An EXAFS Investigation of Local Structure around Rb^+ in Aqueous Solution

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EXAFS spectra have been measured in order to elucidate the local structure around Rb^+ in aqueous solution. It has been found that the Rb^+ is surrounded by ca. six O atoms of H_2O molecules. The Rb–O distance was determined to be 2.90 (3) Å. The coordination number and Rb–O distance compare well with those of the other alkaline metal ions estimated by X-ray diffraction.

1. Introduction

The local structure around various metal ions in aqueous solution has been studied with NMR, X-ray and neutron diffraction techniques [1–7]. Vorgin et al. have reported that on the basis of the NMR spectrum of RbOH in aqueous solution the coordination number, N, of H_2O around Rb^+ is 3.5 [1]. However, it has been pointed out that N was underestimated owing to the weak magnetic interactions between Rb^+ and H_2O [2]; N and the interatomic distance were estimated to be 5 and 2.89 Å, respectively, by molecular dynamics simulation [6–8]. The interatomic distance, r, around Rb^+ in aqueous solution has not been determined experimentally so far.

In the present paper, the local structure around Rb^+ in dilute aqueous solution determined by Rb K-edge extended X-ray absorption fine structure (EXAFS) method is reported.

2. Experimental

EXAFS measurements were performed by using synchrotron radiation from the Photon Factory (PF) at the National Laboratory for High-Energy Physics (KEK, Tsukuba) [9]. The concentration of the solution was 1.0×10^{-2} mol dm^{-3}. As reference samples we measured the EXAFS spectra of solid RbOH and rubidium hydrogen succinate ($RbC_4H_5O_4$; RHS). EXAFS spectra were collected in transmission mode, using beamline BL-7C with two Si(111) flat crystal monochromators in ring operating condition of 2.5 GeV and a ring current 350–200 mA. The photon energy, E, was calibrated with a Cu foil by assigning 8.9788 keV to pre-edge on its absorption edge.

3. Results and Discussion

The EXAFS oscillations, $\chi(k)$, were extracted from the absorption spectra using standard procedures [10]. The programs "XAFS93" and "MBF93" were employed for the EXAFS data analyses [10]. Figs. 1 (a) and (b) show the Fourier transforms, $\Phi(r)$, of the EXAFS oscillations, $k^3 \chi(k)$, of RbOH aqueous solution and solid RbOH at 300 K. The Fourier transforms were performed in the k-range of 1.450–11.100 Å^{-1} and 1.500–8.000 Å^{-1} for $k^3 \chi(k)$ of the aqueous solution and the solid, respectively. The $\Phi(r)$'s of both samples exhibit a pronounced peak around $r = 2.2$ Å corresponding to the nearest neighboring atoms. The X-ray structural analysis of solid RbOH shows that the Rb^+ is coordinated by six O atoms [11]. Thus, the peaks are attributed to the Rb–O scattering. The coordination number, N, and the Rb–O distance, r,

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around Rb^+ in RbOH aqueous solution were obtained by applying the filtering technique [10] to the pronounced peak which corresponds to the range of 1.640–2.510 Å. EXAFS oscillations, $\chi(k)$, are described by the single scattering theory [12–14]. A nonlinear least-squares fitting was applied to the filtered data according to the theoretical equation [14]

$$\begin{aligned}\chi(k) &= \Sigma N_j f_j(k;\pi) \exp[-2r_j/\lambda_j(k)] \exp[-2k^2 \sigma_j(2)] \\ &\quad \times \sin[2kr_j - (2k/r_j)(1 + 2r_j/\lambda_j(k))\, \sigma_j(2) \\ &\quad + \delta_j(k)]\, (kr_j^2)^{-1}, \\ k &= [2m(E-E_0)/\hbar^2]^{1/2},\end{aligned}$$

where k denotes the wave number of the photoelectrons. Each shell, j, has N_j scatterers at a distance r_j from the absorbing atom. The Debye-Waller term, $\sigma_j(2)$, indicates the mean-square relative displacement between the absorbing and backscattering atom. $\lambda_j(k)$ is the mean free path of the photoelectron. $f_j(k;\pi)$ is the backscattering amplitude of atom j, and $\delta_j(k)$ the total phase shift experienced by the excited photoelectron as it travels between the absorbing atom and its neighbors. Theoretical values were used for $f_j(k;\pi)$ and $\delta_j(k)$ [15].

The analysis of EXAFS spectrum of RbOH aqueous solution was carried out with $\lambda(k) = 1.486\,k$, estimated from the EXAFS spectrum of RbOH powder. N and r around Rb^+ in the RbOH aqueous solution have been determined to be 6.6(1.2) and 2.88(5) Å, respectively. Furthermore, we have tried to determine N and r with $\lambda(k) = 1.677\,k$ estimated by using the structural parameters of RHS, in which the Rb^+ is coordinated by eight O atoms [16]. Similar results of $N = 6.3\,(1.1)$ and $r = 2.92\,(2)$ Å were obtained. All best-fit parameters are collected in Table 1. The present results are comparable with those reported for K^+ and Cs^+ in aqueous solutions by means of X-ray and neutron diffraction methods; $N = 6-8$ and $r = 2.60-2.95$ Å for K^+ [2, 3, 7, 17–21], and $N = 6-8$ and $r = 2.95-3.15$ Å for Cs^+ [4, 7, 17, 22, 23]. It is worthwhile to point out that the present EXAFS investigation is performed on dilute aqueous solution. The previous investigations of the local structure around alkaline metal ions in aqueous solition were made at the concentration higher than ca. 1.0 mol dm^{-3}, in which case the counter anion might affect the local structure [7].

Consequently, it can be concluded that the N and r around Rb^+ in aqueous solution is approximately six and 2.90 (3) Å, respectively. The results are consistent with those estimated by molecular dynamics [6–8]. The effective ionic radius, r_{eff}, of Rb^+ in aqueous solution is estimated to be 1.66 Å by subtracting the r_{eff} of a water molecule adjacent to the cation, 1.24 Å [24], from the observed Rb–O distance. The r_{eff} is in good agreement with that determined by Heyrovska [24]. The r_{eff} in aqueous solution is larger than the Pauling radius of Rb^+, 1.48 Å, in crystal [25], while it agrees with that given by Shannon, 1.66 Å [26].

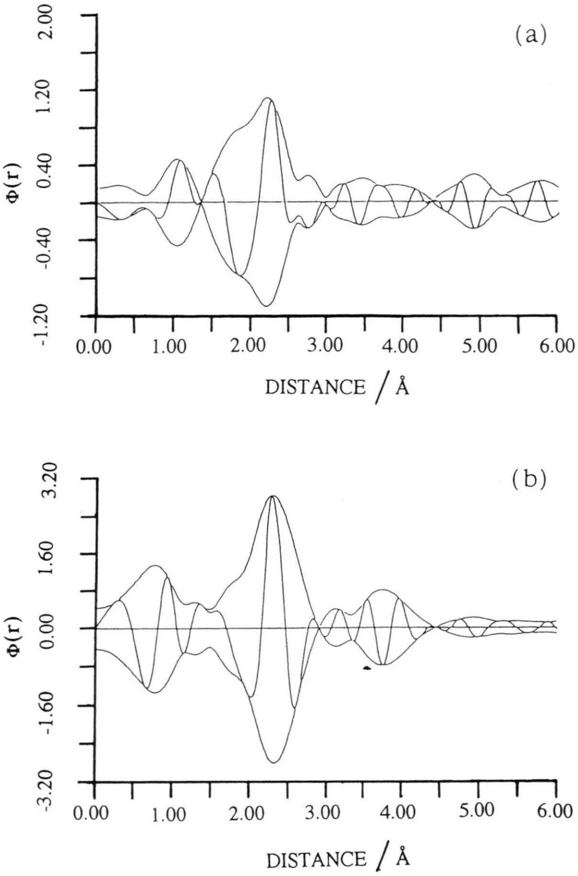

Fig. 1. Magnitude (envelope) and imaginary part of the Fourier transform, $\Phi(r)$, of the EXAFS oscillations at the Rb K-edge absorption in (a) aqueous solution of RbOH and (b) solid RbOH at 300 K.

Table 1. Best-fit least-squares refined interatomic distances (r), coordination number (N) and Debye-Waller factors ($\sigma(2)$) with standard deviations in parentheses.

Sample	T(K)	r_{Rb-O}(Å)	N	$\sigma(2)$(Å^2)	$\lambda(k)$(Å)
RbOH soln.[a]	300	2.88(5)	6.6(1.2)	0.035(4)	1.486 k
RbOH soln.[b]	300	2.92(2)	6.3(1.1)	0.035(4)	1.677 k

[a] The $\lambda(k)$ of RbOH is employed.
[b] The $\lambda(k)$ of $RbC_4H_5O_4$ is employed.

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