Dynamics of the Sulfate Ion in Dilute Water-DMF Solutions

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Z. Naturforsch. **50a**, 7–10 (1995); received November 4, 1994

Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

The Raman band of the $\nu_1(A_1)$ mode of SO_4^{2-} of Li_2SO_4 dissolved in water and water-dimethylformamide mixtures was measured in the concentration range 0.01 to 0.2 mol · dm^{-3}. The central frequency of the sulfate ion increases with sulfate concentration. The limiting frequency at infinite dilution depends on the DMF content. The Raman band becomes asymmetric with increasing concentration of Li_2SO_4 in 20 wt% DMF mixtures and with addition of LiCl to the aqueous solution of Li_2SO_4. The vibrational relaxation behavior of the $\nu_1(A_1)$ mode was investigated by analyzing the vibrational correlation function based on Kubo's stochastic theory.

Introduction

Sulfate ions in aqueous solution associate with divalent cations, forming solvent-separated and/or contact ion pairs. Ultrasonic measurements have confirmed this [1]. The formation of ion pairs influences the arrangement and motion of the nearby water molecules, thus affecting the shape, central frequency, half-width, and intensity of the Raman line. Daly et al. [2] and Davis et al. [3, 4] have observed an asymmetry of the $\nu_1(A_1)$ band of SO_4^{2-} in aqueous solution of $MgSO_4$ and have assigned the shoulder near the $\nu_1(A_1)$ mode to a Raman band due to the formation of contact ion pairs. In our previous work [5, 6] we have investigated the Raman line shape of the $\nu_1(A_1)$ mode of SO_4^{2-} of various sulfates with monovalent, divalent and trivalent cations in water and have found that the shoulder or asymmetry of the mentioned Raman band is not limited to II–II type electrolytes and is not due to the formation of contact ion pairs but rather to the inhomogeneity of the environment around sulfate ion. However, our previous work has been carried out at concentrations >0.5 mol · dm^{-3}, where it is difficult to eliminate the effect of cation-cation interactions.

In this work we have investigated the dynamics of SO_4^{2-} in water-DMF mixtures in order to carity the origin of the asymmetry of the Raman band in the $\nu_1(A_1)$ mode. In particular, we concentrated on the behavior of SO_4^{2-} at concentrations below 0.2 mol · dm^{-3} SO_4^{2-} in order to reduce the inter ionic interactions.

Experimental

Samples: The guaranteed grade Li_2SO_4 and LiCl were used without further purification. Dimethylformamide (DMF) was of spectral grade.

Raman Spectroscopy: Polarized Raman spectra $I_{\parallel}(\omega)$ are measured, using a laser Raman spectrometer (NR-1800, Japan Spectroscopic Co., Ltd) and an argon ion laser (GLG 3300, N.E.C. Co., Ltd) which is operated at 514.5 nm with an output power of 300 mW. The Raman spectra, which are assigned to symmetric SO_4 stretching, were recorded in the frequency range 960 to 1000 cm^{-1} with a slit width of 1 cm^{-1}. The concentrations of SO_4 ranged from 0.01 to 0.2 mol · dm^{-3}. As the half-width of the Raman line is > 6 cm^{-1}, the broadening effect by the slit width is negligible. If the depolarization ratio of the SO_4 stretching is very small, one can assume that the polarized Raman line shape nearly equals the isotropic Raman line shape, $I_{iso}(\omega)$, which involves an information on the vibrational relaxation only.

Vibrational Relaxation: Several interpretations of the isotropic Raman line broadening have been proposed [7–9]. The dephasing model based on binary collisions [7] has been applied to organic liquids if a Raman line shape is expressed by a single Lorentzian function. In electrolyte solutions, however, most of

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Raman bands [5, 6, 10–12] are reproduced by the convolution of Lorentzian and Gaussian functions. In addition, the dephasing model involves an ambiguous parameter, the interaction parameter, which is difficult to obtain experimentally and is estimated from the molecular diameter [7]. Rothschild [9] has derived the following general expression for the vibrational correlation function on the basis of Kubo's stochastic theory:

$$\phi_{\text{vib}}(t) = \exp\left\{-M_2\left[\tau_c^2\left(\exp\left(-\frac{t}{\tau_c}\right)-1\right)\right]+\tau_c t\right\}, \tag{1}$$

where τ_c is the modulation time, which is the correlation decay of the perturbation Hamiltonian, and M_2 is the vibrational second moment given by

$$M_2 = \int_{-\infty}^{\infty} (\omega-\omega_0)^2 I(\omega-\omega_0)\,\mathrm{d}(\omega-\omega_0) \Big/ \int_{-\infty}^{\infty} I(\omega-\omega_0)\,\mathrm{d}(\omega-\omega_0). \tag{2}$$

$I(\omega-\omega_0)$ is the Raman line shape centered at the peak frequency ω_0. In the case of SO_4 stretching, the vibrational correlation function can be obtained from the Fourier transformation of the polarized Raman band. The system shows either the fact or slow modulation, depending on whether

$$M_2^{1/2}\tau_c \ll 1 \quad \text{or} \quad \gg 1\,. \tag{3}$$

Results

The frequencies at maximum intensity and the half-widths of the $\nu_1(A_1)$ band of SO_4^{2-} are summarized in Table 1. In [5] we have reported the asymmetry in the $\nu_1(A_1)$ band for Li_2SO_4 concentrations > 0.6 mol · dm^{-3} in water. However, in the concentration range investigated here, the Raman line is symmetric within experimental error. As pointed out previously [5], the asymmetry of the Raman band appears in the presence of an excess of lithium ions, which affects the arrangement and motion of the water molecules around the SO_4^{2-} ions. Figure 1 shows the slight asymmetry of the Raman band occurring when LiCl is added an aqueous solution of 0.1 mol · dm^{-3} Li_2SO_4. In water-DMF mixtures, the electrostatic interaction between the ions increases with increasing DMF content as a result of the reduction of the dielectric constant of the solvent. Figure 2 shows the Raman spectra of the SO_4 stretching mode for 20 wt% DMF.

Table 1. The peak frequency, half-width, second moment and fitting parameter τ_c of the $\nu_1(A_1)$ mode of Li_2SO_4 in water-DMF mixtures. * Ref. [6].

Solvent	Conc. mol · dm^{-3}	Freq. cm^{-1}	Half-width cm^{-1}	M_2 cm^{-2}	τ_c ps	$M_2^{1/2}\tau_c \cdot 2\pi c$
Water	0.01	981.3	6.1			
	0.05	981.6	6.3	49.4	0.45	0.59
	0.10	981.5	6.3	46.3	0.42	0.54
	0.20	981.7	6.5	43.1	0.46	0.56
	1.20*	981.8	6.9	51.0	0.41	0.56
10% DMF	0.01	980.4	7.4			
	0.05	981.0	7.5	37.2	0.53	0.60
	0.10	981.4	7.6	47.8	0.44	0.58
	0.20	981.6	8.0	54.8	0.43	0.58
20% DMF	0.01	979.1	7.5			
	0.05	980.0	8.2	29.4	0.79	0.80
	0.10	980.6	8.6	43.8	0.53	0.66
	0.20	980.7	9.5	55.6	0.49	0.68

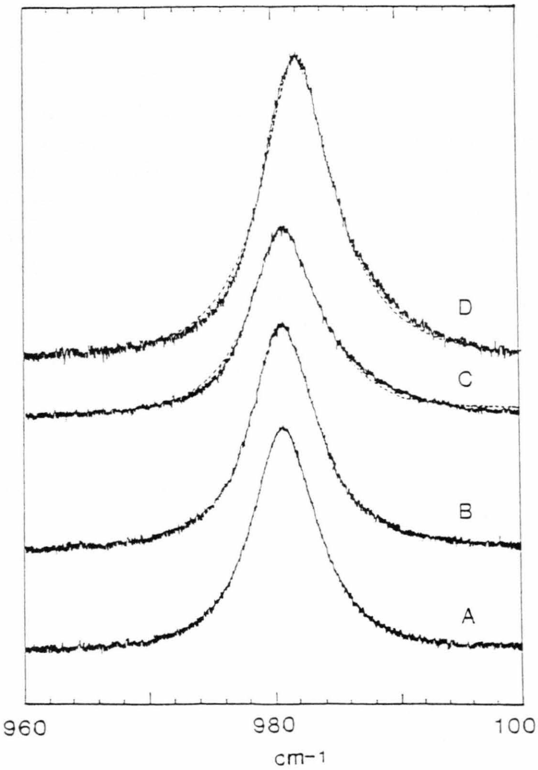

Fig. 1. Raman bands of the $\nu_1(A_1)$ mode of 0.1 mol · dm^{-3} Li_2SO_4 in water. The concentration of LiCl is 0 (A), 0.2 (B), 0.8 (C) and 1.0 (D) mol · dm^{-3}. Symmetry corresponds to the dashed lines.

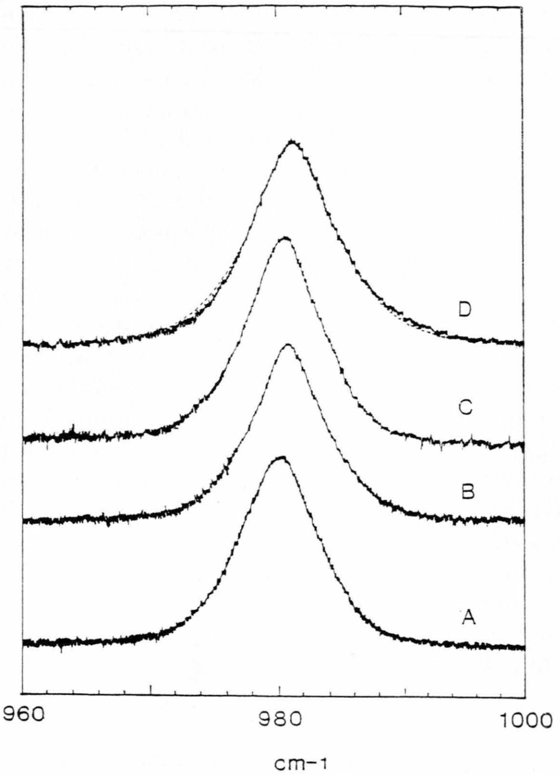

Fig. 2. Raman bands of the $\nu_1(A_1)$ mode of Li_2SO_4 in 20 wt% DMF solution. The concentration of Li_2SO_4 is 0.01 (A), 0.05 (A), 0.1 (C) and 0.2 (D) mol · dm^{-3}. Symmetry corresponds to the dashed lines.

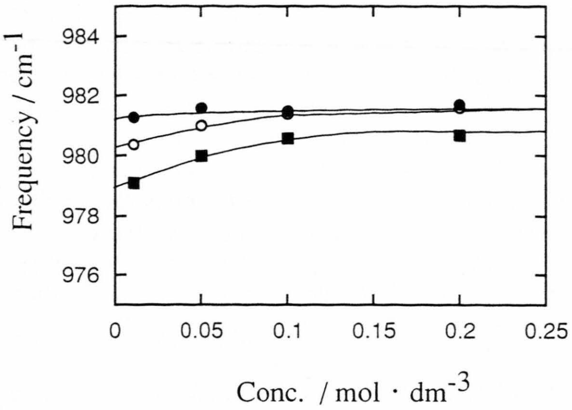

Fig. 3. Concentration dependence of the vibrational frequency at the maximum peak of the $\nu_1(A_1)$ mode. (●): water, (○): 10 wt% DMF and (■): 20 wt% DMF.

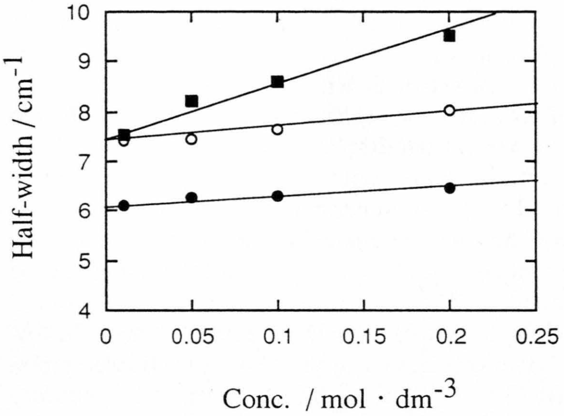

Fig. 4. Concentration dependence of the half-width of the $\nu_1(A_1)$ mode. (●): water, (○): 10 wt% DMF and (■): 20 wt% DMF.

A slightly asymmetric Raman line is observed at 0.2 mol · dm^{-3} of Li_2SO_4.

Figure 3 shows the concentration dependence of the maximum peak frequency of the SO_4 stretching in the mixtures. The frequency increases slightly with the concentration of Li_2SO_4 in water. Below 0.1 mol · dm^{-3} Li_2SO_4 in water-DMF mixtures the frequency decreases with decreasing concentration of Li_2SO_4. The limiting value at infinite dilution gives the vibrational frequency of the SO_4 stretching free from the inter-ionic interaction. The limiting value depends on the composition of the mixture. The lower its dielectric constant, the lower is the limiting value. Replacement of the water molecules around ions by DMF molecules results in blue shift.

Figure 4 shows the concentration dependence of the half-width of the SO_4 stretching mode in solutions. The half-width increases linearly with concentration in water and the mixtures. The linear change in the half-widths with concentration has been observed in the $\nu_1(A'_1)$ mode of NO_3^- in aqueous nitrate solution [12]. The half-width obtained at infinite dilution in DMF solutions is larger than that in pure water. As the vibrational relaxation time is inversely proportional to the half-width, the larger half-width for the mixtures indicates that the stretching of SO_4^- is slower and more restricted in water than in water-DMF mixtures.

The vibrational correlation function was obtained by Fourier transformation of the polarized Raman band of the SO_4 mode. The modulation time was obtained by fitting the vibrational correlation function with (1), where the second moment was estimated from the Raman intensity using (2). The second moment M_2 and the best fitting parameter τ_c are summarized in Table 1. While the second moment of the $\nu_1(A_1)$ mode of SO_4^{2-} is almost independent of the concentration in pure water, it increases with the concentration of Li_2SO_4 in DMF-water mixtures. The modulation times τ_c are independent of the Li_2SO_4 concentration below 0.2 mol · dm^{-3} in water, but in the mixtures they depend on the Li_2SO_4-concentration. As the DMF content increases, the modulation becomes slower.

Discussion

In [5] we have reported that the Raman line of the SO_4^{2-} stretching mode is asymmetric above 0.6 mol · dm^{-3} Li_2SO_4 in water, while in this work, the line was observed at to be symmetric 0.2 mol · dm^{-3} Li_2SO_4 in water. In the concentrated solution lithium ions interact strongly with SO_4^{2-} ions. The correlation time of water molecules around Li^+ [13] is different from that around SO_4^{2-}, and the approach of Li^+ ion to SO_4^{2-} disturbs the water structure around SO_4^{2-}. Therefore the asymmetric Raman line arises. At infinite dilution, the interaction between SO_4^{2-} and the solvent becomes homogeneous and the Raman line is symmetric. The asymmetry appears at 0.2 mol · dm^{-3} Li_2SO_4 in the 20 wt% DMF mixed solvent. In low dielectric media, such as the 20 wt% DMF-water mixture, Li^+ associates with SO_4^{2-} even at low concentration, the environment around SO_4^{2-} becomes inhomogeneous and the Raman line shape becomes asymmetric.

The modulation time τ_c is defined as the correlation decay of the perturbation Hamiltonian, but the physical meaning of the modulation times is not clear. Rothschild [9] has examined the relationship between τ_c and the Enskog collision time. He concluded that, although the order of the τ_c values agrees with the collision times, the consideration of the collision effect alone is insufficient to predict the τ_c values. As is seen in Table 1, τ_c tends to increase with increasing DMF content. τ_c is sensitive to the composition of the mixture. The τ_c values of Li_2SO_4 in water are of the same order as those of SCN^- [6, 11, 14], CO_3^- [14] and NO_3^- [12, 14] in water; they are around 0.3 ~ 0.4 ps, depending slightly on the cation species. τ_c is determined by the solvation and the dynamical local structure around ions. In addition, the modulation due to large size molecules such as DMF is slow, and in such case the vibrational amplitude is affected. As the collision effect depends on the size and mass, it is smaller for water than for DMF molecules. In order to interpret the detailed relationship between the vibrational relaxation of ions and the collision process, further investigation for electrolyte solutions is needed.

In this work, the inequality of $M_2^{1/2}\tau_c < 1$ holds in the concentration ranges investigated. This result means that the vibrational relaxation behavior of SO_4^{2-} is in the intermediate modulation regime.

Acknowledgement

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Area of "Molecular Approaches to Non-equilibrium Process in Solutions" from the Ministry of Education, Science and Culture (No. 0412105).

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