Journal of Molecular Structure 1081 (2015) 38–43

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Study on the structure of aqueous potassium chloride solutions using the X-ray diffraction and Raman spectroscopy methods

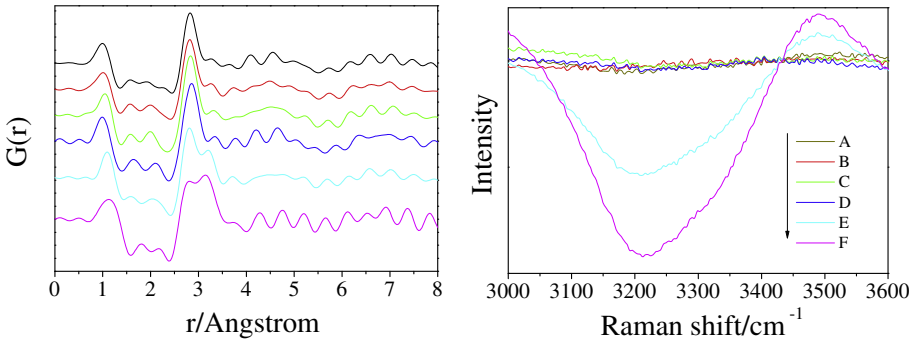
Li Fei [a,b], Yuan Junsheng [a,c,*], Li Dongchan [a,c], Li Shenyu [a,c], Han Zhen [a,b]

[a] Engineering Research Center of Seawater Utilization Technology of Ministry of Education, Tianjin 300130, China
[b] School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, China
[c] School of Marine Science and Engineering, Hebei University of Technology, Tianjin 300130, China

HIGHLIGHTS

- The KCl solution was tested by laboratory and synchrotron X-ray, and Raman spectroscopy.
- The reconstructive laboratory X-ray source is competent for testing KCl solution structure.
- Below 1.00% (include 1.00%), the structure of KCl solution was unchanged.
- Above 15.00% (include 15.00%), the structure change of KCl solution was obvious.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 July 2014
Received in revised form 20 September 2014
Accepted 20 September 2014
Available online 24 October 2014

Keywords:
Potassium chloride
Aqueous solution
Solution structure
Synchrotron
X-ray source
Raman spectroscopy

ABSTRACT

Many researchers have studied potassium chloride aqueous solutions, whereas, for the tests were carried out at different conditions, the results with diverse concentrations were not comparable. In this study, the structure of aqueous potassium chloride solutions were determined by X-ray diffraction (both using the synchrotron beam line and laboratory X-ray source) and Raman spectroscopy. Potassium chloride solutions at the concentrations ranging from 0.07% to 26.00% were systematically tested through these methods. For the solutions studied, a semi quantitative structural analysis was performed at the level of the reduced pair distribution functions (RPDFs) deduced from X-ray diffraction diagrams. The structure features can be seen directly from the RPDFs, which show systematic variations with the increase of the solutions. According to the results, when the concentration was above 15.00%, characteristic peak of K^+–Cl^- contact ion pairs was observed in the RPDFs at 3.15 Å, and their contributions became more and more significant with the increase of the concentrations. Furthermore, O–H bond lengths in water molecules are stretched with the increase of the concentration. Raman spectroscopy was carried out to support the conclusion that the hydrogen bonds in the aqueous solutions were disrupted with the increase of the potassium chloride concentration.

Introduction

Potash is an important fertilizer and industrial raw material. The solid state storage of potassium in the world is finite. Therefore, it is foresighted to pay attention to liquid resources. The composition of liquid potash (e.g. seawater) is intricate, thus,

* Corresponding author at: Engineering Research Center of Seawater Utilization Technology of Ministry of Education, Tianjin 300130, China. Tel.: +86 022 60204598; fax: +86 022 60204274.
E-mail address: jsyuan@hebut.edu.cn (J. Yuan).

http://dx.doi.org/10.1016/j.molstruc.2014.09.062
0022-2860/

potassium extraction and separation are difficult. Furthermore, the physical properties of materials are determined by their atomic structure, so the study of solution structure is conducive to effectively extract potassium from the liquid ore.

It is now over 80 years since water structure under ambient conditions has been studied using X-ray scattering. To our knowledge, people have paid attention to the influence of inorganic ions on the microscopic structure of water for a long time. Therefore, a lot of experimental [1–6] results about the coordination numbers of alkali ions in aqueous solution also have been reported between sixties and eighties in 20th century. Beside X-ray diffraction, aqueous solutions of alkali ions were investigated by many scientists through computer simulations [7–20]. In the early days, unavoidably, there were shortcomings in the early experiments. Thus, in recent years, experimental [21–24] and theoretical investigations [25–32] about potassium ion have increased, which shows that it has become again a popular investigation target.

With the substantial improvements of experimental techniques and data analysis strategies over the past 10 years, researchers drew their attention back to neutron and X-ray scattering method again [22]. Mancinelli et al. [23,24] and Soper and Weckström [21] have used these two methods to investigate the hydration structure of potassium ions in aqueous solution at the ISIS pulsed neutron source (UK). The concentration of most dilute solution in their study was 1.2 ion pairs per 100 water molecules. Soper and Weckström built a three dimensional model of the scattering system consistent with the scattering data using the method of empirical potential structure refinement (EPSR) [21]. Their results showed that, for the potassium ions, the ion hydration number is around 6 water molecules and is fairly stable as a function of concentration, with possibly a slight decrease with increasing salt concentration.

In addition, Spectroscopic methods such as NMR [33–35], EXAFS [36], femtosecond spectroscopy [37–41], Raman spectroscopy [42–48], etc., have been crucial in obtaining structural information of aqueous solution. Sun et al. [44] has recorded the Raman spectrum of NaCl–H_2O, KCl–H_2O, $CaCl_2$–H_2O, $MgCl_2$–H_2O and NaCl–KCl–$CaCl_2$–H_2O, and they found there is an equilibrium phenomenon between various structural species, and the equilibrium constant was obtained. Chumaevskii et al. [42] has received the Raman spectrum of H_2O and aqueous solutions of LiCl, NaCl, KCl, RbCl and CsCl, and a model of five-molecule unit was raised.

Despite much of efforts did by the researchers, the structure of aqueous potassium chloride solutions with different concentrations were not determined systematically, especially for extremely dilute solution. For the test were carried out at different conditions, the results with diverse concentrations were not comparable. Therefore, we carried out, by means of X-ray diffraction and Raman spectroscopy method, a structural investigation of aqueous potassium chloride solutions with the concentrations ranging from 0.07% to 26.00%. It was delightful to highlight that these methods were found to perform very well in describing the structure variation of aqueous potassium chloride solutions with different concentrations.

The outline of the paper is as follows. In the next section we describe some details of the apparatus and experiments. In 'Results and discussion', we discuss the microstructure of the solutions in term of reduced structure functions $F(Q)$, reduced pair distribution functions $G(r)$, and results of Raman spectra. Conclusions and remarks are presented in section 'Conclusions'.

Details of the experiment

Sample preparation

In this letter, deionized water was produced by a UP water purification system (UPHW-I90T), and its electric resistivity was 18.25 MΩ cm. Various aqueous potassium chloride solutions, with the concentrations ranging from 0.07% to 26.00%, were prepared. The solute was guarantee grade reagent (Guangfu Fine Chemical, 99.99% purity) and was used without further purification. The concentrations and densities of the solutions studied are shown in Table 1. The acronyms of these solutions will be used hereafter in this text. X-ray diffraction and Raman spectra data were recorded at room temperature.

Details of the synchrotron X-ray beam line

X-ray diffraction data were recorded in the Shanghai Synchrotron Radiation Facility (Shanghai, China), using Huber 5021 six-circles diffractometer on beam line BL14B1. The sample is 40 m away from the source. A sagittal double crystal monochromator Si (1 1 1) was used to produce an X-ray beam with the energy at 18 keV (corresponding to a wavelength of $\lambda = 0.6889$ Å), with energy resolution 2×10^{-4}@ 10 keV. This incident energy of X-ray photons allowed the Q (diffraction vector $Q = 4\pi \sin\theta/\lambda$) reach up to 17 $Å^{-1}$. The scattering radiation was collected by a CsI scintillation crystal detector. The samples holder was a thin walled (0.01 mm) special glass capillary (Charles super company) with a diameter of 1.5 mm, which can efficiently avoid sample container scattering. A goniometer was used to allow precise placement of the capillary tube on the goniometer axis. The scattering angle of this measurement was between 2° and 150° corresponding Q value was between 0.3 and 17.6. The data were collected with an angle step of 0.2°/step. Over 100,000 counts were taken for each step by the CsI detector.

Details of the laboratory X-ray source

The laboratory X-ray facility used in this study was D8 Focus produced by Bruker. The detector installed on the laboratory XRD system was called LYNXEYE, which can record a high quality data in approximately 1/200th of the time required using a point detector. Original assembled goniometer of this equipment was a vertical Bragg–Brentano geometry. In order to solve the background deduction problem, we choose special glass capillary as sample holder. Therefore, a rotating sample stage system (Fig. 1) was designed special for D8 Focus to accomplish capillary geometry (Fig. 2). As it is shown in Fig. 1, the central parts of this system are as follows, I: rotating stage (self-designed); II: capillary; III: microscope; IV: goniometer head; V: X-ray tube; VI: detector. In this measurement, D8 Focus was equipped with an X-ray tube with a molybdenum anode ($K\alpha$ radiation $\lambda = 0.7107$ Å). The scattering angle was the same as that on synchrotron beam line.

Raman spectral measurements

The potassium chloride solutions were the same sample as used in the X-ray diffraction measurement. Additionally, the Raman spectra of pure water at the same condition were also recorded. The DXR Raman Microscope (made by ThemoFisher Company in

Table 1
Physical properties of potassium chloride solutions studied.

Sample name	Mass percentage wt%	Molarity mol/L	Density g cm^{-3}	KCl: H_2O
A	0.07	0.94×10^{-2}	0.9966	1: 5874.9
B	0.21	0.28×10^{-1}	0.9969	1: 1971.5
C	0.42	0.56×10^{-1}	0.9985	1: 983.4
D	1.00	0.13	1.0001	1: 410.0
E	15.00	2.20	1.0923	1: 23.5
F	26.00	4.08	1.1698	1: 11.8