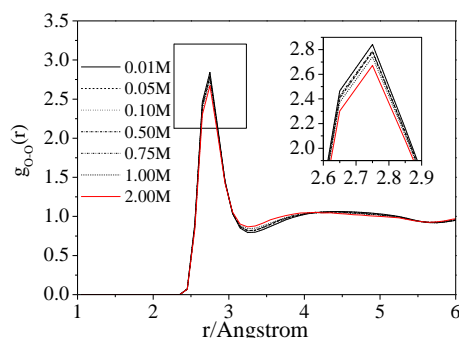


Figure 3: Pair distribution functions of KCl solution system at different concentrations for O-O

In general, the peak positions and coordination numbers listed above agrees well with the published experimental results (Table 1). Their experiments were performed at the same condition ( $T = 298$  K,  $p = 1$  bar) as our simulation. Comparison between results from this work and NDIS method performed by Soper and Weckström (2006) were reasonable and reliable. The results obtained from this work were also in good consist with that got from the more sophisticated method QM/MM and QMCF (Table 1). This consistency indicates clearly that the COMPASS force fields used in classical molecular simulations are sufficient to describe the hydration of simple metal cations.

Overall, in MD simulation study, when the concentration is below 0.10 M (include 0.10 M), the coordination shell structures around  $K^+$  did not change obviously with the increase of concentration. While the concentration of KCl aqueous solution was 0.50 M, 0.75 M, 1.00 M, and 2.00 M, apparent shape changes

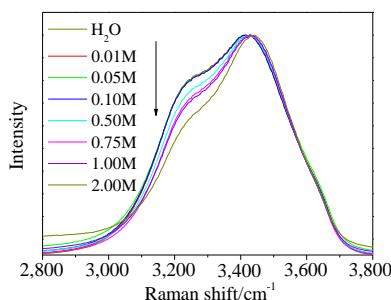
were observed. The authors proposed that water molecules around the  $K^+$  in the dilute aqueous solution (below 0.10 M) may be at the same dynamical state.

*Table 1: Comparison of first peak positions ( $r_{peak}$ ) and coordination numbers for K-O from this work and literatures*

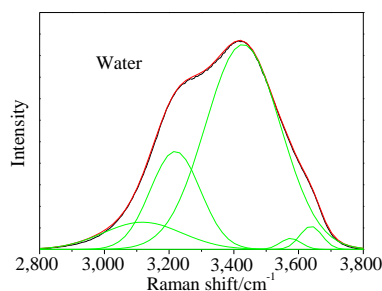
solute	Concentration	method	$r_{peak}/\text{\AA}$	$n_{KO}$	ref
KCl	0.01 M (1/5536)	MD	2.65	6.43	This work
KCl	0.05 M (1/1104)	MD	2.65	6.41	This work
KCl	0.10 M (1/552)	MD	2.65	6.41	This work
KCl	0.50 M (1/109)	MD	2.65	6.36	This work
KCl	0.75 M (1/71)	MD	2.65	6.27	This work
KCl	1.00 M (1/53)	MD	2.65	6.24	This work
KCl	2.00 M (1/26)	MD	2.65	5.73	This work
K	1/255	MD	2.86	6.1	Zhou et al. (2002)
K	1/48	CPMD	2.82	6.24	Liu et al. (2010)
KCl	1/499	QM/MM	2.8	6.2	Azam et al. (2009)
KCl	1/499	QMCF	2.8	6.8	Azam et al. (2009)
K		MC		5-7	Kistenmacher (1974)
K	1/215	MC		$6.27 \pm 0.25$	Mezei and Beveridge (1981)
KCl	1.2/100	NDIS	2.65	6.2	Soper and Weckström (2006)

### 3.2 Raman spectroscopy

To give a reliable idea of the structural properties of aqueous KCl solutions, we performed Raman spectrum study on the same concentration series described in former models.



*Figure 4: Comparison of the Raman spectrum of water and KCl solutions*



*Figure 5: Gaussian deconvolution of Raman spectrum into five sub-bands for pure water*

Raman spectra (2,800–3,800  $\text{cm}^{-1}$ ) of pure water and KCl solution with concentration of 0.01 M, 0.05 M, 0.10 M, 0.50 M, 0.75 M, 1.00 M and 2.00 M are shown in Figure 4. With the rising concentration of KCl solution, the relative intensity of the patterns roughly at the frequency 3,264  $\text{cm}^{-1}$  decreased gradually. When the concentration of KCl solution was 2.00 M, the shoulder peak almost disappeared, and the profile of the spectrum became narrow. At the same time, the frequency of the major peak gradually shifted from 3,415  $\text{cm}^{-1}$  to 3,440  $\text{cm}^{-1}$  with the increase of the concentration. It was reported that, in Raman spectrum, O-H stretching vibration of the water molecules appears at 2,800  $\text{cm}^{-1}$  - 3,800  $\text{cm}^{-1}$  (Sun et al., 2010). According to the

reported assumption, the Raman OH stretching band can be deconvoluted by Gaussian method into two, four or five sub-bands. Recently, Sun (2013) gave a five deconvoluted fit, with the centre frequency at 3,041, 3,220, 3,430, 3,572, and 3,636  $\text{cm}^{-1}$ . In order to do a meaningful comparison, we deconvoluted the Raman pattern of pure water into five sub-bands (Figure 5) as Sun (2013) did. As it is shown in Figure 5, the OH stretching Raman spectra of water are deconvoluted into five components, whose centre frequency are 3,105, 3,219, 3,428, 3,575 and 3,638  $\text{cm}^{-1}$ . This comparison proves the data reliability of this work.

From the spectrum in Figure 5, it can be seen that the maximum position of O-H stretching vibration of water appeared near 3,415  $\text{cm}^{-1}$ , and a shoulder peak (hydrogen bonds) occurred near 3,264  $\text{cm}^{-1}$ . These results were consistent with other researches (Sun et al., 2010). Deducing from former research (Li et al., 2003), two kinds of O-H stretching vibration mode exist: inter-molecular O-H interactions and intra-molecular O-H interactions. The inter-molecular interactions make up the lower frequency shift intensity, and the intra-molecular interactions dominate the higher frequency shift intensity. Consider just illustrating the changes of inter-molecular interactions with the increase of KCl aqueous solutions, it is feasible to deconvolute the Raman spectra into two sub-bands.

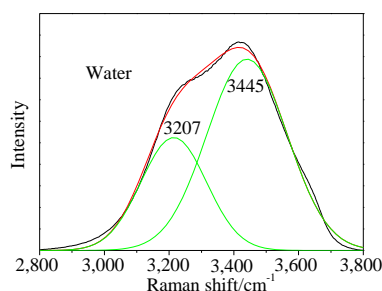


Figure 6: Gaussian fit results of the Raman spectrum into two sub-bands for pure water

Figure 6 and Figure 7 show Gaussian deconvolution of Raman spectra of pure water and shoulder peaks of KCl solutions at different concentrations. It was seen that the two peak positions of water were 3,207  $\text{cm}^{-1}$  and 3,445  $\text{cm}^{-1}$ . The hydrogen bonds are at low-frequency: 3,207  $\text{cm}^{-1}$ . High-frequency is the O-H stretching vibration of the intra-molecular.

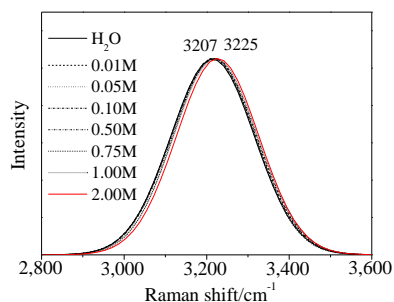


Figure 7: Shoulder peaks of KCl solutions at different concentrations

From Figure 7, it was obtained that when the concentration was below 0.10 M, the Raman shift of the shoulder peak was 3,207  $\text{cm}^{-1}$ . While the concentration increased from 0.50 M to 2.00 M, the Raman shift gradually moved to 3,225  $\text{cm}^{-1}$ . This result showed that the hydrogen bonding interactions were not changed significantly with the concentration lower than 0.10 M (include 0.10 M). Above 0.50 M, the hydrogen bonds were disturbed more and more with the increase of the concentration. At 2.00 M, the hydrogen bonding interactions were weakened most remarkably among these solutions. These results were consistent with the MD simulation results. It can be extrapolated that, when the concentration of KCl aqueous solution rose from 0.50 M to 2.00 M, the percentage of hydrogen bonded OH decreased in water. While the concentrations ranging from 0.01 M to 0.10 M, the structure of bulk water kept steady.

#### 4. Conclusions

In this work, we have investigated the structures of dilute KCl aqueous solutions by MD simulation and Raman spectroscopy. The calculated coordination numbers from this work were compared with newly NDIS

determined results, they are in good agreement. It was speculated that MD simulation could be used to predict coordination numbers for those systems, which cannot be easily determined by experimental measurements. The coordination number of  $K^+$  in 0.01 M KCl solution determined by MD simulation is useful for the interpretation of experimental data.

Raman spectra of these solutions modelled by MD simulation were tested to justify the validity of the results got from computer simulation. The Raman spectra results reproduce the tendency that hydrogen bonds between water molecules would decrease with the increase of the concentration (from 0.50 M to 2.00 M). With the concentration increase from 0.01 M to 0.10 M, few changes could be observed. This is in general accordance with the MD simulation findings in this work.

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### References

- Azam S.S., Hofer T.S., Randolf B.R., Rode B.M., 2009. Hydration of sodium(I) and potassium(I) revisited: A comparative QM/MM and QMCF MD simulation study of weakly hydrated Ions, *Journal of Physical Chemistry A*, 113(9), 1827-1834.
- Chumaevskii N.A., Rodnikova M.N., Sirotkin D.A., 2001. Cationic effect in aqueous solutions of 1:1 electrolytes by Raman spectral data, *Journal of Molecular Liquids*, 91, 81-90.
- Fishkis M.Y., Soboleva T.E., 1974. X-ray structural investigation of aqueous solutions of KI and LiI, *J. of Struct. Chem.*, 15(2), 175-180.
- Kistenmacher H., Popkie H., Clementi E., 1974. Study of the structure of molecular complexes. VIII. small clusters of water molecules surrounding  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $F^-$ , and  $Cl^-$  ions, *The Journal of Chemical Physics*, 61, 799.
- Lawrence R.M., Kruh R.F., 1967. X-Ray diffraction studies of aqueous alkali-metal halide solutions, *The Journal of Chemical Physics*, 47(11), 4758.
- Li F., Yuan J.S., Li D.C., Li S.Y., Han Z., 2015. Study on the structure of aqueous potassium chloride solutions using the X-ray diffraction and Raman spectroscopy methods, *Journal of Molecular Structure*, 1081, 38-43.
- Li R.H., Jiang Z.P., Shi S.Q., Yang H.W., 2003. Raman spectra and  $^{17}O$  NMR study effects of  $CaCl_2$  and  $MgCl_2$  on water structure, *Journal of Molecular Structure*, 645, 69-75.
- Liu Y., Lu H.G., Wu Y.B., Hu T.P., Li Q.L., 2010. Hydration and coordination of  $K^+$  solvation in water from ab initio molecular-dynamics simulation, *The Journal of Chemical Physics*, 132, 124503.
- Marcus Y., 2009. Effect of ions on the structure of water: structure making and breaking, *Chemical Reviews*, 109, 1346-1370.
- Megyes T., Bakó I., Bálint S., Grósz T., Radnai T., 2006. Ion pairing in aqueous calcium chloride solution: molecular dynamics simulation and diffraction studies, *Journal of Molecular Liquids*, 129, 63-74.
- Mezei M., Beveridge D.L., 1981. Monte Carlo studies of the structure of dilute aqueous solutions of  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $F^-$ , and  $Cl^-$ , *The Journal of Chemical Physics*, 74(12), 6902-6910.
- Muradova G.G., Gadjeva S.R., Palma L.D., Vilardi G., 2016. Nitrates removal by bimetallic nanoparticles in water, *Chemical Engineering Transactions*, 47, 205-210.
- Obst S., Bradaczek H., 1996. Molecular dynamics study of the structure and dynamics of the hydration shell of alkaline and alkaline-Earth Metal Cations, *The Journal of Physical Chemistry*, 100, 15677-15687.
- Sechi E., Vacca A., Mascia M., Palmas S., 2016. Nickel-based nanoporous electrodes for water treatment, *Chemical Engineering Transactions*, 47, 97-102.
- Soper A.K., Weckström K., 2006. Ion solvation and water structure in potassium halide aqueous solutions, *Biophysical Chemistry*, 124, 180-191.
- Sun Q., Zhao L., Li N., Liu J., 2010. Raman spectroscopic study for the determination of  $Cl^-$  concentration (molarity scale) in aqueous solutions: application to fluid inclusions, *Chemical Geology*, 272, 55-61.
- Sun Q., 2013. Local statistical interpretation for water structure, *Chemical Physics Letters*, 568–569, 90-94.
- Zhou J., Lu X.H., Wang Y.R., Shi J., 2002. Molecular dynamics simulation on ionic hydration, *Fluid Phase Equilibria*, 194–197, 257-270.
- Zhou Q., Yuan J.S., Bao J., Li F., 2011. Molecular dynamics simulation of ionic concentration effects on ionic hydration in aqueous KCl solutions, *Computers and Applied Chemistry*, 28(9), 1189-1193.