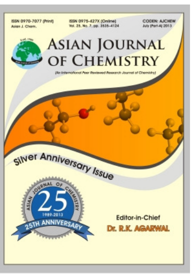
Asian Journal of Chemistry; Vol. 25, No. 11 (2013), 6109-6111

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14274



Molecular Dynamics Simulations of Aqueous Solutions of KCl at Remote Sensing Frequencies

LEI FENG[1], KE LI[2] and XIAO-QING YANG[2,*]

[1]China Academy of Engineering Physics, Mianyang 621900, Sichuan Province, P.R. China
[2]College of Electronics and Information Engineering, Sichuan University, Chengdu 610064, P.R. China

*Corresponding author: E-mail: yyxxqq_mail@163.com; likeman815@qq.com

(*Received*: 7 July 2012; *Accepted*: 29 April 2013) AJC-13413

In this study, molecular dynamics simulations of aqueous solutions of KCl at mass concentrations between 1 and 8 % and at the temperature ranges from 20 to 30 ºC were investigated. Debye relaxation spectrum equation was used to describe the frequency-dependent complex permittivity. The simulated results were compared with experimental results at 5.1 GHz and 13.6 GHz (frequencies that are commonly used by ocean remote sensing satellites) and proved to approximatively agree with the experimental results.

Key Words: Molecular dynamics, Complex permittivity, Dielectric relaxation, Aqueous solution of KCl, Ocean remote sensing.

INTRODUCTION

Seawater is a multi-electrolyte solution, the main ingredient of multi-electrolyte is sodium chloride with the mass concentration of about 78 %. It is usual to replace the seawater with the sodium chloride solution for research[1], nevertheless, many other electrolyte solutions could be ignored, such as potassium chloride, magnesium chloride, magnesium sulfate, *etc*. Thus, we carry out the study of the dielectric properties of aqueous solution of KCl at remote sensing frequencies.

Currently, most of the data of complex permittivity of aqueous electrolytes are the results from experiments[2-8], only a small part of that were obtained *via* molecular dynamics simulation[9-11]. Nevertheless, for experimental measurement of the data, the requirement of so many electrolyte specimens will consume much time for the preparation as well as the measurement. Molecular dynamics simulation method is conducted in this study to replace experimental measurement to obtain more data, the method also has the advantage of revealing molecular motions on the picoseconds time scale which is particularly important for the study of the solvation dynamics.

EXPERIMENTAL

Models and simulations: The simulations were run in the NVT ensemble on systems consisting of 540 molecules (520 water, 10 K and 10 Cl)[9] placed in a cubic box with periodic boundary conditions at temperature between 293 K and 303 K. The box length was chosen to match the experimental density of aqueous potassium chloride solutions at 293-303 K and 1 atm. The SPC/E model was used for water and the ions were modeled as charged Lennard-Jones particles[12,13] and Lennard-Jones interactions were cutoff at 1/2 box length and the long-ranged portions of the electrostatic potentials were treated by Ewald sums with conducting boundaries[14,15]. The equations of motion were integrated using the leap-frog algorithm[16] with a time step of 1 fs, while the molecular geometries were restored using SHAKE[17]. The results reported here are based on the average of 200 000 molecular dynamics time steps for each model.

Theoretical method: The theory underlying the calculation and analysis of the (frequency-dependent) dielectric properties of multicomponent systems by molecular dynamics simulations has been described earlier[18,19]. Thus, here we just briefly introduce the relevant principles used in this study and present the pertinent results.

We selected a useful monoexponential function to do fits for all raw time correlation functions $\phi(t)$[20],

$$\phi(t) = Ae^{(-t/\tau)} \quad (1)$$

where A is the parameter, τ is the relaxation time, $\phi(t)$ is time auto-correlation function of the dipole moment M, obtained from molecular dynamics simulations.

The static dielectric constant is related to the mean square fluctuations in the dipole moment M of the simulation cell by the relation[21].

$$\varepsilon_s - 1 = \frac{4\pi}{3kV}[< M^2 > + < M >^2] \quad (2)$$

where ε_s is static dielectric constant, M is the total dipole moment of the system, k is the Boltzmann's constant and V is the volume of the simulation cell. The mean-square value for

M and $< M^2 >$ can be obtained from molecular dynamics simulation with the system size of 540 particles in the conducting boundary conditions. The static dielectric constant decreases with rising temperature and increasing concentration.

Finally, frequency-dependent dielectric properties of KCl solutions were investigated, $\varepsilon(\omega) = \varepsilon'(\omega) + j\varepsilon''(\omega)$. The complex permittivities can be described by the following single Cole-Cole equation[3,4,7,8,15].

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+(j\omega\tau)^{1-\alpha}} + \frac{\sigma_i}{j\omega\varepsilon_0} \qquad (3)$$

where $\varepsilon(\omega)$ is the complex permittivity at an angular frequency ω, $\omega = 2\pi f$ and ε_s and ε_∞[7] are the limit of the permittivity at low and high frequencies respectively, ε_0 is the permittivity of free space, τ is the relaxation time, σ_i[22] is the ionic conductivity and α is the shape parameter representing symmetrical distribution of relaxation time, $0 \le \alpha < 1$, which is very small[7]. The simulated value of real $\varepsilon'(\omega)$ and imaginary $\varepsilon''(\omega)$ are presented in Figs. 1 and 2.

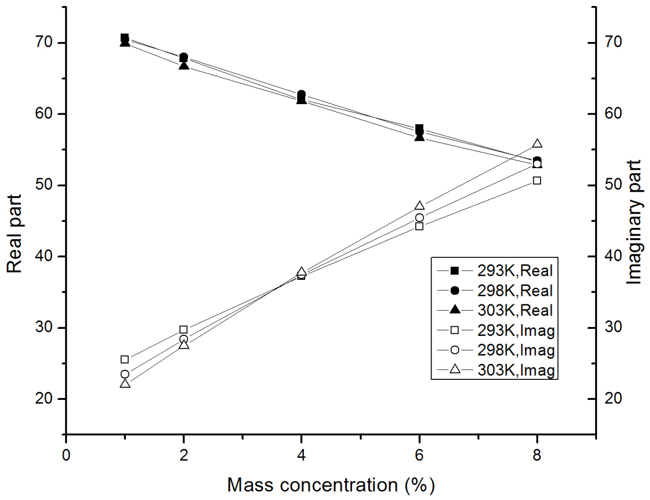


Fig. 1. Real part ε′ (closed symbols) and imaginary part ε″ (open symbols) of simulation values at 5.1 GHz

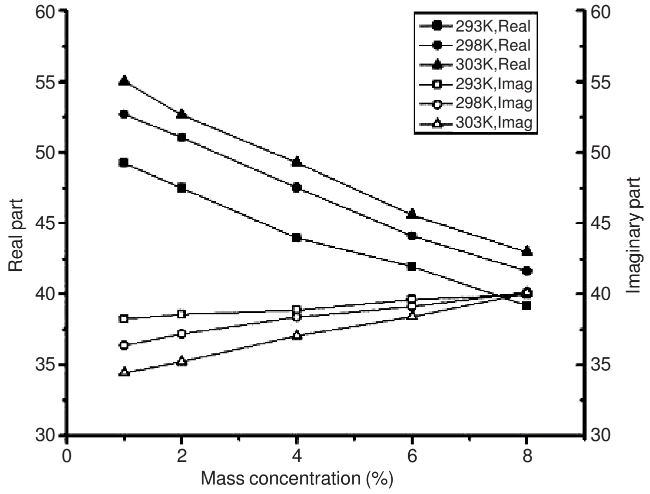


Fig. 2. Real part ε′ (closed symbols) and imaginary part ε″ (open symbols) of simulation values at 13.6 GHz

RESULTS AND DISCUSSION

Some relative experiments were carried out in order to validate the accuracy of the simulations in this study. A vector network analyzer Agilent N5230A, with an Agilent open-ended coaxial cable connected to a Agilent 85070E dielectric probe was employed to measure dielectric properties of these KCl solutions. The experimental value of real $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ imaginary are presented in Figs. 3 and 4.

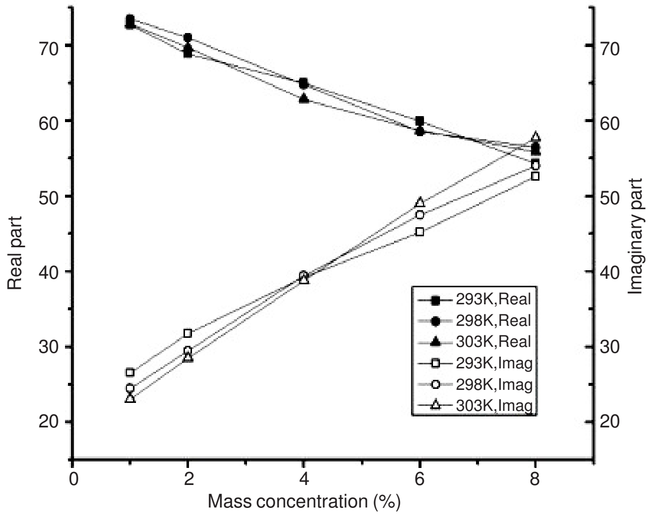


Fig. 3. Real part ε′ (closed symbols) and imaginary part ε″ (open symbols) of measure values at 5.1 GHz

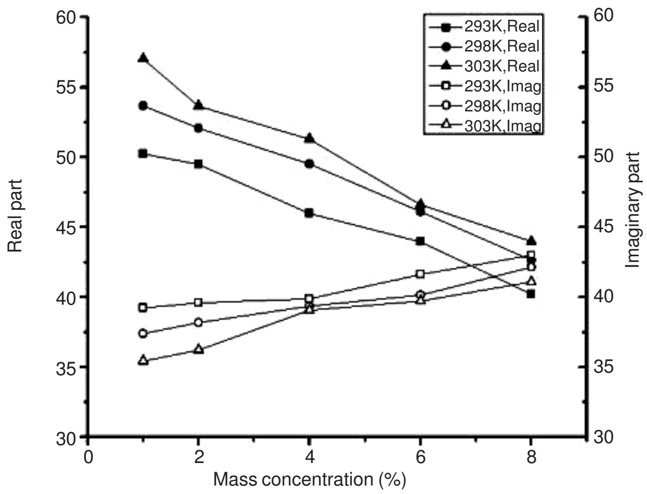


Fig. 4. Real part ε′ (closed symbols) and imaginary part ε″ (open symbols) of measure values at 13.6 GHz

The comparison of the simulated and experimental results reveals the simulated results approximatively agree with experimental results at 5.1 GHz and 13.6 GHz. The error of the simulated and experimental results can be induced from the following reasons: firstly, the error from the experimental measures is inevitable due to reflection and system loss; secondly, the time steps of molecular dynamics simulations are limited by computer performance.

Conclusion

The study on dielectric properties of aqueous solutions of KCl is also important for ocean remote sensing. The static dielectric constant, dielectric relaxation in the frequency of microwave, as well as the microwave spectra of KCl solutions have been investigated through molecular dynamics simulation and the results approximatively agree with experimental measurements. This simulation has been proved to be an efficient tool for the study of molecular processes in solutions on the picoseconds time scale under the sufficiently wide frequency range.

ACKNOWLEDGEMENTS

This project was supported by the National Science Foundation of China (No. 61001019 and No. 21076230), Major State Basic Research Development Program (No. 2013CB328900 and No. 2013CB328905) and Sichuan Province Science and Technology Plan (No. 2013GZX0149).

REFERENCES

1. R.A. Cox, in eds.: J.P. Riley and G. Skirrow, The Physical Properties of Seawater, Ch. 3 in Chemical Oceanography, New York: Academic Press, vol. 1 (1965).
2. A. Peyman, C. Gabriel and E.H. Grant, *Bioelectromagnetics*, **28**, 264 (2007).
3. R. Buchner, G.T. Hefter and P.M. May, *J. Phys. Chem. A*, **103**, 1 (1999).
4. K. Nörtemann, J. Hilland and U. Kaatze, *J. Phys. Chem. A*, **101**, 6864 (1997).
5. T. Meissner and F.J. Wentz, *IEEE Trans. on GRS*, **42**, 1836 (2004).
6. R. Buchner, G.T. Hefter and J. Barthel, *J. Chem. Soc. Faraday Trans.*, **90**, 2475 (1994).
7. T. Chen and G. Hefter and R. Buchner, *J. Phys. Chem. A*, **107**, 4025 (2003).
8. R. Buchner, G. Hefter, P.M. May and P. Sipos, *J. Phys. Chem. B*, **103**, 11186 (1999).
9. A. Yu. Zasetsky and I.M. Svishchev, *J. Chem. Phys*., **115**, 1448 (2001).
10. S. Koneshan and J.C. Rasaiah, *J. Chem. Phys*., **113**, 8125 (2000).
11. G. Hummer, D.M. Soumpasis and M. Neumann, *J. Phys.: Condens. Matter*., **23A**, A141 (1994).
12. S. Chowdhuri and A. Chandra, *J. Chem. Phys.*, **115**, 3732 (2001).
13. A. Chandra and G.N. Patey, *J. Chem. Phys*., **100**, 8385 (1994).
14. S.W. De Leeuw, J.M. Perram and E.R. Smith, *Ann. Rev. Phys. Chem*., **37**, 245 (1986).
15. Richard Buchner and Josef Barthel, *Annu. Rep. Prog. Chem*., **97**, 349 (2001).
16. M.P. Allen and D.J. Tildesley, Computer Simulation of Liquids. Clarendon Press, Oxford (1986); R.W. Hockney, *Methods Comput. Phys*., **9**, 136 (1970).
17. G. Ciccotti and J.P. Ryckaert, *Comput. Phys. Rep*., **4**, 345 (1986).
18. M.S. Skaf and B.M. Ladanyi, *J. Chem. Phys.*, **102**, 6542 (1995).
19. P. Höchtl, S. Boresch and O. Steinhauser, *J. Chem. Phys.*, **112**, 9810 (2000).
20. S. Boresch, M. Willensdorfer and O.Steinhauser, *J. Chem. Phys*., **120**, 3333 (2004).
21. J. Anderson, J. Ullo and S. Yip, *Chem. Phys. Lett*., **152**, 447 (1998).
22. A. Stogryn, *IEEE Transact. Microw. Theory Techniq.*, 733-736 (1971).