

## Inelastic x-ray scattering measurements of liquid water-glycerol mixtures

Yukio Kajihara<sup>1,\*</sup>, Nanako Shibata<sup>1</sup>, Masanori Inui<sup>1</sup>, Kazuhiro Matsuda<sup>2</sup>, and Satoshi Tsutsui<sup>3</sup>

<sup>1</sup>Graduate School of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan

<sup>2</sup>Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

<sup>3</sup>Japan Synchrotron Radiation Research Institute, SPring-8, Sayo, Hyogo 679-5198, Japan

**Abstract.** We have carried out inelastic x-ray scattering measurements on liquid water-glycerol mixtures. The data are analyzed by a damped harmonic oscillator model with two excitations, longitudinal and transverse modes. The sound velocity of the longitudinal mode is almost constant (about 3.1 km/s), being independent of the composition. Thus the strength of 'fast sound' which we define the ratio of this IXS sound velocity to ultrasonic one is largest at pure water and gradually decrease with increasing mole fraction of glycerol. This result indicates that the relaxation phenomena of pure water gradually reduce with increasing the fraction of the solute: the scenario which we proposed for water-monohydric alcohol mixtures hold true for this water-trihydric alcohol mixtures.

### 1 Introduction

Liquid water-monohydric alcohol mixtures exhibit many thermodynamic anomalies [1]. For example, a maximum appears at around 10-20% alcohol mole fraction in the concentration dependence of the ultrasonic sound velocity ( $v_{US}$ , frequency in MHz) [2–4] in water-ethanol and water-methanol mixtures. The anomalies have been believed to be of structural origin [1] and the relation between clathrate structure such like Ethanol-17H<sub>2</sub>O and Ethanol-5.75H<sub>2</sub>O [2, 5] or the special cage structure has been discussed [2, 6]. Anyway, there has been no direct experimental evidence and the discussion has not been concluded.

On the other hand, it is well known that water itself has many thermodynamic anomalies: The density shows a maximum at 4 °C and the ultrasonic sound velocity exhibits anomalous increase below 80 °C. There is an opinion that these anomalies of pure water should affect the properties of water-alcohol mixtures [7]. The so-called 'fast sound' problem is one of such anomalies of pure water [9]. The sound velocity of water at ambient conditions which is obtained by microscopic methods (molecular dynamics and inelastic neutron / x-ray scattering) is much faster (about by a factor of two) than the one obtained by a macroscopic method like ultrasonic measurements. The advent of inelastic X-ray (IXS) and ultraviolet scattering technique lead to the conclusion that a relaxation phenomena, which is assigned to making and breaking hydrogen bond, is the essence of the 'fast sound' of water [10–13].

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\*e-mail: kajihara@hiroshima-u.ac.jp

The strength of the relaxation is so large as to slow down the ultrasonic sound velocity by half compared to the IXS sound velocity. From this fact, it is natural that the question of how this strength will change when alcohol is added to water. We speculated that it should be the origin of the ultrasonic and also the thermodynamics anomalies of water-(monohydric) alcohol mixtures, which is the same scenario to [7]. We recently carried out IXS experiment on water-ethanol mixtures at ambient condition [8] and on water-methanol mixtures from ambient to low temperature conditions [4]. The concentration dependence of the strength of the relaxation exhibits a maximum for pure water and gradually decreases with increasing alcohol concentration in both water-ethanol and water-methanol mixtures. From these experimental results, we concluded that the ultrasonic anomalies of the water-monohydric alcohol mixtures are derived from the pure water itself, not from the complex mixing state of water and alcohols.

In the present study, we carried out IXS measurement of water-glycerol mixtures, to verify whether the same scenario as observed for water-monohydric alcohol mixtures holds also true for water-trihydric alcohol mixtures.

## 2 Experimental details and Results

The IXS experiment is performed at SPring-8/BL35XU in Japan [14] with standard beamline conditions for liquids. Si (11 11 11) reflection is used as a backscattering monochromator and the energy of the incident beam is 21.747 keV. The energy resolution of the spectrometer is about 1.5 meV and the scan ranges of energy transfer ( $E$ ) is  $\pm 35$  meV. There are 12 analyzers (and corresponding 12 detectors) in total, four in the horizontal direction and three in the vertical direction, which enables us to measure 12 data at once whose momentum transfer ( $Q$ ) are different. We set 2 horizontal angles of the analyzers to cover  $Q$  range from 1.5 to 11  $\text{nm}^{-1}$ . An aluminum cell with two sapphire single crystal windows of diameter 8 mm and thickness 0.5 mm each is used to hold the liquid samples. The flat samples have a thickness of 2 mm.

Figure 1 shows  $S(Q, E)$  of the water-10 mol% glycerol sample recorded at a temperature of 25 °C. Closed circles, open circles, closed triangles and open triangles correspond to  $Q$  equal to 1.56, 4.24, 6.56 and 9.25  $\text{nm}^{-1}$ , respectively. In the spectra, we can see the shoulders correspond to the longitudinal acoustic mode at around the energy of  $\pm 2$ ,  $\pm 8$ ,  $\pm 14$  and  $\pm 20$  for  $Q$  equals to 1.58, 4.24, 6.56 and 9.25  $\text{nm}^{-1}$ , respectively. In pure water, it was concluded that IXS spectrum has two collective modes (longitudinal and transverse acoustic excitations) [10, 15]. Thus we analyzed the spectrum by a damped harmonic oscillator (DHO) model which has two DHO components correspond to these two modes in addition to a Lorentzian component corresponds to quasi-elastic scattering as shown in the following equation.

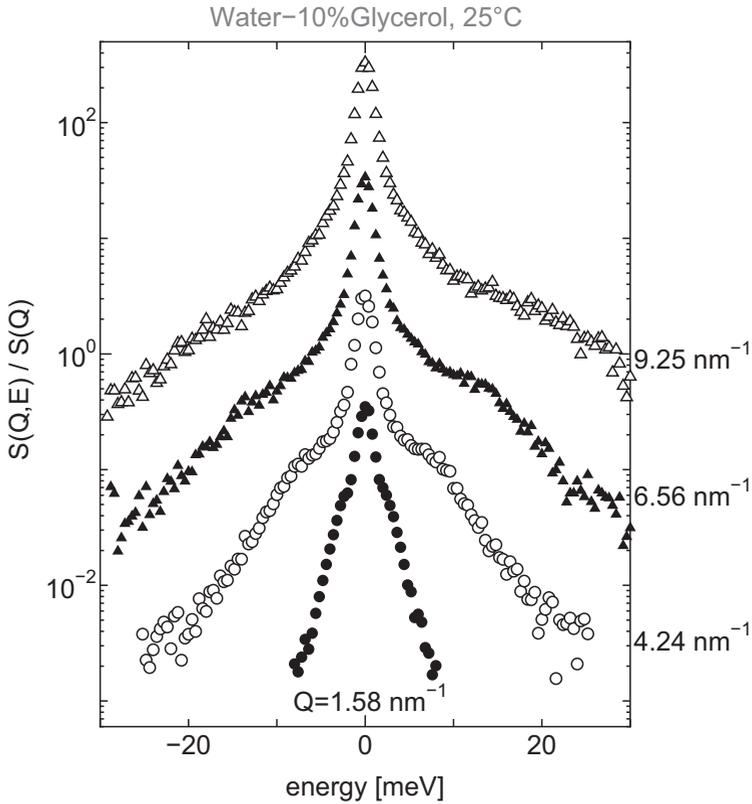
$$\frac{I(Q, E)}{I(Q)} = \int \frac{S(Q, E)}{S(Q)} R(E - E') dE'$$

$$\left( \frac{S(Q, E)}{S(Q)} \right) = \left( \frac{E/k_B T}{1 - e^{-E/k_B T}} \right) \times \left( (1 - A_1 - A_2) f_0 + \sum_i^{1-2} A_i f_i \right)$$

$$f_0 = \frac{1}{\pi \Gamma_0} \frac{\Gamma_0}{E^2 + \Gamma_0^2}$$

$$f_{i=1,2} = \frac{k_B T}{\pi} \frac{4\Gamma_i \sqrt{E_i^2 - \Gamma_i^2}}{(E^2 - E_i^2)^2 + 4\Gamma_i^2 E^2} \quad (1)$$

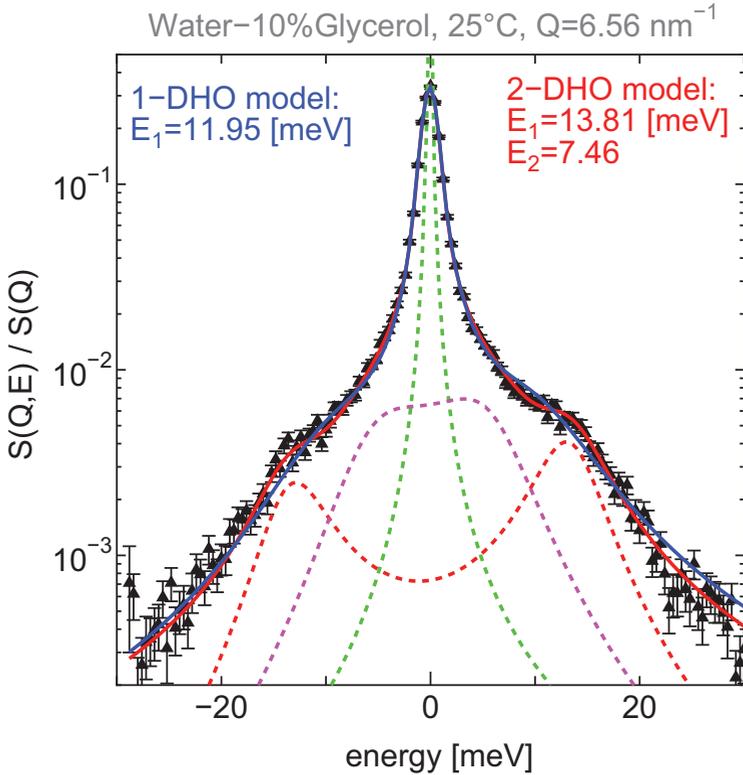
Here  $\Gamma_0$  is the width of the central Lorentzian and  $A_i$ ,  $\Gamma_i$  and  $E_i$  are the amplitude, width and energy of the DHO for longitudinal ( $i = 1$ ) and transverse ( $i = 2$ ) modes, respectively.



**Figure 1.**  $S(Q, E)$  of water-10 mole % glycerol mixture at 25 °C. Closed circles, open circles, closed triangles and open triangles correspond to  $Q$  equal to 1.58, 4.24, 6.56 and 9.25  $\text{nm}^{-1}$ , respectively. Each spectra is shifted by a factor of 5 for clarity.

$k_B$  is Boltzmann constant and  $T$  is the temperature of the sample.  $R(E)$  represents the resolution function experimentally determined from the measurements of PMMA (polymethyl methacrylate). We fitted the experimentally obtained spectrum by this model function  $I(Q, E)$  and optimized these parameters by the non-linear least squares method. In figure 2, the calculated model spectra are plotted by solid lines; the spectra with two-DHO components are plotted by the red line and that with one-DHO (only longitudinal mode) by the blue one. The shoulder of the spectrum at around 14 meV, which corresponds to the longitudinal mode, is better described by the red line than the blue one, which means that there exists a transverse mode in addition to a longitudinal one in this mixture. The estimated energy ( $E_1=13.81$  meV) correspond to the longitudinal mode of 2-DHO model is slightly higher than that (11.95 meV) of 1-DHO model. Dashed lines are the components of the calculated spectrum (without considering resolution function); the green, red and pink lines correspond to the Lorentzian component, DHO for the longitudinal mode and DHO for the transverse mode, respectively.

Figure 3(a) shows dispersion curves for water-10 mole % glycerol mixture at 25 °C. Closed and open circles indicate the estimated energies of the DHO function for longitudinal ( $E_1(Q)$ ) and transverse modes ( $E_2(Q)$ ), respectively. From the curve of longitudinal mode, we estimate the  $Q$ -dependent sound velocity  $v(Q) = E_1(Q)/Q$  as shown in figure 3(b).  $v(Q)$  is almost constant in the higher- $Q$  region above 4  $\text{nm}^{-1}$  and shows a decrease approaching

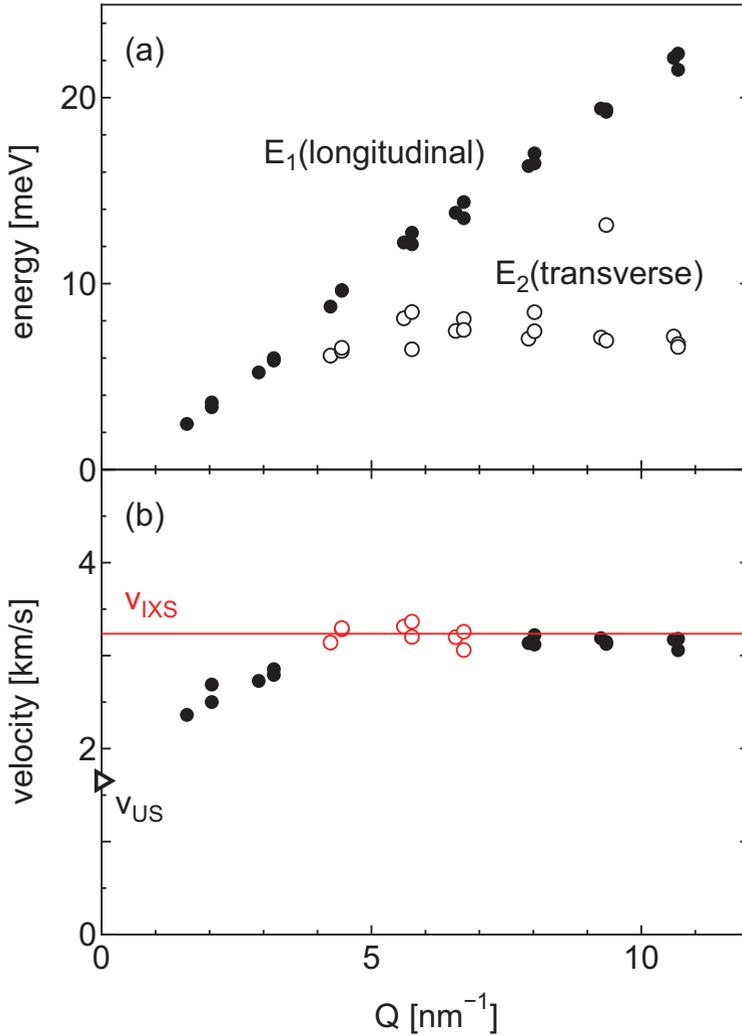


**Figure 2.**  $S(Q, E)$  of water-10 mole % glycerol mixture at temperature of 25 °C and  $Q$  equal to 6.56  $\text{nm}^{-1}$ . Open circles are experimental values. The blue and red solid lines represent the calculated model functions of 1-DHO and 2-DHO models, respectively. Dashed lines are the components for 2-DHO model function without convolution of the resolution function; the green, red and pink lines correspond to a Lorentzian component, DHO for longitudinal mode and DHO for transverse one, respectively.

$v_{\text{US}}$  (indicated by triangle in the figure) at lower  $Q$ - values. But for mixtures containing more than 60 mole % glycerol  $v(Q)$  gradually decrease with increasing  $Q$  above about 8  $\text{nm}^{-1}$ . Thus we determined IXS sound velocity  $v_{\text{IXS}}$  by only averaging  $v(Q)$  in the range of 4 to 7  $\text{nm}^{-1}$  for all the mixtures as indicated by the red open circles in figure 3.

Figure 4 (a) shows the concentration dependence of  $v_{\text{IXS}}$  at 25 °C.  $v_{\text{US}}$  [18] is also plotted in the figure represented by a solid line. Irrespective of concentration, the present  $v_{\text{IXS}}$ , indicated by closed circles, is almost constant with a value of 3.1 km/s which compares well with literature data [10, 16, 17] denoted by open marks. This result suggests that there does not exist special structure or characteristic mixing state in this system. To characterize the relaxation phenomena in this system, we define the simple parameter as the strength of 'fast sound'  $S_f \equiv v_{\text{IXS}}/v_{\text{US}}$ . This is a measure for the strength of the relaxation processes that exist in the frequency range between that of US (MHz) and that of IXS (THz) measurements as followings. Sound velocity  $v$  can be related with the apparent longitudinal elastic modulus  $M$  as  $M = \rho v^2$ . Frequency ( $\omega$ ) dependence of the elastic modulus is expressed by the Debye approximation as,

$$M(\omega) = M_{\infty} + \frac{M_0 - M_{\infty}}{1 + i\omega\tau}. \quad (2)$$

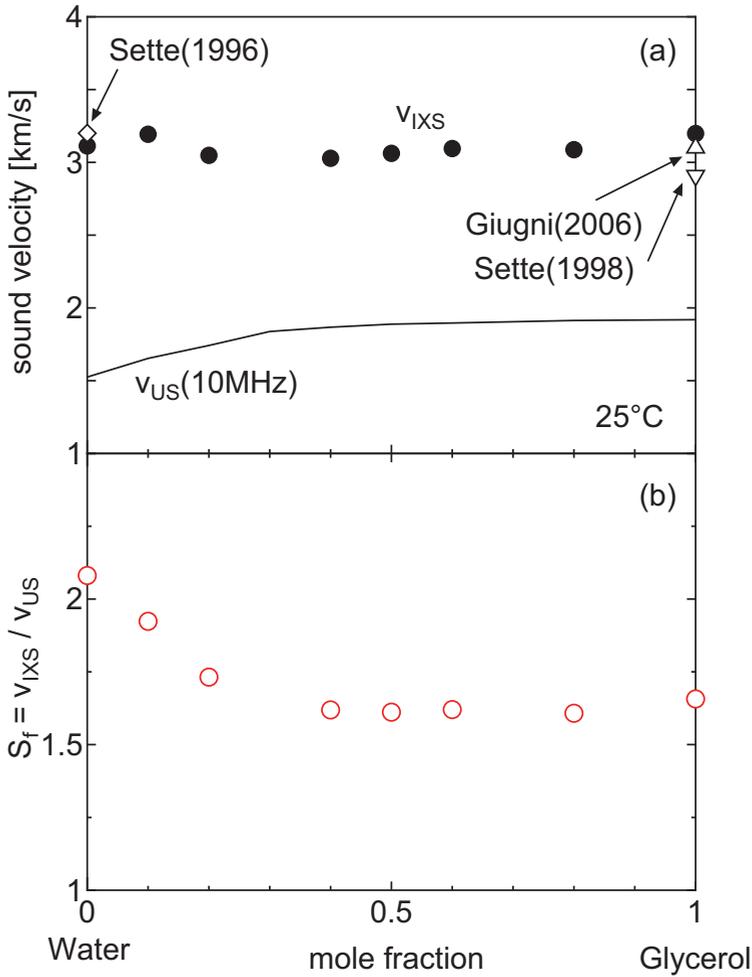


**Figure 3.** (a) Dispersion curve of water-10%glycerol mixture at 25 °C. Closed and open circles indicate the estimated energies of DHO function for longitudinal and transverse modes, respectively. (b)  $Q$ -dependent sound velocity of the longitudinal mode  $v(Q)$ . IXS velocity  $v_{\text{IXS}}$  is determined by the average of  $v(Q)$  in the  $Q$  range between 4 and 7  $\text{nm}^{-1}$  denoted by red open circles. In the low- $Q$  region,  $v(Q)$  approaches to the ultrasonic sound velocity  $v_{\text{US}}$ .

where the  $M_0$  and  $M_\infty$  are bulk modulus for  $\omega=0$  and  $\omega \rightarrow \infty$ , respectively, and  $\tau$  is the characteristic time of the relaxation. Similar formalism was adopted and the characteristic time and other parameters were discussed for liquid water [11]. Here we focus on the strength of the relaxation  $\epsilon$ , which is related with the strength of fast sound as,

$$\epsilon \equiv \frac{M_\infty - M_0}{M_0} = \frac{v_\infty^2 - v_0^2}{v_0^2} \approx \frac{v_{\text{IXS}}^2 - v_{\text{US}}^2}{v_{\text{US}}^2} = S_f^2 - 1. \quad (3)$$

In this equation, we assume that the frequency of IXS (THz) and that of US (MHz) is enough fast and slow compared to the characteristic frequency of the system  $1/\tau$ . Thus the parameter



**Figure 4.** (a) Concentration dependence of sound velocity of water-glycerol mixtures. Marks are obtained by IXS measurement: closed circles are by us and open marks are by others [10, 16, 17]. Solid line shows ultrasonic sound velocity [18]. (b) Ratio of the two sound velocities.

$S_f$  is a good measure for the strength of the relaxation processes that exist in the frequency range between that of US and that of IXS measurements.  $S_f$  is plotted in figure 4 (b) by open circles, which is largest for pure water and gradually decrease with increasing glycerol content in the water-rich region (mole fraction of glycerol  $x_g < 0.5$ ). In the glycerol rich region ( $x_g > 0.5$ ),  $S_f$  is almost constant. We conclude that the concentration dependence of  $v_{US}$  is mainly characterized by the relaxation, not by the characteristic mixing state or special structure of these two molecule (water and glycerol). In the low-alcohol mixtures, the relaxation should be caused by pure water because the strength of the relaxation is largest. These conclusion is same as that for the water-monohydric alcohol mixtures [4, 8] and thus should be universal in water-alcohol mixtures. We believe that the origin of this relaxation of pure water is the critical fluctuations for liquid-liquid phase transition whose critical point is suggested to locate in the deep supercooled region (critical temperature is about  $-50^\circ\text{C}$  and

pressure is from 100 MPa to 150 MPa) [19, 20]. Because  $S_f$  increases with decreasing temperature in water-rich region of water-methanol mixtures. There is one difference between these monohydric- and trihydric- alcohol solutions :  $S_f$  is from 1.6 to 1.7 for glycerol-rich mixtures which is not so small as compared to that of high monohydric-alcohol mixtures ( $S_f$  is about 1.2 to 1.3). This is because the glycerol is a well-known glass forming liquid and has a substantial value of the strength of relaxation [17], which should affect the relaxation of glycerol-rich samples.

### 3 Summary

We have carried out IXS measurements on liquid water-glycerol mixtures. The IXS determined sound velocity is almost constant irrespective of the glycerol concentration. The strength of the relaxation for the mixtures, which is estimated by taking the ratio of this IXS velocity and the one measured by the ultrasonic method, is largest at pure water and gradually decreases with increasing the concentration of glycerol. We conclude that our scenario, that the ultrasonic feature (and we believe all the other thermodynamic anomalies) in water-alcohol mixtures is characterized by the relaxation phenomena, not by the special mixing state of the two materials (water and alcohol). We believe that the fluctuations of pure water corresponding to liquid-liquid phase transition should be dominant in the low alcohol (both monohydric-alcohol and glycerol) mixtures. In the glycerol-rich samples, the relaxation is thought to be characterized by the glass forming ability of pure glycerol.

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