

Study on Structural Fluctuations of Binary Solutions

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Chapter 1

General introduction

1.1 Background of the present study

Materials exist as solids, liquids or gases. The position of molecules is fixed in the solid state and the molecules, especially in crystals, are arranged in periodic order. For this periodicity, it is possible to discuss the properties of crystal based on the arrangement of molecules in a unit cell. For crystals, many studies have been carried out from the both points of theory and experiment. It is possible to say that they are established systems. In a gaseous state, we can treat a molecule as free one. In that case, interaction between particles can be neglected. In the study of gaseous states, a lot of information were also obtained from various investigations with good accuracy.

As the density of the liquid is almost the same as that of the crystal, the interaction between molecules in the liquid is not negligible. The disorder in molecular arrangement makes also it difficult to discuss liquid structure quantitatively. Though a lot of investigations on liquids have been made, neither structural expression with good accuracy nor determinate discussion can be done, compared with gaseous and crystalline states. The establishment in theoretical treatment of liquid has been left far behind the ones of the gaseous and crystalline states. Even for a pure liquid of one component system, the discussion on determinate liquid structure is difficult. A new parameter, namely concentration, joins for two component system, and more difficulty in physicochemical treatments is added. In the solution, mixing state changes in dependence on the concentration and the temperature, and it is the one of most important factors to rule the properties of the solutions. Usually, we utilized multi component systems of liquids rather than pure liquids. Therefore, it seems to be important to develop the methodology how to elucidate the mixing state of solutions and to apply it to actual systems.

1.2 Objective of the present study

Wide-angle x-ray scattering is used to obtain information on micro structure of liquid or solution and gives the radial distribution function as general expression of the structure. This radial distribution function shows how the other atoms are distributed around a central atom. In microscopic view, the structure of liquid or solution is anisotropic. In macroscopic view, however, the structure of liquid or solution is isotropic. The obtained data from a radial distribution function gives one-dimensional information that is depending on only distance. The radial distribution function obtained from diffraction experiments contains the information on distance correlation up to about 20 Å.

On the other hand, the data obtained from small-angle x-ray scattering (SAXS) gives information on structural correlation ranging wider than that from wide-angle x-ray scattering. The wider region, namely semi-micro region, just corresponds to that where clustering or aggregation of molecules are discussed. The mixing state of solution can be discussed qualitatively using the conception of fluctuation as expression of structure.

Thermodynamic data give macroscopic information about mixing state in solution. As for the solution chemistries, thermodynamic experiments and the discussion have occupied majority up to now. Systematic discussion connecting the microscopic, semi-microscopic and macroscopic views has been little. The objective of the present study is to investigate information on mixing state in binary solution in more detail by combining information of microscopic and semi-microscopic views given from diffraction experiments and that of macroscopic view given from thermodynamic data.

In Chapter 2, the mixing state in dimethyl sulfoxide aqueous solution is mainly investigated by using a wide-angle x-ray scattering experiment. Macroscopic information from thermodynamic data is also discussed in relating to the radial distribution function from the scattering experiments.

It is necessary to add the semi-microscopic information in order to discuss the structure of solutions. Small-angle x-ray scattering experiment just gives the information.

In Chapter 3, it is reported on the design and construction of SAXS apparatus. It was aimed to use conveniently and to have overall efficiency at laboratory.

In Chapter 4, the results of SAXS experiments on acetonitrile aqueous solution is summarized. The solution system exhibits phase separation at the upper critical solution

temperature (UCST), at mole fraction is 0.38 and 272K. From macroscopic viewpoint, acetonitrile is mixing with water well at room temperature. However, mixing state of the solution is changing drastically as close to UCST. The discussion on the structure of the solution is made by use of the conception of fluctuations. The fluctuation is a conception, which shows the difference from the average value. In solution system, density and concentration fluctuations are defined as difference from the average number of density and the average concentration, respectively. I carried out SAXS experiments for acetonitrile aqueous solutions with changing temperature and concentration. In the chapter, I discussed the mixing state of the solution by using the value of fluctuations obtained from SAXS experiments.

In Chapter 5, I obtained the second derivative of Gibbs's free energy for acetonitrile aqueous solutions from measurement of vapor pressures. The quantities of derivatives of Gibbs's free energy gives more detailed information for the mixing state of solution as being higher derivatives. The second derivative of Gibbs's free energy in present chapter corresponds to the fluctuation of the solution, and that is compared to ones obtained from SAXS experiment in Chapter 4.

In Chapter 6, finally, all the information on structure of solutions is discussed and summarized comprehensively.

Chapter 2

Mixing Schemes of Aqueous Dimethyl Sulfoxide Studied by X-ray Diffraction

2.1 Introduction

The scattering technique has been useful in obtaining structural information of liquids and liquid mixtures. Its application to aqueous solutions up to early 1980's has been reviewed.¹ More recent works include the studies of aqueous tert-butanol² and 1-, and 2-propanol³ by Nishikawa. On the other hand, thermodynamic studies on aqueous solutions have served a supplementary, yet an important role in understanding molecular processes in aqueous solutions. Numerous reviews are available in literature and works up to early 1980's were also summarized in ref.(1). More recently, however, Koga measured partial molar quantities in aqueous solutions accurately and in small increments in composition.^{4, 5} As a result, it was possible to evaluate the composition derivatives of these partial molar quantities. The latter signifies the effect of a solute upon the partial molar quantities of solute. Thus such derivatives convey information about the solute-solute interactions as discussed at some length earlier. As a consequence, some "structural" information on the mixing schemes of aqueous solutions was obtained.^{4, 5}

The same thermodynamic methodology was applied to aqueous dimethyl sulfoxide (abbreviated as DMSO).⁶ It was shown that there are three composition regions, in each of which the mixing scheme is qualitatively different from those of other regions. The details of each mixing schemes were described earlier.⁴⁻⁶ Briefly, mixing scheme I in the most water-rich region is characterized as retaining characteristics of liquid H₂O. Namely, the influence of DMSO molecules is minimized by H₂O's forming an "iceberg" around them but sacrificing the hydrogen bond probability of bulk H₂O away from solutes. The bulk H₂O still holds the basic characteristics as liquid H₂O in that the hydrogen bond probability is still high enough for bond percolation, *i.e.* the hydrogen bond network is still connected. The iceberg portions form a building unit for an addition compound when the solution is cooled to solid.^{4, 5} In the most DMSO-rich region, DMSO molecules cluster together in the same environment as in pure DMSO and H₂O molecules interact with such DMSO clusters as a

single molecule. Mixing scheme **II** in the intermediate region is that by which the solution consists of two kinds of clusters, one rich in H_2O and the other in DMSO, reminiscent of mixing schemes **I** and **III** respectively. The boundary between mixing schemes **I** and **II** was found $x = 0.28$ and that between **II** and **III** is $x = 0.56$ at 25°C .⁶

This chapter deals with an x-ray diffraction study of aqueous DMSO at room temperature. The structural aspect suggested by the thermodynamic studies mentioned above⁴⁻⁶ is put to test. Aqueous DMSO is a convenient system for such a study, since the solute contains S atom which has a larger x-ray cross section than C or O. Thus, the mode of aggregation of DMSO molecules in aqueous solution could be learned more clearly than for other solutes, alcohols for example. A drawback is, however, O-O or O-C interference, which might otherwise provide some structural information about "iceberg" or bulk portion of H_2O , is masked by strong interference involving S atoms.

2.2 Experimental

DMSO (Wako, Special Grade) was used as supplied. H_2O was distilled immediately before use. The diffraction experiments were carried out in a transmission geometry using Ag $\text{K}\alpha$ ($\lambda = 0.5608 \text{ \AA}$). The present setup covered the range in momentum transfer of scattering, s ($= (4\pi/\lambda)\sin\theta$), from 0.4 to $9 \text{ \AA}^{-1}$, where θ is a half of scattering angle. An imaging plate (DIP-100, Mac Science) was used for detection. 2000 seconds were allowed for data accumulation. The thickness of the sample was 0.72 mm held by two $25\mu\text{m}$ Mylar windows. Diffraction measurements were taken at $22 \pm 1^\circ\text{C}$ for pure DMSO, pure H_2O and aqueous DMSO at $x = 0.07, 0.15, 0.28, 0.38, 0.50, 0.60$, and 0.80 , where x is the mole fraction of DMSO.

The details of data analysis pertinent to detection by an imaging plate has been described elsewhere.⁷ Briefly, the measured intensity was corrected for the background scattering, the polarization and the non-uniformity caused by our readout system of the used imaging plate. The two-dimensional intensity data were circularly averaged. The corrections for the absorption, the geometry factor and the incoherent scattering followed. The absolute coherent intensity, $I(s)$, was obtained by normalizing the asymptotic value of the resulting intensity at large s to that from independent atoms in the stoichiometric ratio, $(\text{DMSO})_x(\text{H}_2\text{O})_{1-x}$.

2.3 Results and discussions

2.3.1 Structure of Liquid DMSO

First the "structure" of pure liquid DMSO is discussed, which is later used as a reference in studying the "structure" of aqueous DMSO. Itoh *et al.* found by x-ray diffraction that the local molecular arrangement in liquid was same as the packing of crystal.⁸ The experiment was duplicated and the results are shown below. Further discussion on the structure of liquid DMSO is based on present data.

The experimental weighted structure function, $si(s)$, for liquid DMSO was calculated by,

$$si(s) = s (I(s) - \sum f_k^2(s)), \quad (1)$$

where $I(s)$ is the observed total coherent intensity, and f_k is the atomic scattering factor of the k -th atom. The resulting $si(s)$ is shown in Fig. 1 as a function of s . They agree with the data of Itoh *et al.*⁸

Next, the radial distribution function, $4\pi r^2 (\rho(r) - \rho_0)$ is calculated, by the following Fourier transformation.

$$4\pi r^2 (\rho(r) - \rho_0) = (2r/\pi) \int (s i(s) / \sum Z_k^2) \sin(sr) \exp(-Bs^2) ds \quad (2)$$

ρ_0 is the bulk number density of the molecule, Z_k is the number of electrons in the k -th atom, and the factor $\exp(-Bs^2)$ is the damping factor to minimize the termination effect in Fourier transformation. Note in eq.(2) that I Fourier-transformed $(si(s) / \sum Z_k^2)$, rather than $(si(s) / \sum f_k^2)$, a common practice. This is again to minimize the termination error coming otherwise from a strong s -dependence of the modification function $(1 / \sum f_k^2)$.⁹ Furthermore, $I(s)$ is calculated at a large angle region, $s > 9 \text{ \AA}^{-1}$, by using the intramolecular structure parameters for gas molecule¹⁰ and is smoothly connected to the observed $I(s)$. This is

justified since $I(s)$ of liquid commonly approaches to that of the free molecule in a large s range, $s > 6 \text{ \AA}^{-1}$. As a result, I obtained a well-behaving, free from cutoff error, radial distribution function, $4\pi r^2(\rho(r) - \rho_0)$, as shown in Fig. 2.

In Fig. 2, the peak at $r \approx 1.7 \text{ \AA}$ is attributed to an intramolecular S=O and two intramolecular S-C interferences. The weak shoulder at $r \approx 2.7 \text{ \AA}$ is due to two nonbinding O...C and a C...C intramolecular interferences. The peaks at $r > 3 \text{ \AA}$ are of intermolecular origin. As shown in Fig. 2, there is correlation apparent up to the fourth nearest neighbors, up to about $20 \text{ \AA}$.

Liquid structure may be viewed as having a certain nearest neighbor configuration around a central molecule.^{11, 12} Unlike crystal, however, repetition of this nearest neighbor unit is imperfect, and thus the positional correlation is lost rapidly as the distance from the central molecule increases. This effect is embodied in the mean square deviation of the distribution of separation between atoms that increases rapidly with r . Namely, the mean square deviation between the j -th and the k -th atoms, I_{jk}^2 , is assumed, following Prins¹¹ as,

$$I_{jk}^2 = 2 D r_{jk}^2, \quad (3)$$

where D is an adjustable parameter and r_{jk} is the mean distance between the j -th and the k -th atoms. Beyond several molecular distance, R_C , away from a chosen central molecule, the structure can be regarded as continuum. R_C is another adjustable parameter. The details of calculation of scattering intensity from a model structure of liquid were described elsewhere.¹²

In search for an appropriate structure model, I systematically changed the local arrangement and the intermolecular distances from those of crystal.¹³ It is found, as Itoh *et al.* did,⁸ that the same molecular arrangement as crystal with a 3 % increase in molecular distance in three-dimensional directions resulted the best fit for the weighted structure function, $si(s)$. This 3 % expansion is consistent with the liquid density, 1.1 g cm^{-3} , about $(1.03)^{-3}$ times that of crystal calculated at 5°C .⁷ The resulting adjustable parameters were $D = 0.046 \text{ \AA}$ and $R_C = 8.8 \text{ \AA}$. The resulting $si(s)$ is shown in Fig. 1 as the broken curve. The

match with the observed (open circle) is satisfactory.

The local molecular arrangement thus elucidated is shown in Fig. 3. The parallelogram represents the imaginary unit cell, reminiscent of crystal structure. Fig. 3(a) shows basically *b-c* plane, and Fig. 3(b) *a-c* plane. The molecule #1 is chosen as the central molecule, and its ten nearest neighbors numbered from #2 to #11 are shown in the figure. The interatomic distances from S or O atom of molecule 1 to O or S of the *n*-th (*n* = 2, ..., 11) nearest neighbor molecules are given in Table 1. These ten (eleven including molecule 1) nearest neighbor molecules are responsible for the peak at about 5.6 Å in the distribution function, Fig. 2. Unlike crystal, positional correlation dies down rapidly through Prins deviation relation (eq.(3)) and past the sphere of radius R_C (= 8.8 Å), the location of other molecules is completely blurred. There are total of 25 molecules within this sphere. This sphere is called the "structure region", within which the central molecule feels the structure around itself.¹²

A DMSO molecule has a strong dipole along S=O bond.¹⁴ Fig. 3 suggests that the intermolecular S=O dipole interaction plays a key role in this molecular arrangement. Namely, molecules 3, 1 and 2 (or 5, 7 and 4) seem to form a zigzag chain due to S=O dipole attraction. The intermolecular distances from S atom of molecule 1 (denoted as S(1)) to O atom of molecules 2 and 3 (O(2) and O(3)) are 3.8 Å, as shown in Table 1. Conversely, those from O(1) to S(2) and S(3) are the same. This indicates that S=O of molecule 1 and O=S of molecules 2 and 3 are parallel. Molecules 6 and 9 form another chain equivalent to 3-1-2 chain and 11 is a part of the chain below 5-7-4 along *c*-axis in the figure. Thus, in a general direction of *b*-axis there are four chains running through the unit cell bonded by S=O dipole attraction. In liquid, integrity as a chain dies down past the sphere of radius R_C , however. The inter-chain interaction seems to occur via van der Waals or weak hydrogen bonding between two CH₃ of molecule 3 and O of molecule 5, *etc.* Thus, when mixed with H₂O, H₂O molecules may penetrate into the space between the chains to form preferential hydrogen bonds with O of DMSO, while intra-chain molecule may stay intact. Hence, out of total of 10 nearest neighbors, molecules # 6, 9, 10, and 11 may lose correlation with molecule #1 and thus the locus of the first intermolecular peak may shift to a shorter *r* value. This seems indeed to happen as will be discussed below.

2.3.2 Structure of Aqueous DMSO

The weighted structure functions, $si(s)$, and the distribution functions, $4\pi r^2(\rho(r) - \rho_0)$, for aqueous solutions are plotted in Fig. 4 and Fig. 5, together with those of pure H_2O and DMSO. Earlier thermodynamic studies⁴⁻⁶ indicated that the mixing scheme changes from **I** to **II** at $x = 0.28$ and **II** to **III** at $x = 0.56$. Fig. 6 shows the shift of the locus of the first peak of intermolecular origin. The dotted vertical line shows the mixing scheme boundaries. If this shift is due only to dilution effect, the plots in Fig. 6 should be the straight line tying both extremes, $x=0$ and $x=1$, as shown by a broken line. Clearly the characteristics of the distribution function are different in each of mixing schemes **I**, **II** and **III**. Thus, in Figs. 4 and 5, graphs are grouped together in three corresponding to each mixing scheme **I**, **II** and **III**.

2.3.3 Mixing Scheme III

Let us start with mixing scheme **III**. It is striking that the distribution function for aqueous solution at $x = 0.6$ or 0.8 in Fig. 5 seems identical to that of pure DMSO if scaled with x . This indicates that DMSO retains its liquid structure intact, and H_2O does not form any structure remarkable enough to disturb the distribution function of liquid DMSO. H_2O molecules in this region are working as simple diluent. This is in complete agreement with the conclusion drawn by thermodynamic studies.⁴⁻⁶ Namely, the excess partial molar enthalpy and entropy of DMSO and H_2O suggested that DMSO molecules cluster together in the same manner as in pure DMSO and H_2O molecules interact with DMSO clusters as a single molecule.

2.3.4 Mixing Scheme I

Let us now turn to mixing scheme **I**. The $2.8 \text{ \AA}$ peak in distribution function for pure H_2O , Fig. 5, is due to the hydrogen bonded O-O interference. Other characteristic O-O interferences of liquid H_2O appear at 4.5 and $7.1 \text{ \AA}$. They are due to strong correlation from a central O to the second and the third neighbor O atoms through the hydrogen bond network prevalent in liquid H_2O . On addition of DMSO, these peaks characteristic to H_2O diminish rapidly, indicating loss of the H_2O -like character. At $x = 0.07$ the $2.8 \text{ \AA}$ and $7.1 \text{ \AA}$ peaks

decrease, while the 4.5 Å peak grows and shifts to a larger r value. The trend continues at $x = 0.15$ but at $x = 0.28$, the boundary to mixing scheme **II**, the peak at about 5.3 Å is the most conspicuous and no correlation is apparent for $r > 9$ Å. I suggest that this peak is mainly due to involvement of S in DMSO. The 7.1 Å O-O peak definitely dies down at $x = 0.28$, indicating the loss of the nature of liquid H₂O. The 2.8 Å peak, on the other hand, remains even at $x = 0.28$, which may be coming from the "iceberg" portion. Or perhaps the hydrogen bonds between O of H₂O and O of DMSO are possible which would make rather a strong contribution to the 2.8 Å peak. However, the O-O interference is masked by a much stronger interference involving S due to S's much larger scattering cross section. Thus, any more detailed discussion on O-O interference which might shed light on structure of "iceberg" and bulk portion of H₂O is not possible.

It is noted that at $x = 0.28$ the peak presumably due to interference involving S is at $r = 5.3$ Å, shorter than 5.6 Å as for the case in Mixing scheme **III** and pure DMSO. As discussed above, the total ten nearest neighbors (#2-#11 in Fig. 3) are responsible for the peak in distribution function at $r = 5.6$ Å for pure DMSO. I noted above that molecules 3-1-2 or 5-4-7 form a zigzag chain more tightly bound together by S=O dipole interactions than the average. The inter-chain interactions, on the other hand, may be of van der Waals or a weak hydrogen bonds between H on methyl group and O on the other DMSO molecule. When H₂O molecules are added, they are likely to penetrate in some of these loosely bound spaces to form stronger hydrogen bonds with O on DMSO. Typically space between 1 and 6, or 7 and 11 could be most likely. As a result, correlation between 1 and 6 or 11 is lost. Hence the interferences responsible for 5.3 Å peak in distribution function at $x = 0.28$ are smaller in number and more tightly "bound" together than 11 molecules shown in Fig.3 for pure liquid. The upshot of all these is that even in this H₂O-rich region, mixing scheme **I**, DMSO molecules are clustered together, smaller in size than that in mixing scheme **III**. (For distinction, I call this in Mixing scheme **I** a "small" cluster and that in mixing scheme **III** a "large" cluster). While the detailed form of this small cluster is not known, it must be mainly held together by S=O dipoles, (2-1-3, in Fig. 3, for example). If so, then hydrophobic CH₃ groups point outward of such a small cluster, and hence DMSO works as a hydrophobic solute. This is consistent with the finding of earlier thermodynamic studies, in that the x -dependence of the excess partial molar volume clearly showed a signature of a hydrophobic

solute.⁴⁻⁶ Furthermore, a small DMSO cluster existing in mixing scheme **I** sheds some additional light onto the mixing scheme **I** for aqueous DMSO. Generally, mixing scheme **I** has been understood as "preparing" for formation of an addition compound, a clathrate, of the type $S(H_2O)_m$ on freezing, where S stands for a solute.^{4,5} The value of m is typically 30,^{4,5} which is a reasonable number for H_2O molecules to surround a solute *i.e.* an "iceberg" formation. Turning to aqueous DMSO, the threshold value of mixing scheme **I** is $x = 0.28$. In terms of an addition compound, $DMSO(H_2O)_m$, the value of m is about 3, a much smaller number to form an "iceberg", while addition compounds, $DMSO \cdot 3H_2O$, $DMSO \cdot 2.5H_2O$, and $DMSO \cdot 0.5H_2O$ are known.¹⁵ The present work suggests DMSO exists as a "small" cluster in mixing scheme **I**. If the size of this "small" cluster is z, then 3z molecules of H_2O would surround this cluster; more reasonable situation. It would be interesting to determine the crystal structures of addition compounds, $DMSO \cdot 3H_2O$, $DMSO \cdot 2.5H_2O$, and $DMSO \cdot 0.5H_2O$ to see if indeed reminiscence of a "small" cluster exists in these compounds.

2.3.5 Mixing Scheme II

The distribution function, Fig. 5, in mixing scheme **II** changes gradually from that at $x = 0.28$ to that at $x = 0.5$. The peak at 5.3 Å shifts almost linearly with x to 5.6 Å, Fig. 6. At the same time, the pattern develops to that corresponding to mixing scheme **III** and to pure DMSO. Earlier thermodynamic studies suggested that mixing scheme **II** is such that two kinds of clusters, one rich in H_2O and the other rich in DMSO. In terms of terminology of the present work, mixing scheme **II** is a mixture of "small" and "large" clusters and the relative amount changes gradually. Alternatively, the gradual change in distribution function as x decreases shows the gradual process of collapse of a "large" cluster to a "small" one by H_2O gradually penetrating into inter-chain spaces in Fig.3. However, the present observation alone does not distinguish the above two alternative explanations.

2.4 Conclusions

In conclusion, the present study confirms mixing scheme **III** suggested by earlier thermodynamic studies.⁴⁻⁶ Namely, DMSO molecules make a "large" cluster with the same local structure as pure DMSO in the DMSO-rich region, $x > 0.56$. H_2O does not form any

structure to be conspicuous in the distribution function. These findings are in complete agreement with the conclusion by thermodynamic studies.⁴⁻⁶ In the H₂O-rich region, where mixing scheme I was suggested,⁴⁻⁶ it was found that DMSO form a "small" cluster via dipole attraction of hydrophilic S=O in aqueous solution rather than dissolved as a single molecule. As a result, hydrophobic CH₃ sticks outward, while hydrophilic S=O is hidden inside such a cluster. This provides a good reason why DMSO show a strong hydrophobic signature in the x -dependence of the partial molar volume of DMSO.⁴⁻⁶ The structure of H₂O is not very conspicuous in the present study, due to a large scattering cross section of S in solute DMSO. Thus, interferences involving O and C atoms are masked. Nevertheless, the present findings are not inconsistent with mixing scheme I suggested earlier.⁴⁻⁶ Rather, the present findings provided a deeper understanding to mixing scheme I for aqueous DMSO. For mixing scheme II, the present observation is also consistent with the thermodynamic understanding.⁴⁻⁶

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Table 1

The intermolecular S $\cdots$ S and S $\cdots$ O distances relative to the central molecule **1**. The results of structure simulation for pure DMSO. The numbering for molecules corresponds to the one shown in Figure 3. S(n) signifies the S atom on the n-th DMSO molecule. The underlines show the S $\cdots$ O distances shorter than 4.0 Å. The molecules with asterisk have hydrogen atoms which is near oxygen atom of the central molecule **1** or *vice versa*.

n	distance / Å		
	S(1) $\cdots$ S(n)	S(1) $\cdots$ O(n)	O(1) $\cdots$ S(n)
2*	4.3	<u>3.8</u>	<u>4.0</u>
3*	4.3	<u>3.7</u>	<u>3.8</u>
4	5.2	6.3	6.4
5	5.2	6.4	6.3
6*	5.4	4.6	4.7
7*	5.4	<u>4.0</u>	6.9
8*	5.4	6.9	<u>4.0</u>
9	6.1	6.6	6.0
10	6.1	6.0	6.6
11	6.1	6.9	6.9

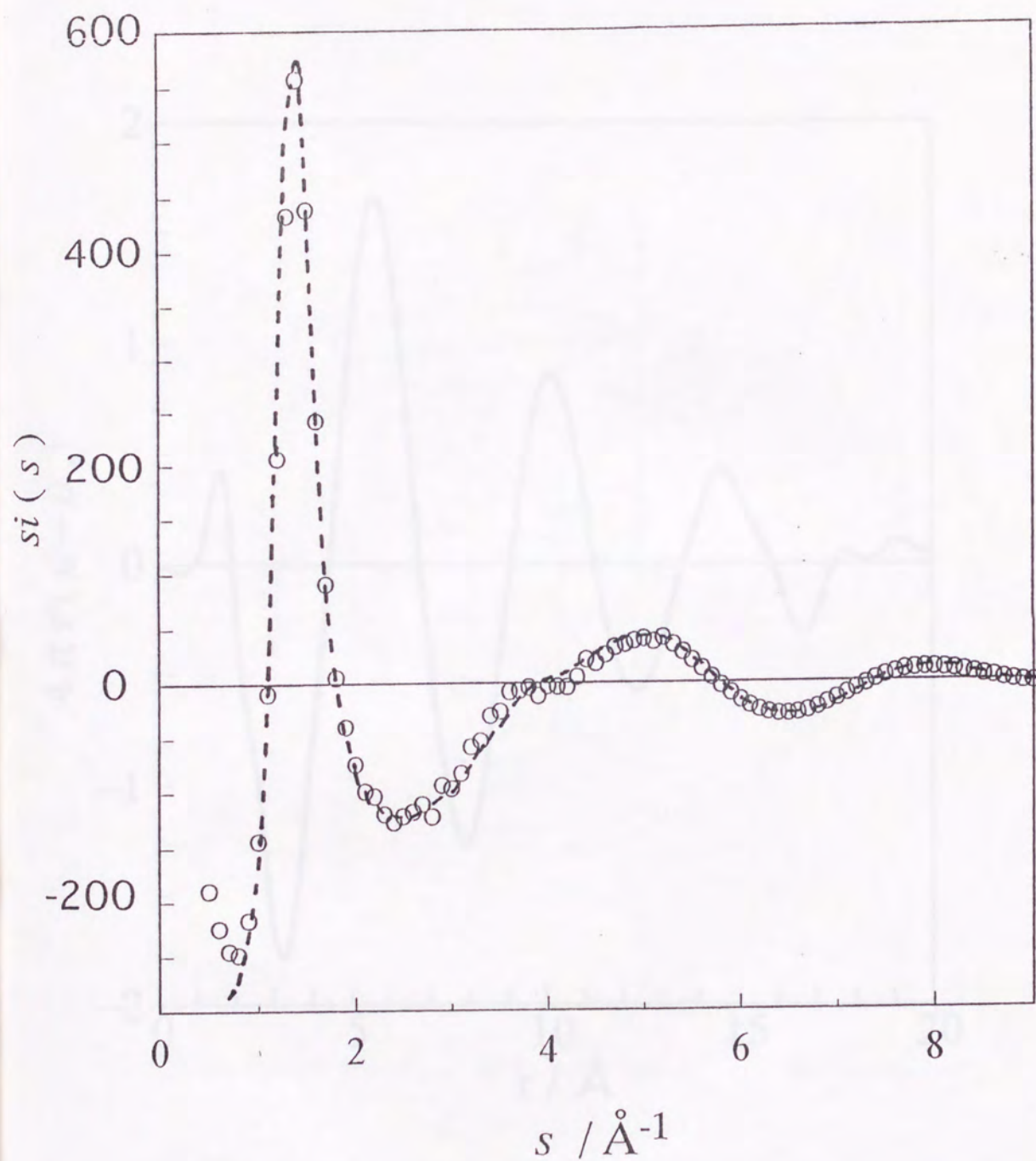


Fig. 1 The observed weighted structure function $si(s)$ for pure liquid DMSO (open circles) and the simulated one (broken curve).

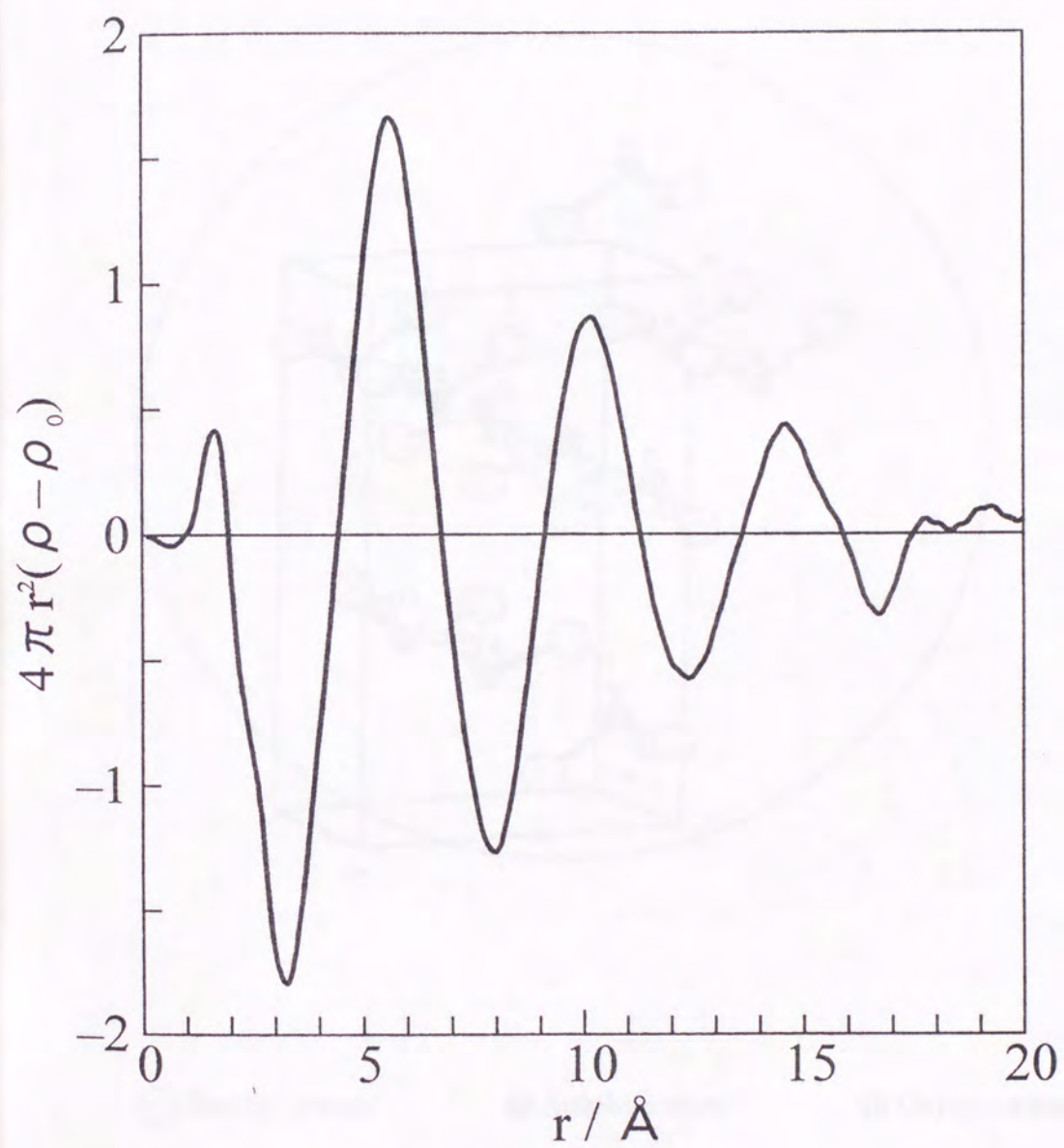
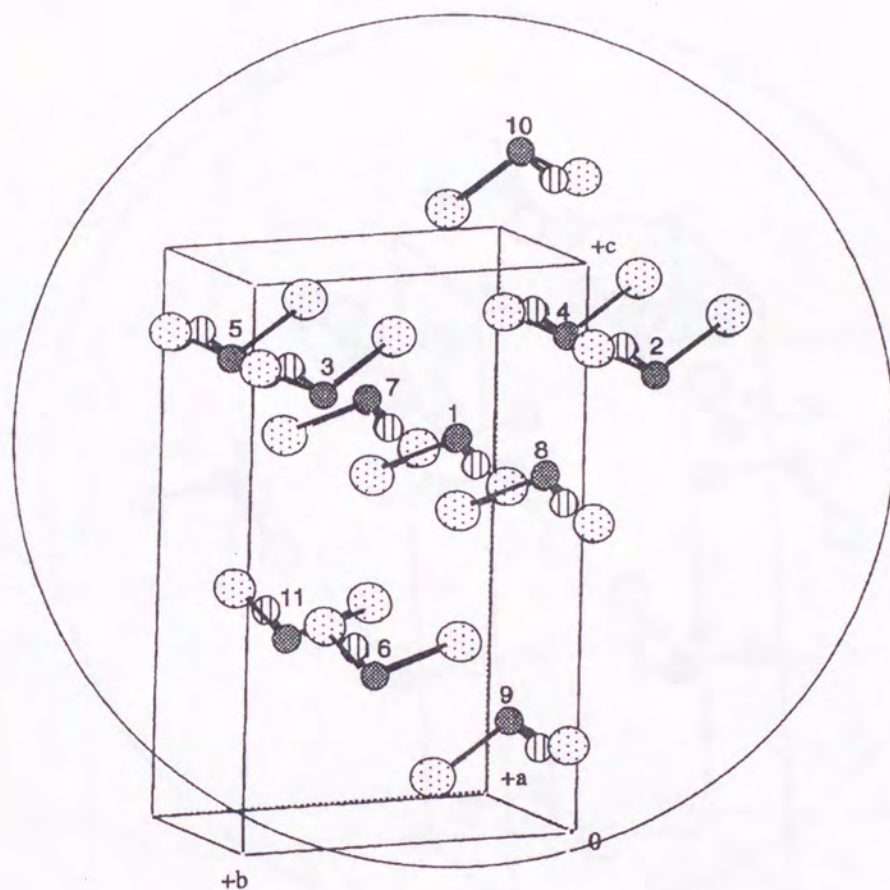


Fig. 2 The distribution function of pure liquid DMSO.



● Methyl group

● Sulphur atom

⦶ Oxygen atom

Fig. 3(a)

The local molecular arrangement for pure liquid DMSO. The neighboring molecules are numbered around the central molecule 1. The rectangular solid represents the imaginary "unit cell". The sphere of radius R_c is figured with the center at S atom of the molecule 1.

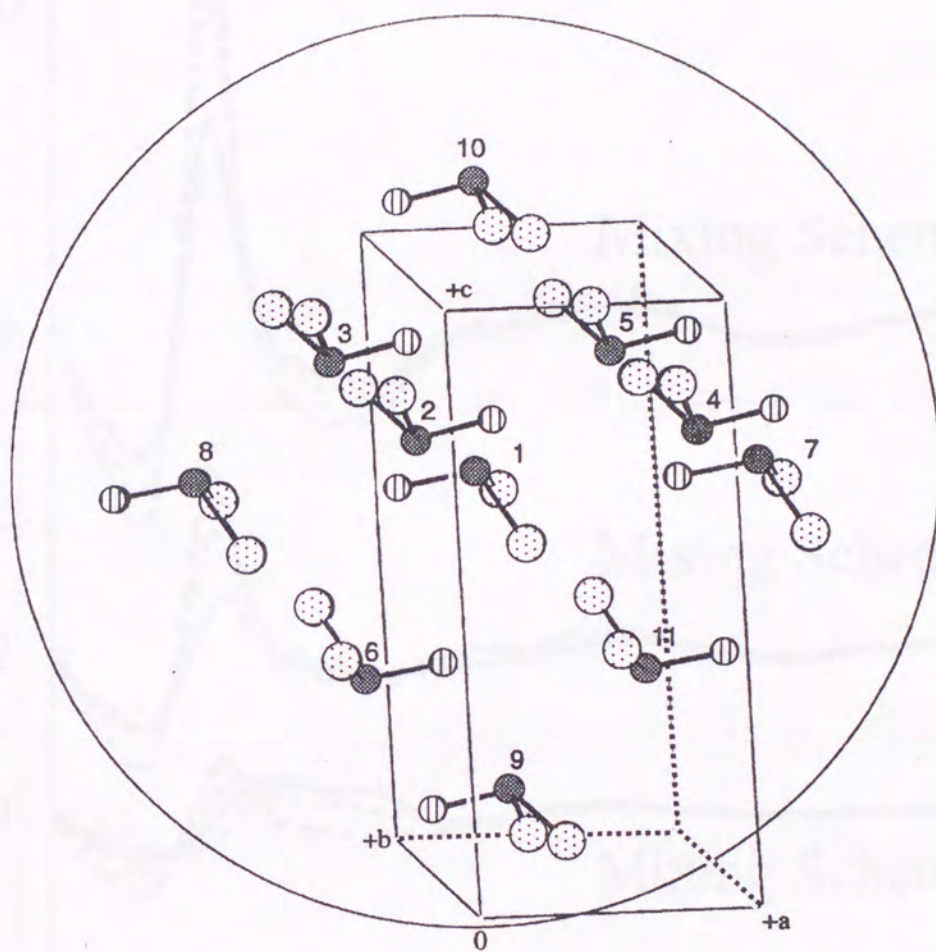


Fig3.(b)

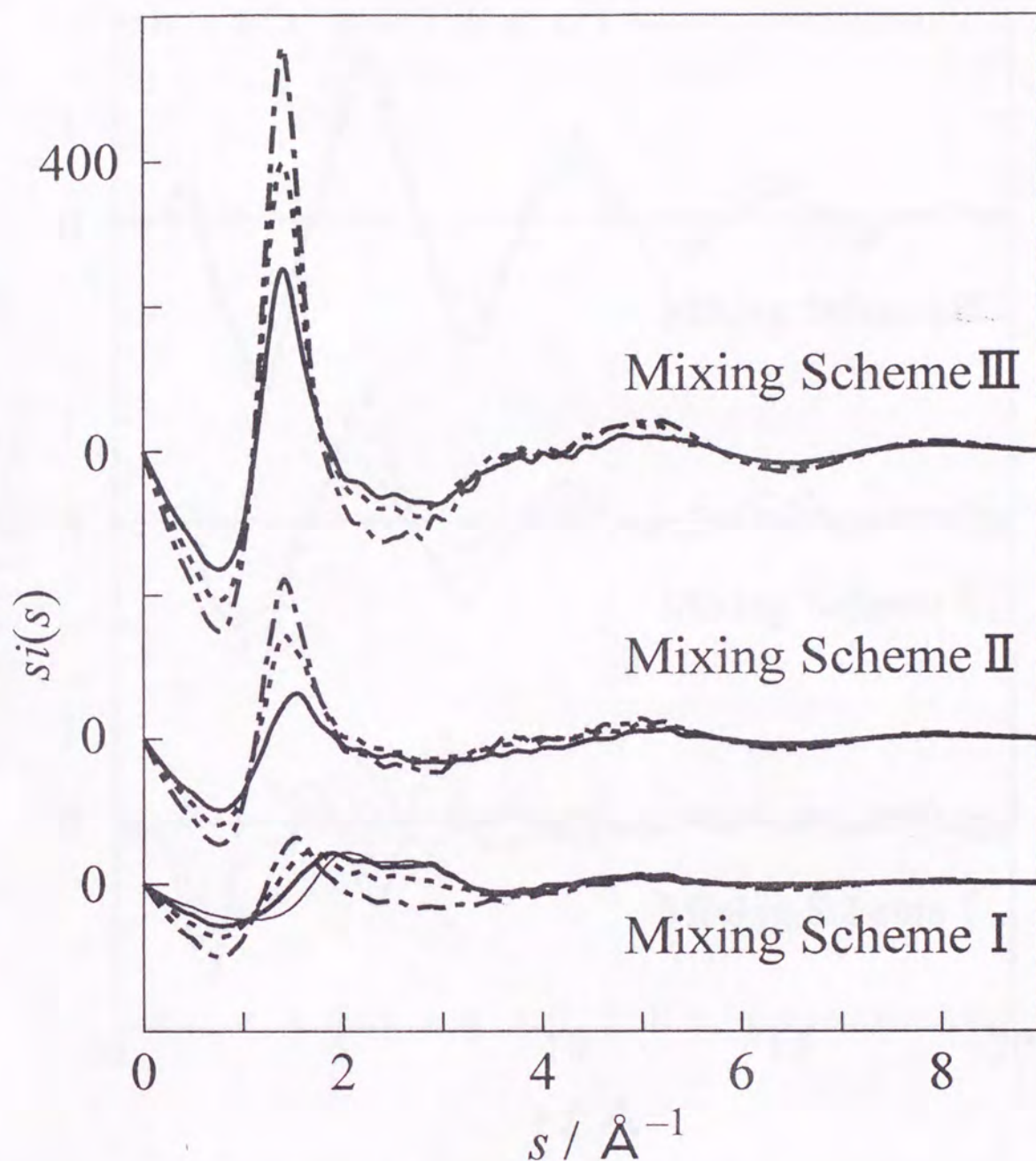


Fig. 4 The observed weighted structure functions $si(s)$ for aqueous DMSO solution, and pure DMSO and H_2O . The weighted structure functions are grouped into three mixing schemes I, II and III. In mixing scheme III, the chain curve, dotted curve, and full curve refer to pure DMSO and solution of $x = 0.80$ and 0.60 , respectively. In mixing scheme II, the chain curve, dotted curve and full curve refer to the solutions of $x = 0.50$, 0.38 , and 0.28 . In mixing scheme I, chain curve, dotted curve, thick full curve, and thin full curve represent the solutions of $x = 0.28$, 0.15 , 0.07 , and pure water.

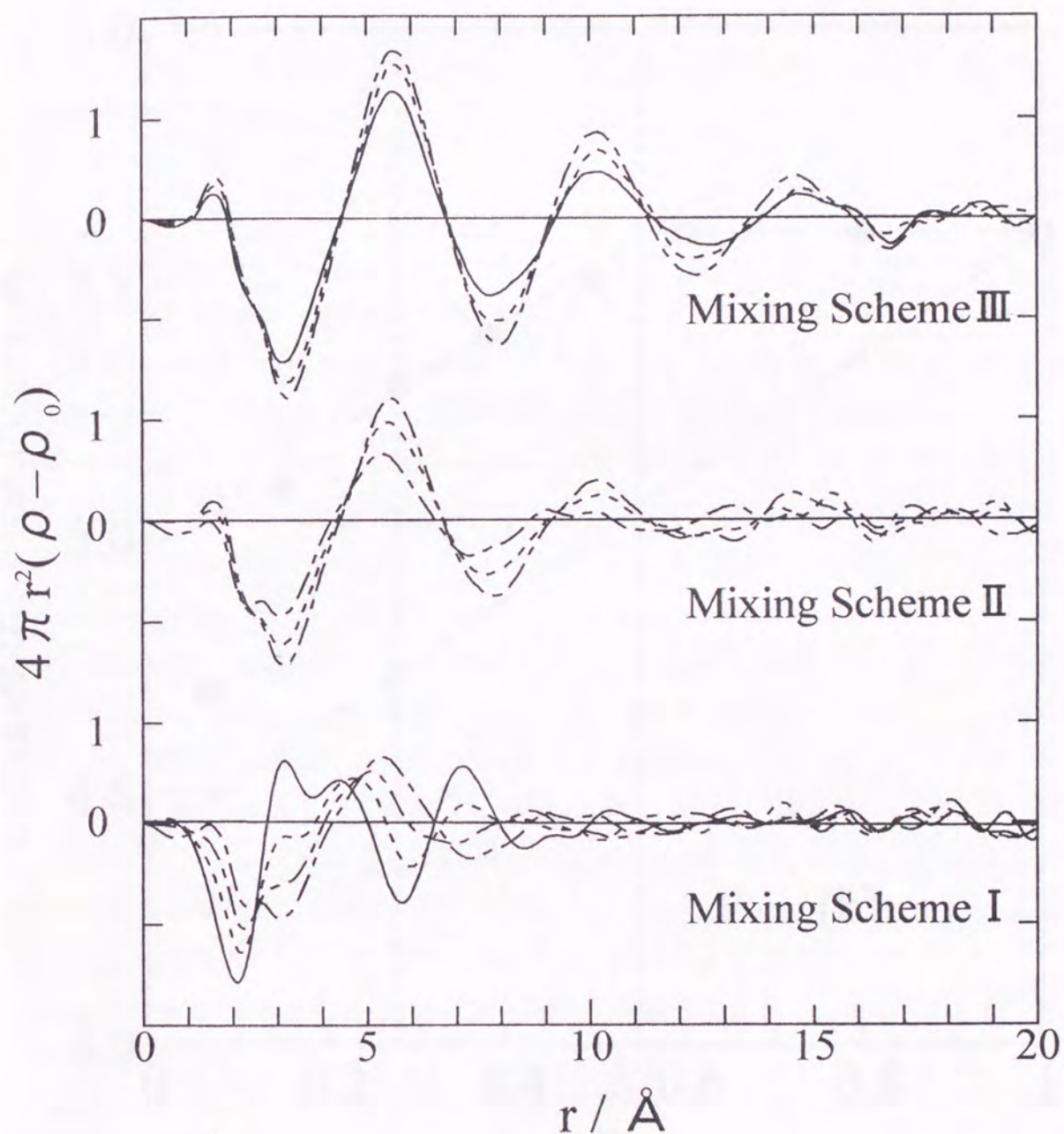


Fig. 5 The distribution functions of aqueous DMSO solutions, and pure DMSO and water. The curves are grouped into the mixing schemes I, II and III. The representation of the curves corresponds to that in Figure 4.

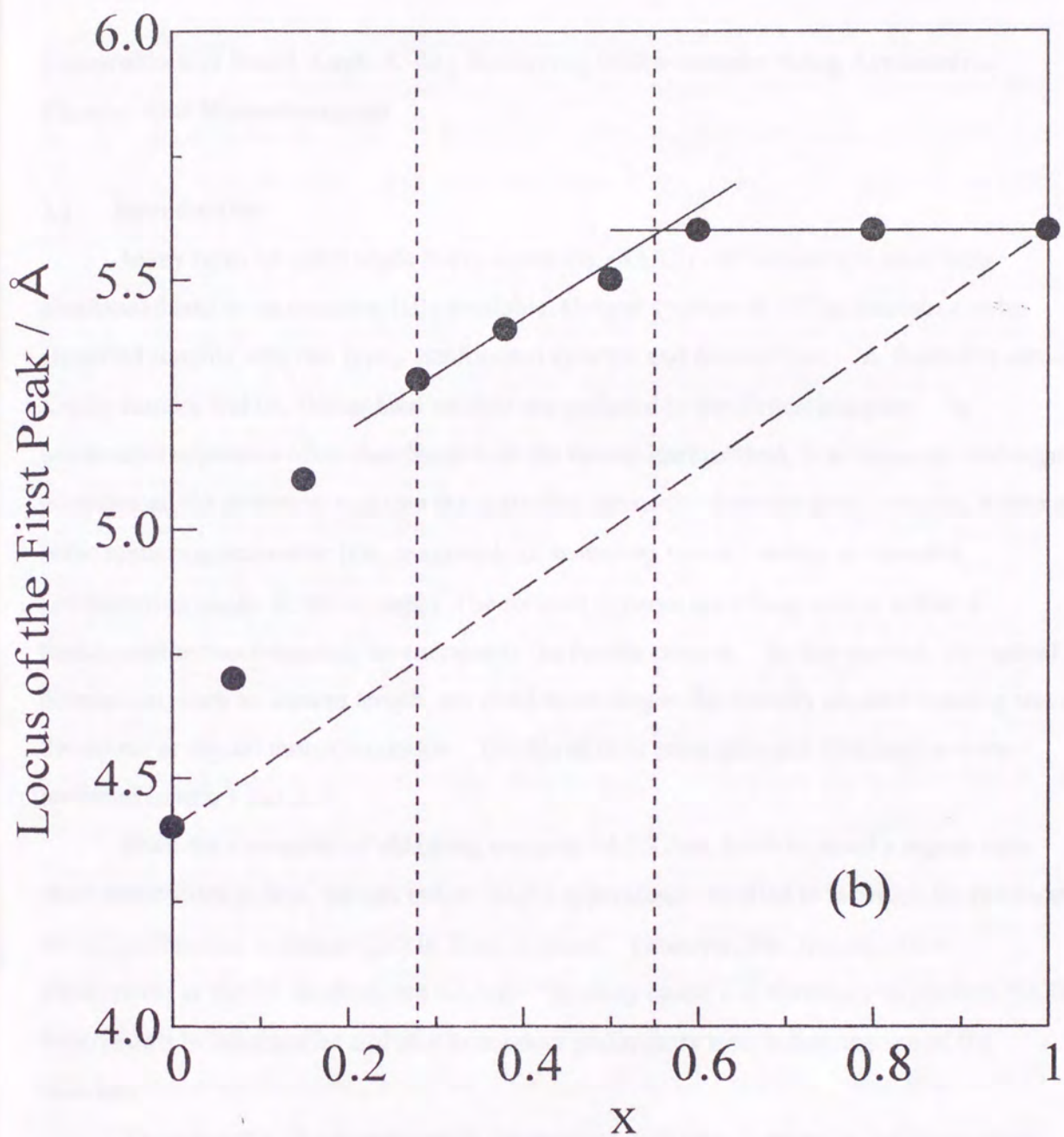


Fig. 6 Locus of the first peak of the distribution function for aqueous DMSO solutions.

Chapter 3

Construction of Small-Angle X-Ray Scattering Diffractometer using Asymmetric Channel-Cut Monochromator

3.1 Introduction

Many types of small angle X-ray scattering (SAXS) diffractometers have been constructed and some commercially available. Optical systems of diffractometers can be classified roughly into two types: nonfocused systems and focused one. A three-slits camera, Kratky camera and the Bonse-Hart method are included in the former category. In nonfocused apparatus other than those with the Bonse-Hart method, it is necessary to design complicated slit system to measure the scattering intensities down to small s region, where s is the scattering parameter (*i.e.*, magnitude of scattering vector) defined as $4\pi\sin\theta/\lambda$ (2θ : scattering angle, λ : wavelength). The focused systems use a bent-mirror and/or a bent-crystal monochromator; an example is the Franks camera. In this method, the optical dimensions, such as camera length, are fixed according to the initially decided bending rate of the mirror or crystal monochromator. Details of their principles and efficiencies were reviewed in refs. 1 and 2.

From the viewpoint of obtaining accurate SAXS data down to small s region with short accumulation time, we can utilize SAXS apparatuses installed at facilities for common use of synchrotron radiation (SR) in X-ray regions. However, the chances of the experiments at the SR facilities are limited. In many cases, it is necessary to perform SAXS experiments in laboratories and also to conduct preliminary tests before the use of the facilities.

To enable SAXS experiments in laboratories with easy treatments, a diffractometer was constructed. The aims concerning the design of the apparatus are the following:

- (1) the treatments, including the alignment of the optical system, are easy,
- (2) data down to similar low s values can be obtained, compared with the data commonly obtained at SR facilities,
- (3) the accuracy of the data is sufficient,
- (4) experiments can be carried out with a reasonable accumulation time,

(5) the measurable s region can be changed easily according to the requirement of samples, and

(6) the beam size is suitable small for the measurement of a small sample.

Complicated slit systems are not suitable to aim (1). Aim (4) requires employing a one- or two-dimensional detector. A one-dimensional PSPC(position sensitive proportional counter) is selected for ease. To satisfy aim (2) under the condition of the use of the PSPC, a narrow beam is unavoidable. For this requirement, an asymmetrically cut crystal was employed as a monochromator. It also enabled us to obtain a parallel beam after reflection by it, which satisfied aim (5), because any camera length can be selected without considering the focused length. A narrow, parallel beam is also effective for satisfying aim (6).

3.2 Constructing apparatus

A scheme of the apparatus is shown in Fig.1. The brightness of X-rays should be higher, and for that reason the rotating-anode X-ray generator with a fine focus system (M06XHF,MAC Science) was used. A copper anode was used. The point-focus geometry was employed and the focus size of X-ray was $0.3 \times 3 \text{ mm}^2$. The detector was a PSPC of 100 mm wide (PSPC-100,MAC Science). All paths of X-ray from the first slit to the beam stopper were in vacuum in order to avoid scattering from air and lose due to absorption by it. The vacuum chamber, monochromator box and pipes were made of aluminum alloy for its lightness (Matsuo Kogyosyo) and Capton films of $25 \mu\text{m}$ thickness were used as windows for X-ray paths. We can change the camera length simply by adding or removing the vacuum pipes in front of the PSPC. When the sample is set 1200 mm from the detector, it can measure s region from 0.01 to $0.4 \text{ \AA}^{-1}$.

A schematic representation of the monochromator is given in Fig.2. It is made of a Ge(220) single crystal with an asymmetric cut and a symmetric one (Fujitoku). The angle α between the incident beam and the asymmetric crystal surface was chosen to be 16.7° . The value of the asymmetric factor b is given by

$$b = \sin(\theta_B - \alpha) / \sin(\theta_B + \alpha) \quad (1)$$

where θ_B is the Bragg angle [22.65° for the Ge(220) and $\text{Cu } K\alpha_1$]. Its value becomes 0.16;

namely, the incident beam was narrowed to 1/6 its original size for the component parallel to the scattering plane. The subsequent reflection by the symmetric surface was aimed at achieving a simple and compact arrangement of the optical system. Although the appearance of the present optical system resembles that of the Bonse-Hart diffractometer³ from the viewpoint of the monochromatization of the incident X-ray beam by multireflections, the aim is quite different. The present purpose is to carry out SAXS experiments with ease and at the same time, to obtain data with proper measurable s region, while the aim of the Bonse-Hart diffractometer is to obtain data with higher resolution down to a small s region; I thereby employ multireflections by crystals for incident as well as scattered beams. As an application of the Bonse-Hart diffractometer, the use of an asymmetric monochromator has been proposed,^{3,4} with the aim of obtaining higher angle resolution of the incident beam by expanding the beam with a monochromator cut inversely to that in the present case, while the aim of the present case, while the aim of present optical system is to obtain a narrow beam using the asymmetrically cut monochromator.

The distance between the center of the monochromator and the second slit was chosen to be 90 mm, so that the incident beam was separated into $K\alpha_1$ and $K\alpha_2$ radiations. When only $K\alpha_1$ radiation was taken out through the second slit, the full-width at half maximum of the direct beam was about 0.3 mm at the position of the PSPC.

A beam stopper is set in the vacuum side in front of the PSPC, in order avoid scattering from air by the strong direct beam. The beam stopper is made of lead and a hole is bored at its center, at which a thin copper disk is attached. The direct beam passes through the disk, and the resulting attenuated beam reaches the PSPC. By measuring the attenuated intensity of the direct beam in the case where the sample is in and the case where the sample holder is empty, the absorption coefficient and l the path length of the sample. This determination is important for the correction of data such as absorption and subtraction of the background intensity or parasitic scattering.

To estimate the efficiency of new diffractometer, I measured a sample that had been measured using the SAXS equipment at the BL-15A station, Photon Factory(PF) at High Energy Accelerator Research Organization, Tsukuba.⁵ It employs the focused optical system with a bent mirror and a bent Si single crystal. The sample was glass-like carbon obtained by heat treatment at 3000°C.⁶ Figure 3 shows the results obtained using the present

diffractometer(dark curve),⁶ and those obtained using the equipment at PF(pale curve). The agreement between the two data sets is very good except in the low s region. The observable undulation in the scattering pattern of PF around $s \sim 0.03 \text{ \AA}^{-1}$ is due to the noise of the used detector. The enhancement in the intensity of PF data in the lowest s region is probably due to the contamination of scattering by air, because the X-ray path in PF was not in vacuum at the position where the sample was set.

The s resolution is comparable with that of the BL-15A equipment at PF. This was ascertained from the fact that the diffracted peaks from the collagen with periodic spacing of $653 \text{ \AA}$ appeared with the same distinctness. On the other hand, the peaks were smeared out in the case of using a commercial three slit camera.

The scattering intensity obtained using the present diffractometer is estimated to be about 1/500 of that in PF, when the X-ray generator is operated at 40 kV and 100 mA. Although the intensity is weak, samples with relatively strong SAXS powers can be measured in a reasonable accumulation time: e.g. porous materials such as various carbon materials, in 30 ~ 60 minutes, and solutions with micelles or colloids, in several hours. As a result, it is concluded that the diffractometer enables us to carry out SAXS experiments with easy treatment and provides data with a proper measurable s region and proper high s resolution.

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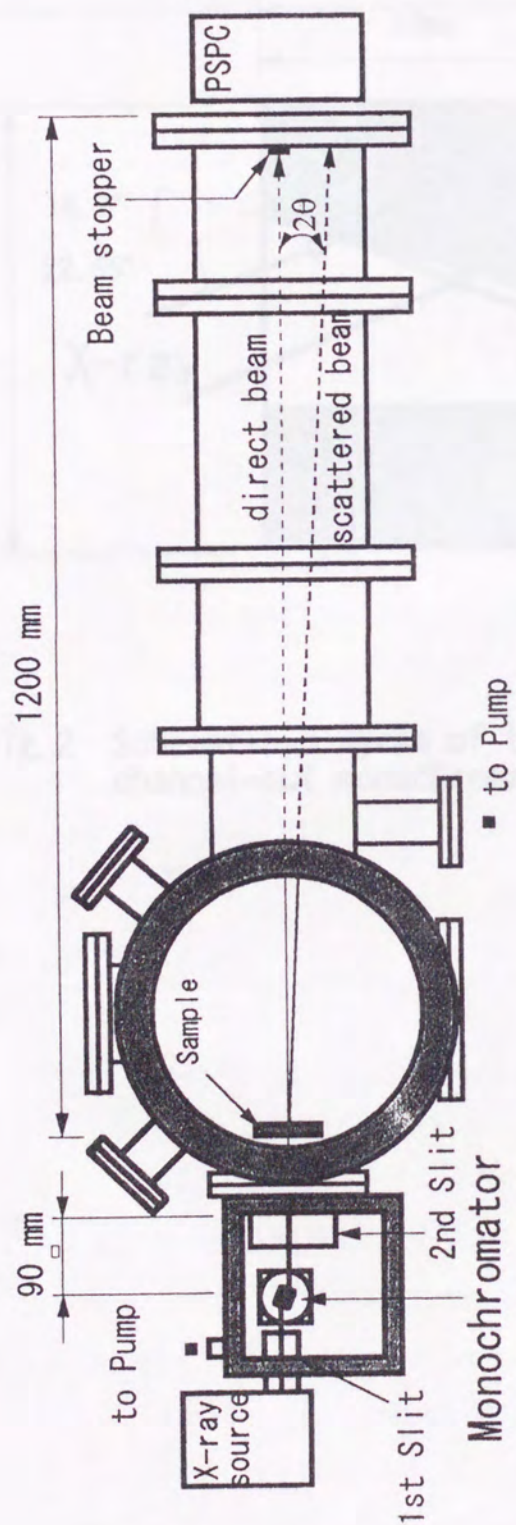


Fig.1 Schematic diagram of the SAXS diffractometer. The monochromator box and main chamber are represented in cross section.

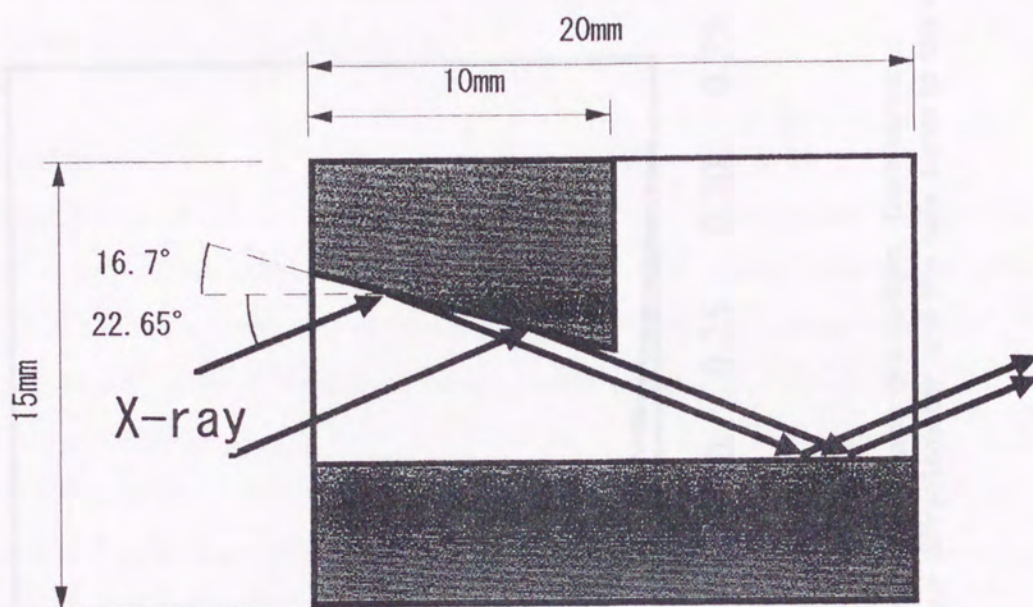


Fig.2 Schematic diagram of the asymmetric channel-cut monochromator.

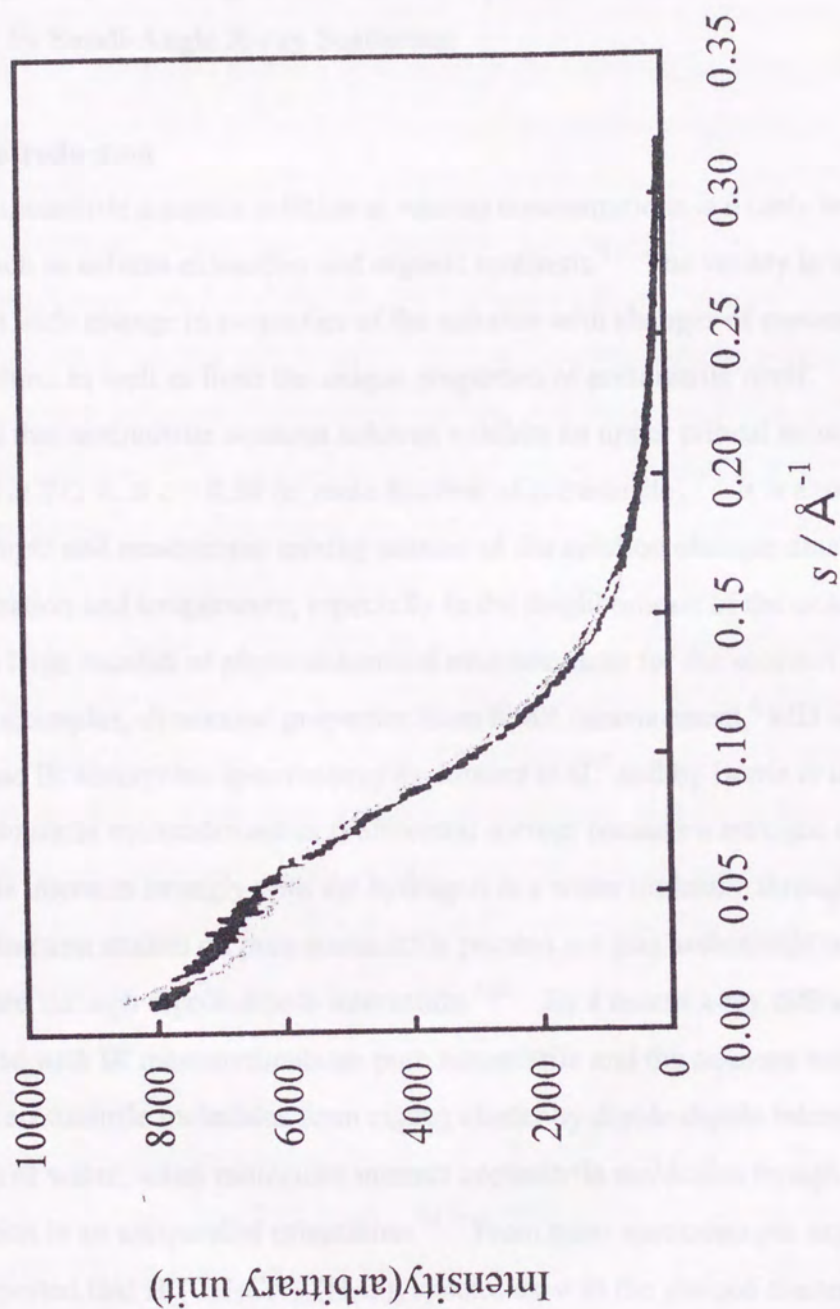


Fig.3 Comparison of the scattering intensity from glass-like carbon. Dark curve corresponds to the data obtained using our diffractometer, and the pale curve to the data obtained at BL-15A of PF.⁶

Chapter 4

Inhomogeneity of Mixing in Acetonitrile Aqueous Solution Studied by Small-Angle X-ray Scattering

4.1 Introduction

Acetonitrile aqueous solution at various concentrations is widely used as chemical fields such as solvent extraction and organic synthesis.¹ The variety in use will originate from the wide change in properties of the solution with changes of concentration and temperature, as well as from the unique properties of acetonitrile itself. Amitage *et al.* reported that acetonitrile aqueous solution exhibits an upper critical solution temperature (UCST) at 272 K at $c = 0.38$ (c : mole fraction of acetonitrile).² It is expected that the microscopic and mesoscopic mixing scheme of the solution changes drastically dependent on concentration and temperature, especially in the neighborhood of the critical point.

A large number of physicochemical measurements for the solution have been carried out; for examples, dynamical properties from NMR measurement,³ MD simulation by Kovacs *et al.*⁴ and IR absorption spectroscopy by Jomorz *et al.*⁵ and by Bertie *et al.*⁶ They reported that acetonitrile molecules act as preferential solvent because a nitrogen in an acetonitrile molecule interacts strongly with the hydrogen in a water molecule through hydrogen bonding. The diffraction studies on pure acetonitrile pointed out that acetonitrile molecules are weakly associated through dipole-dipole interaction.⁷⁻¹⁰ By a recent x-ray diffraction study combined with IR measurements on pure acetonitrile and the aqueous solution,¹¹ it is pointed out that acetonitrile molecules form zigzag cluster by dipole-dipole interaction, and that, on addition of water, water molecules interact acetonitrile molecules though dipole-dipole interaction in an antiparallel orientation.¹¹ From mass spectroscopic experiments¹²⁻¹⁴, Nishi *et al.* reported that $H^+(CH_3CN)_m(H_2O)_n$ species exist in the ionized clusters which are prepared by adiabatic expansion of the aqueous solution. From the macroscopic viewpoint, various thermodynamic studies^{2,15-20} pointed out unusual features of acetonitrile aqueous solution and most of them claimed that acetonitrile molecules act as a structure breaker.

Though many studies on acetonitrile aqueous solution have been performed as mentioned above, there are few reports on temperature dependence of the mixing scheme.

Blandamer *et al.* reported temperature dependence on the fluctuation in the solutions,^{2, 15} which were not so quantitative. Many studies, except Nishi's reports,¹²⁻¹⁴ focused on one or few molecules at the most in acetonitrile aqueous solutions, or, on the other hand, discussed macroscopic behaviors of water or acetonitrile molecules. The inhomogeneity of mixing in the solution will grow up with approaching to UCST and then the solution separates into two phases. In order to investigate the change of the mixing scheme of the solution with a critical point, it is necessary to comprehensively discuss the mixing scheme of the solution from microscopic, mesoscopic and macroscopic viewpoints.

Nishikawa has shown that the information from small-angle x-ray scattering (SAXS) is mesoscopic in size, and that the concentration fluctuation obtained by SAXS method is quantitative description of the mixing scheme, and then applied the method to some alcohol aqueous solutions.²¹⁻²⁴ In the present report, the present author applies the method to acetonitrile aqueous solution systems, and study 1) how the mixing state of this solution changes with the change of concentration and temperature and 2) how the phase separation occurs in the solution. The SAXS intensities of the solutions were measured at 273, 279, and 298 K in the range of $0.0 \leq c \leq 0.5$. Concentration and density fluctuations and cross term of these fluctuations, the Kirkwood-Buff parameters, and individual density fluctuations for acetonitrile and water were obtained by using zero-angle scattering intensities $I(0)$ and thermodynamic data such as partial molar volumes and isothermal compressibilities. The Ornstein-Zernike correlation lengths were also determined for some of the solutions for which it is possible to make the Ornstein-Zernike plot.

4.2 Experimental section

Scattering experiments were carried out at BL-15A Station, Photon Factory (PF) at National Laboratory for High Energy Accelerator Research Organization (KEK), Tsukuba, using a SAXS apparatus constructed at the station.²⁵ By a bent mirror and a bent monochromator made of Si single crystal, X-rays of 1.5 Å in wavelength were selected and the beam was focused to $1.0 \times 0.5 \text{ mm}^2$ at the position sensitive proportional counter (PSPC). The camera length was 2100 mm, and x-ray path was evacuated except at the position where the sample cell was set. The s region ($s = 4\pi \sin \theta / \lambda$, 2θ : scattering angle, λ : x-ray wavelength) ranging from 0.036 to 0.16 Å^{-1} was covered.

The sample was enclosed in a stainless sample cell with diamond windows of 0.1 mm in thickness. The thickness of the sample was *ca.* 1.0 mm. The temperature of the sample was kept constant by flow of temperature-controlled water through a jacket of the sample cell. The scattering intensities from the solutions of $c = 0.2, 0.3, 0.35, 0.38, 0.4, 0.45$ and 0.5 were measured at 273, 279, and 298 K. Intensities from pure water and acetonitrile, and background from the empty cell, were also measured as well as those from the solutions. The intensities from pure water and acetonitrile were used as the standard intensities to calibrate those of the solutions to absolute scale.

A beam stopper is made of lead. A hole is bored at the center of the stopper, at which a copper disk of 0.4 mm in thickness is stuck. Direct beam passes through the disk and the attenuated beam by it reaches to the PSPC. By comparing the attenuated intensity of the direct beam for the case that the sample is in the holder and the one for the case that the holder is empty, the absorption factor μl of the sample (μ : the linear absorption coefficient of the sample, l : the path length of the sample) can be obtained experimentally. For all the samples the absorption factors were determined in this way.

The data was corrected for the fluctuation in intensity of incident X-rays, background intensities, the effects of multiple scattering and absorption.

4.3 Results and Discussion

4.3.1 Zero-Angle X-ray Scattering Intensity. The scattered intensities of acetonitrile aqueous solutions after the necessary corrections are shown in Fig. 1 (a) - (c). Though the intensities are not converted to absolute scale yet, they are normalized to the intensities from the same volume. At small s -region, the scattering intensities increase as decreasing temperature. Especially, scattering intensity of $c = 0.38$ at 273 K (Fig. 1(c)) is the largest. The scattering intensities of pure water and acetonitrile are much weaker than those of solutions. In next section, it is shown that the concentration and density fluctuations which are related to the zero-angle x-ray scattering intensity, $I(0)$. The value of $I(0)$ needs to be obtained for each sample. According to the Ornstein-Zernike theory,²⁶ the scattering intensity near $s = 0$ is represented by the following equation for the sample at the neighborhood of the critical point,

$$I(s) = \frac{I(0)}{1 + \xi^2 s^2} \quad (1)$$

where ξ is the Ornstein-Zernike correlation length. The so-called Ornstein-Zernike plots of $1/I(s)$ vs. s^2 for the present solutions formed straight lines for $c = 0.3, 0.35, 0.38, 0.4, 0.45, 0.5$ at 273 and 279 K. From the intensities extrapolated to $s = 0$ for the plots, the values of $I(0)$ were determined. For the other solutions where the Ornstein-Zernike description is not a good approximation, $I(0)$'s were obtained from the extrapolation to $s = 0$ of polynomial fitting curves for scattered intensities.

The obtained $I(0)$'s must be converted into absolute scale. For one component system, $I(0)$ is related to the isothermal compressibility given by

$$I^{TD}(0) = Z^2 \left(\frac{N^2}{V} \right) \kappa_T k_B T, \quad (2)$$

where superscript "TD" at $I(0)$ means the zero-angle X-ray scattering intensity calculated from thermodynamic values, Z is the number of electrons in a molecule, and N is the number of molecules in the corresponding volume V . T is the thermodynamic temperature, k_B the Boltzmann constant, and κ_T is the isothermal compressibility. $I_W^{TD}(0)$ and $I_{AN}^{TD}(0)$ of water and acetonitrile are calculated from eq. 2 by use of the values of κ_T which were reported by Grant-Taylor *et al.*, namely 451 for water and 1154 TPa⁻¹ for acetonitrile at 298 K.²⁷ Zero-angle intensities $I^{TD}(0)$'s of water and acetonitrile obtained from eq. 2 are 2.06×10^{23} and 3.02×10^{23} e.u./cm³ respectively, where "e.u." means electron unit. The ratio of $I_{AN}^{TD}(0) / I_W^{TD}(0)$ is 1.47. The ratio of $I_{AN}(0) / I_W(0)$, where $I_{AN}(0)$ and $I_W(0)$ are the obtained values from the present SAXS experiments, is 1.48. It can be concluded that SAXS experiments and some corrections for data were made adequately, because the ratio of the intensities by experiments was in good agreement with that by calculation. By comparing $I_W(0)$ and $I_W^{TD}(0)$, $I(0)$'s of all solutions were converted into absolute scales. The

temperature dependence of $I(0)$'s is shown in Fig. 2, where the values are normalized to the intensities per cm^3 . The $I(0)$ values have maximum near $c = 0.38$ for all isotherms and increase remarkably as decreasing temperature.

4.3.2 Fluctuations Bhatia and Thornton gave a theoretical relation between the fluctuations and intensity of X-ray scattering.²⁸ Applying their theorem actually, Nishikawa obtained the fluctuations of some binary mixtures by SAXS experiments and discussed their mixing states.²¹⁻²⁴ The concentration and density fluctuations and cross term of these fluctuations are presented by $\overline{N} \langle (\Delta c)^2 \rangle$, $\langle (\Delta N)^2 \rangle / \overline{N}$ and $\langle (\Delta c)(\Delta N) \rangle$, respectively. The brackets and overline upper letters mean the average. The relation between the zero-angle intensity, $I(0)$, and concentration fluctuation, $\langle (\Delta c)^2 \rangle$, is given by²⁸

$$I(0)/\overline{N} = \overline{Z}^2 (N/V) k_B T \kappa_T + \{ \overline{Z} \delta - (Z_\alpha - Z_\beta) \}^2 \overline{N} \langle (\Delta c)^2 \rangle \quad (3)$$

where Z_α and Z_β is the number of electrons in an α molecule and a β molecule, respectively.

$\overline{Z}$ is given by

$$\overline{Z} = c_\alpha Z_\alpha + c_\beta Z_\beta, \quad (4)$$

where c_α and c_β are mole fractions of α and β . The concentration and density fluctuations and cross term of these fluctuations are related to some thermodynamics parameters, as shown in following equations,

$$\overline{N} \langle (\Delta c)^2 \rangle = \overline{N} k_B T / \left(\frac{\partial^2 G}{\partial c^2} \right)_{T,P,N} \quad (5)$$

$$\langle (\Delta N)^2 \rangle / \overline{N} = (\overline{N}/V) k_B T \kappa_T + \delta^2 [\overline{N} \langle (\Delta c)^2 \rangle] \quad (6)$$

$$\langle(\Delta N)(\Delta c)\rangle = -\delta \left[\overline{N} \langle(\Delta c)^2\rangle \right] \quad (7)$$

where G is the Gibbs free energy. The δ is the term correcting the size difference of α and β molecules, which is given by

$$\delta = (v_\alpha - v_\beta) \overline{N} / V, \quad (8)$$

where v_α and v_β is partial molar volumes of α and β molecules, respectively.

The partial molar volumes for the acetonitrile-water mixtures were obtained from reported excess molar volumes of the solution at 298 and 279 K.² The partial molar volumes at 273 K, whose values were not reported, were substituted for by those at 279 K. The isothermal compressibilities, κ_T , of acetonitrile aqueous solution were obtained at a few concentrations in the whole range at 298 K by Grant-Taylor *et al.*²⁷ The values of isothermal compressibility for the solution at the concentration necessary to the analyses, were obtained by extrapolation. The isothermal compressibilities at 273 and 279 K were substituted for by those of at 298 K because of small temperature dependence of the values in solution. The concentration fluctuations for the solutions were calculated from eq. 3 with $I(0)$ values obtained by the present experiment, and thermodynamic data of κ_T , v_W and v_{AN} . The density fluctuations and the cross term of these fluctuations were also calculated from eqs. 6 and 7. The concentration and density fluctuations and the cross term of these fluctuations are shown in Fig. 3 (a), (b) and (c), respectively. The values are also listed in Table 1. The absolute values of these parameters for fluctuations have maxima or minimum around $c = 0.38$, whose trends resemble the $I(0)$ behavior shown in Fig. 2

The concentration fluctuation for the binary ideal solution is given by $c(1 - c)$. Here, the ideal solution means the one where the volumes of the component molecules are the same and they are mixed randomly. The maximum value of the concentration fluctuation for the ideal solution is given by 0.25 at $c = 0.5$. At the neighborhood of UCST, the fluctuation for acetonitrile solution is several hundred times larger than the ideal solution, which shows the

extremely large inhomogeneity of mixing in the solution. The concentration fluctuations were obtained quantitatively and reported only for the aqueous solutions of ethanol,²⁴ *n*-propanol and *iso*-propanol,²³ and *tert*-butanol^{21,22}, which are miscible with water in any proportion and at any temperature.²⁴ The values of acetonitrile solutions are much larger than the ones of these alcohol solutions. As mentioned above, the partial molar volumes of v_{AN} and v_W for the solutions at 273 K were substituted for by those at 279 K. The author expects that the values of fluctuation at 273 K will become larger than the present values by use of the v_{AN} , v_W and κ_T values at the temperature. The present work is the first report for the concentration fluctuation of the solution which has the critical point.

The contour lines of the concentration fluctuation are drawn in Fig. 4, with the miscibility curve by Amitage *et al.*² This is rough map, because the measured points are not sufficient enough to draw contour lines. However, the map is useful sketch, which directly shows the inhomogeneity of molecular distribution for the solution in the phase diagram of concentration and temperature.

4.3.3 The Kirkwood-Buff parameters The Kirkwood-Buff parameters are defined by²⁹

$$G_{\alpha\beta} = \int (g_{\alpha\beta}(r) - 1) dV \quad (9)$$

where $g_{\alpha\beta}(r)$ is the partial distribution function. Ben-Naim pointed out importance of the Kirkwood-Buff parameters for solution chemistry and interpreted that the parameters are a measure of the affinity of α molecules around a β molecule and *vice versa*.³⁰ For a binary solution system, he showed that the Kirkwood-Buff parameters are obtained from three kinds of thermodynamic parameters, $\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P,N}$, v_i ($i = \alpha$ or β) and κ_T , and then discussed the mixing state in ethanol aqueous solution.³⁰ After his paper, some papers were published, reporting the Kirkwood-Buff parameters of various solutions by using of thermodynamic data only.^{31,32} However, there were some questions in accuracy, because it is difficult to obtain

accurate values from the second derivatives for the Gibbs free energy with respect to concentration.

The concentration fluctuation obtained by SAXS is directly related to the Kirkwood-Buff parameters,³³

$$G_{\alpha,\alpha} = -\frac{1}{n_\alpha} + \kappa_T k_B T + \frac{v_\alpha^2 n}{c_\alpha^2} \left[\overline{N} \langle (\Delta c)^2 \rangle \right] \quad (10)$$

$$G_{\beta,\beta} = -\frac{1}{n_\beta} + \kappa_T k_B T + \frac{v_\beta^2 n}{c_\beta^2} \left[\overline{N} \langle (\Delta c)^2 \rangle \right] \quad (11)$$

$$G_{\alpha,\beta} = \kappa_T k_B T + \frac{v_\alpha v_\beta n}{c_\alpha c_\beta} \left[\overline{N} \langle (\Delta c)^2 \rangle \right] \quad (12)$$

where n_α and n_β are the number densities of species α and β , and n is the one when molecules are not distinguished. Three Kirkwood-Buff parameters, $G_{\alpha\beta}$ are obtained separately from the combination of κ_T , v_i and $I(0)$ from SAXS experiments; namely, the values of the second derivative of the Gibbs free energy by concentration can be substituted for by the SAXS intensity which is possible to be directly measured.

The concentration and temperature dependence of these Kirkwood-Buff parameters for acetonitrile aqueous solutions are shown in Fig. 5 (a), (b) and (c) and listed in Table 2. Though values of the $G_{AN,AN}$ exhibit maximum at $c = 0.30$ and 298 K, the position of maximum shifts to $c = 0.38$ as decreasing temperature. The maxima of $G_{W,W}$ show inverse shift; namely at $c = 0.45$ for 298 K and at $c = 0.38$ for 273 K. Even at 30 K higher than UCST, the affinities of same kinds of molecules are considerably large and are increasing as approaching the critical temperature.

There are reports on the Kirkwood-Buff parameters of the solution by Matteoli *et al.* (at 303 K),³¹ and by Blandamer *et al.*,³² both of which were obtained by thermodynamic values only. The agreement of the present data with these data is not quantitative but qualitative. It is predicted that the disagreement originates from not the difference between mesoscopic

probe (SAXS data) and macroscopic one (thermodynamic data) but the data treatments especially in the second derivative of the Gibbs free energy. Satoh and Nakanishi also reported the parameters by Monte Carlo simulation at 298 K and 1 atmosphere with a NPT ensemble.³⁴ The values are much smaller than the present results and the maximum and minimum positions are not in agreement. It is thought that the system size (216 molecules in total) of the simulation is too small to investigate the mesoscopic fluctuations. Moreover, it is regrettable that the simulation for the solution in the neighborhood of $c = 0.38$ is missing.

With the average number density n_α of molecule α , the quantities $n_\alpha G_{\alpha\beta}$ are obtained, the physical meaning of which is the fluctuation of the particle numbers of each component. Namely, for $\alpha = \beta$, the quantity $(n_\alpha G_{\alpha\alpha} + 1)$ is the fluctuation of the particle number of α molecules and for $\alpha \neq \beta$ the quantity $n_\alpha G_{\alpha\beta}$ is the cross fluctuation between the particle number of α molecules and β molecules.²²⁻²⁴ The number fluctuation (density fluctuation) of each component is shown in Fig. 6 (a) and (b). Note that the density fluctuation $\langle(\Delta N)^2\rangle/\bar{N}$ given by eq. 6 and shown in Fig. 3 (b) refers to the fluctuation of numbers of molecules when the acetonitrile and water molecules are not distinguished. While the density fluctuation in the undistinguished case and that for water have maxima at $c = 0.38$ for all isotherms, the peak for acetonitrile has temperature dependence; namely it is positioned at lower concentration at higher temperature and shifts to $c = 0.38$ as approach to the critical temperature. The loci of the peaks of the density fluctuations are shown by lines in Fig. 4. The magnitude of the fluctuation of water molecules is much larger than that of acetonitrile molecules. Therefore, the contribution of the fluctuation of water is dominant in the total particle number fluctuation and the concentration fluctuation in the system. Same behaviors are found in the some alcohol aqueous solutions.²²⁻²⁴

4.3.4 Correlation length. From SAXS experiments, other information can be obtained; it is the correlation length which shows inhomogeneity of the system from the viewpoint of size. In the case of the system which is near the critical point, it is well known that the Ornstein-Zernike description is suitable. The relation between the SAXS intensity and the

Ornstein-Zernike correlation length ξ is given by eq. 1. The length is related to the correlation function of the density as given by²⁶

$$\langle (n(r_0) - \bar{n})(n(r_0 + r) - \bar{n}) \rangle \propto \exp\left(-\frac{r}{\xi}\right) / r \quad (13)$$

where $n(\mathbf{r})$ and $\bar{n}$ is the one-body density function at $\mathbf{r}$ and its average value, respectively. Equation 13 indicates that there is no aggregate with the characteristic size, and that the number of aggregates decreases exponentially with increase of their size and the correlation length ξ is the parameter of the decrease.

In the present aqueous acetonitrile solution, the function $(n(\mathbf{r}) - \bar{n})$ will refer to the difference of mean electron density for the aggregates made of acetonitrile and water molecules and that for surroundings. The lengths for the solutions at some concentrations and temperatures are obtained, where the Ornstein-Zernike description is a good approximation and are listed in Table 3. The value of ξ for the solutions, of course, increases with approach to the UCST and reaches to 30 several Å at the thermodynamic state of 1 K higher than the critical point. A rough sketch of the Ornstein-Zernike region for the solution is given in Fig. 4. The Ornstein-Zernike region means the thermodynamic states in the phase diagram where the Ornstein-Zernike description is realized.

4.3.5 Mixing state. For acetonitrile-water mixtures, the author obtained temperature and concentration dependence of the concentration fluctuation, density fluctuation, divided density fluctuations of acetonitrile and water, and correlation length for acetonitrile-water mixtures. The fluctuations of density and concentration and correlation length represent directly the inhomogeneity of the distribution of molecules in mesoscopic region. The fluctuations give information on the inhomogeneity from the viewpoint of number of each molecule, and the correlation length gives that on the inhomogeneity in the viewpoint of size of aggregates.

Koga *et al.* have also reported a comprehensive thermodynamic study on the solution by measuring excess chemical potentials and the second derivatives of the Gibbs free energy such as partial molar enthalpies, entropies and volumes.²⁰ They divided the solution into three composition regions in each of which the mixing scheme is quantitatively different from those of other regions. The composition region of the present SAXS study corresponds to Mixing Scheme II of Koga's definition.^{20,35} In the region, there is no hydrogen-bond-network of water molecules perfectly connected in the system (*i.e.* bond-percolation), and the solution consists of two kinds of clusters, each rich in acetonitrile or water. The clusters grow rapidly as decrease of temperature and separated at 272 K at $c = 0.38$ when the clusters reach the macroscopic size.

Koga *et al.* compared the mixing behavior in the aqueous acetonitrile with those of aqueous alcohols, and concluded that the thermodynamic behavior of aqueous acetonitrile is resembles with that of aqueous 1-propanol rather than that of ethanol or methanol in spite of that the molar volume of acetonitrile ($52.9 \text{ cm}^3 \text{ mol}^{-1}$) is close to that of methanol ($40.8 \text{ cm}^3 \text{ mol}^{-1}$) or that of ethanol ($58.7 \text{ cm}^3 \text{ mol}^{-1}$). This behavior will be caused by the difference of the effect of CN group in an acetonitrile molecule and OH group in an alcohol molecule. Nishikawa carried out the comprehensive studies on the mixing schemes of some aqueous alcohols by SAXS measurements,²¹⁻²⁴ being short of aqueous methanol. For aqueous *tert*-butyl alcohol solution, the characteristic factor determining the mixing state seems to be the formation of the cage structure of water molecules around a *tert*-butyl alcohol, such as clathrate-hydrate-like structure.^{21,22} For aqueous 1-propanol, the prominent factor is probably the formation of micelle by hydrophobic interaction.²³ For ethanol-water systems, the factor will take the balance of hydrogen bonding energies between ethanol-ethanol and water-ethanol.²⁴ The inhomogeneity of aqueous alcohols becomes smaller in order of 1-propanol, *tert*-butyl alcohol and ethanol. The inhomogeneity of aqueous ethanol is several 10 times smaller than that of aqueous acetonitrile. In the case of aqueous methanol, which was not studied, the fluctuation will be less compared with aqueous ethanol, and the mixing scheme is expected to be close to the ideal mixing. The methyl group in acetonitrile is too small to form aggregations by hydrophobic interaction. Then, it is expected that the acetonitrile molecules aggregate with dipole-dipole interaction of CN groups. In fact, it is dominant interaction to form the structure of neat liquid acetonitrile.⁷⁻¹¹ In the aqueous

solution, of course, the hydrogen bonding between CN group and OH group exists.

However, the bonding will be weaker than the one between OH and OH. Consequently water molecules aggregate with themselves and acetonitrile molecules do. This will be the mechanism of large inhomogeneity of the mixing in the solution and at last reach to the phase separation. The important factor which determines the mixing scheme of the acetonitrile-water system is expected to be strong hydrogen bonding of water molecules, weak one of water and acetonitrile molecules and dipole-dipole interaction of acetonitrile molecules.

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Table 1 Zero-Angle X-ray scattering intensities and fluctuations of aqueous acetonitrile solutions.

298K

c	$I(0)$ (10^{21} e.u./cm ³)	$N\langle(\Delta c)^2\rangle$	$\langle(\Delta N)^2\rangle/N$	$\langle(\Delta c)(\Delta N)\rangle$
0.0	2.06	-	-	-
0.2	13.5	1.70	3.34	-2.37
0.3	27.5	4.82	7.52	-6.00
0.35	30.3	6.17	8.63	-7.27
0.38	28.0	6.17	8.08	-7.04
0.40	26.7	6.17	7.77	-6.90
0.45	22.5	5.86	6.67	-6.23
0.5	15.7	4.40	4.55	-4.45
1.0	3.02	-	-	-

279K

c	$I(0)$ (10^{21} e.u./cm ³)	$N\langle(\Delta c)^2\rangle$	$\langle(\Delta N)^2\rangle/N$	$\langle(\Delta c)(\Delta N)\rangle$
0.0	1.94	-	-	-
0.2	19.7	3.4	6.2	-4.55
0.3	62.7	12.6	19.1	-15.5
0.35	79.7	18.6	25.3	-21.6
0.38	79.9	20.5	26.0	-23.0
0.40	69.7	18.8	23.0	-20.7
0.45	52.2	16.2	17.8	-16.9
0.5	30.0	10.3	10.3	-10.3
1.0	2.83	-	-	-

273K

c	$I(0)$ (10^{21} e.u./cm ³)	$N\langle(\Delta c)^2\rangle$	$\langle(\Delta N)^2\rangle/N$	$\langle(\Delta c)(\Delta N)\rangle$
0.0	1.9	-	-	-
0.2	28.0	5.0	8.97	-6.66
0.3	108	22.1	33.4	-27.1
0.35	206	49.0	66.4	-56.9
0.38	252	65.9	83.4	-74.1
0.40	170	46.8	57.0	-51.6
0.45	113	39.1	39.1	-37.3
0.5	48.2	17.0	17.0	-17.0
1.0	2.8	-	-	-

Table 2 The Kirkwood-Buff parameters and density fluctuations of acetonitrile ($n_{AN}G_{AN,AN}+1$) and water ($n_WG_{W,W}+1$) of aqueous acetonitrile solutions.

298K

c	$G_{AN,AN}$ ($\text{\AA}^3\text{molecule}^{-1}$)	$G_{W,W}$ ($\text{\AA}^3\text{molecule}^{-1}$)	$G_{AN,W}$ ($\text{\AA}^3\text{molecule}^{-1}$)	$n_{AN}G_{AN,AN}+1$	$N_WG_{W,W}+1$
0.20	698	433	-656	4.44	9.53
0.30	829	1527	-1247	6.36	24.2
0.35	730	2155	-1389	6.18	29.6
0.38	573	2299	-1292	5.27	29.0
0.40	496	2397	-1242	4.80	28.7
0.45	321	2566	-1080	3.61	26.7
0.50	137	2206	-759	2.18	19.9

279K

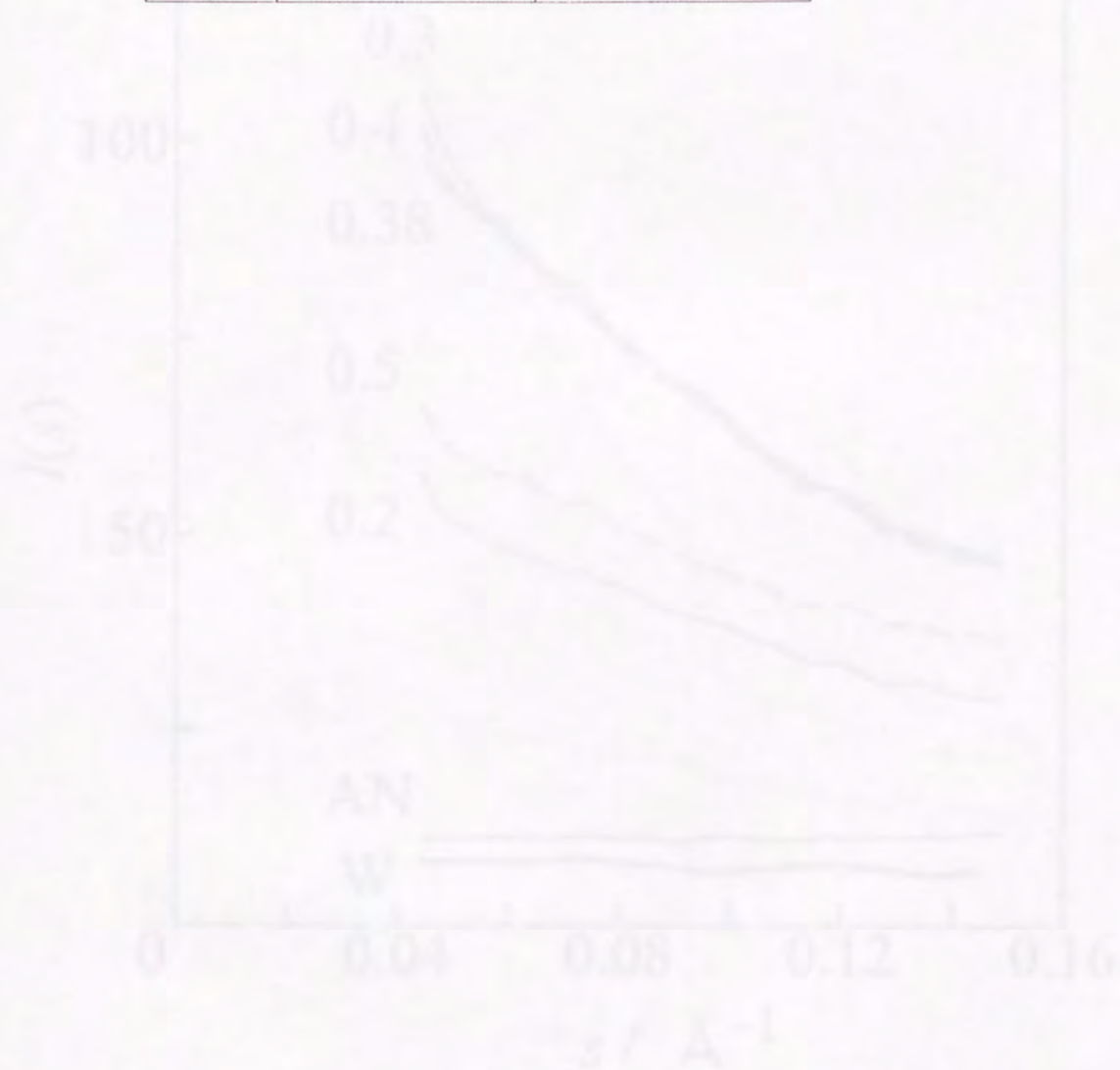
c	$G_{AN,AN}$ ($\text{\AA}^3\text{molecule}^{-1}$)	$G_{W,W}$ ($\text{\AA}^3\text{molecule}^{-1}$)	$G_{AN,W}$ ($\text{\AA}^3\text{molecule}^{-1}$)	$n_{AN}G_{AN,AN}+1$	$N_WG_{W,W}+1$
0.20	1634	869	-1295	9.12	18.3
0.30	2440	4013	-3248	16.9	62.6
0.35	2500	6491	-4158	18.9	88.3
0.38	2226	7619	-4256	17.8	95.2
0.40	1795	7298	-3763	14.9	86.6
0.45	1112	7060	-2964	10.2	72.9
0.50	486	5192	-1777	5.3	46.4

273K

c	$G_{AN,AN}$ ($\text{\AA}^3\text{molecule}^{-1}$)	$G_{W,W}$ ($\text{\AA}^3\text{molecule}^{-1}$)	$G_{AN,W}$ ($\text{\AA}^3\text{molecule}^{-1}$)	$n_{AN}G_{AN,AN}+1$	$N_WG_{W,W}+1$
0.20	2483	1294	-1896	13.3	26.7
0.30	4376	7056	-5675	29.6	109.2
0.35	6799	17188	-10940	49.8	232.3
0.38	7444	24660	-13686	57.2	306.0
0.40	4648	18259	-9356	37.1	215.3
0.45	2592	15668	-6534	22.4	160.7
0.50	879	8678	-2948	8.69	76.9

Table3 The Correlation lengths of the Orstein-Zernike for aqueous acetonitrile solutions.

c	273K(Å)	279K(Å)
0.2	-	-
0.3	21.3	14.4
0.35	28.8	16.7
0.38	31.9	16.6
0.4	25.5	15.3
0.45	21.6	13.9
0.5	13.6	10.0



Fig(1a) Scattering intensity of aqueous acetonitrile and water at 273K.

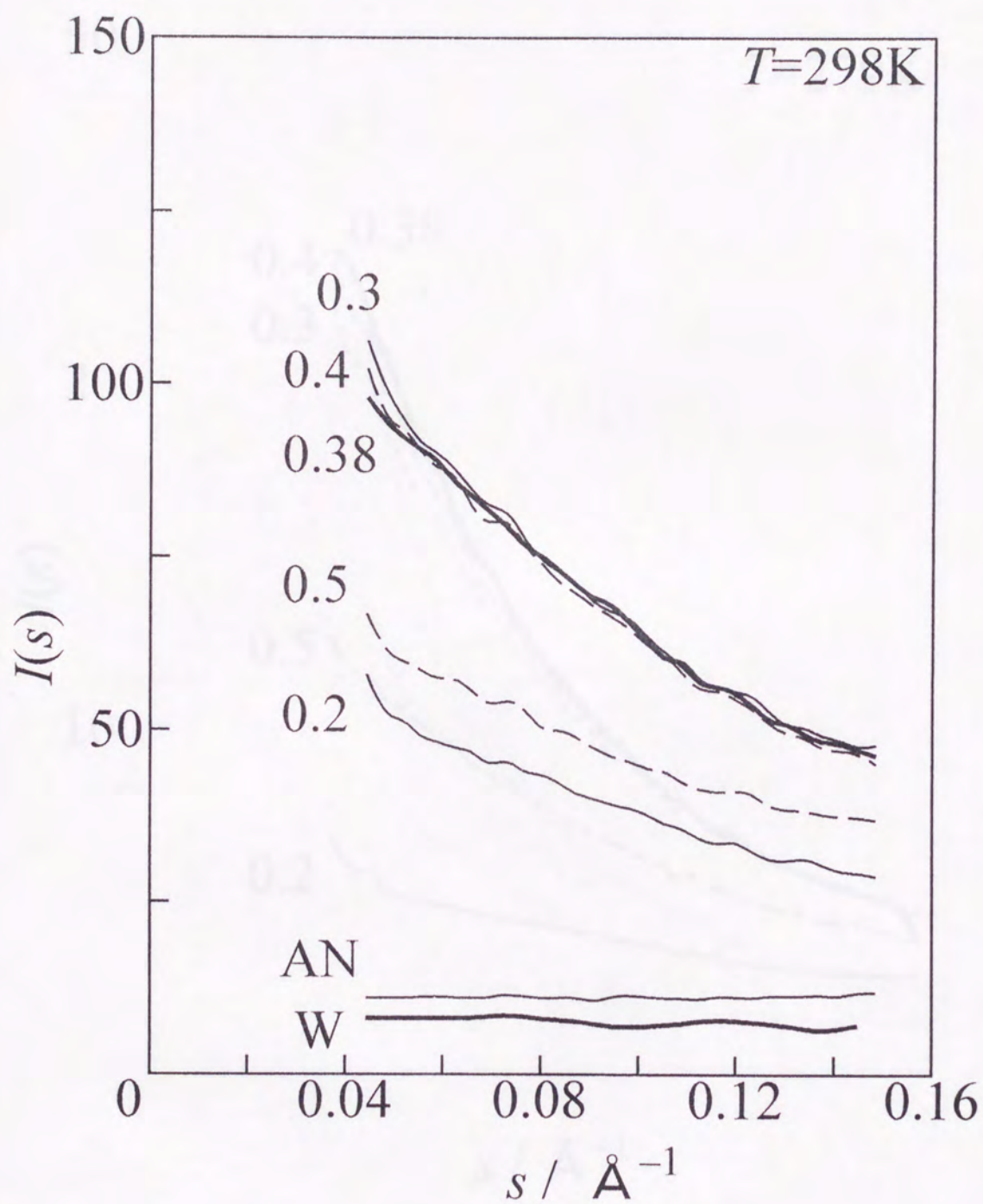


Fig1(a) Scattering intensities of aqueous acetonitrile solutions at 298K

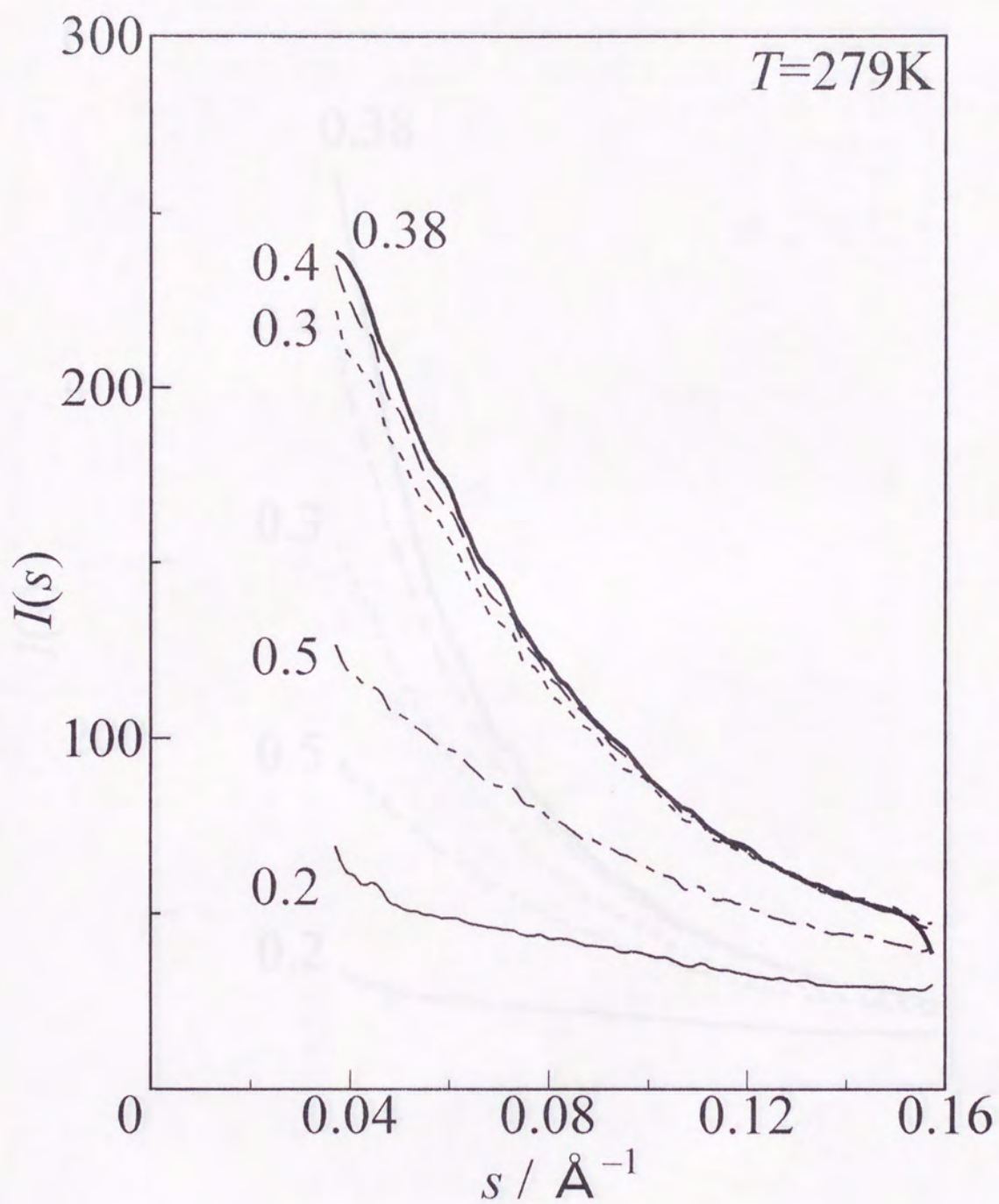


Fig1(b) Scattering intensities of aqueous acetonitrile solutions at 279K

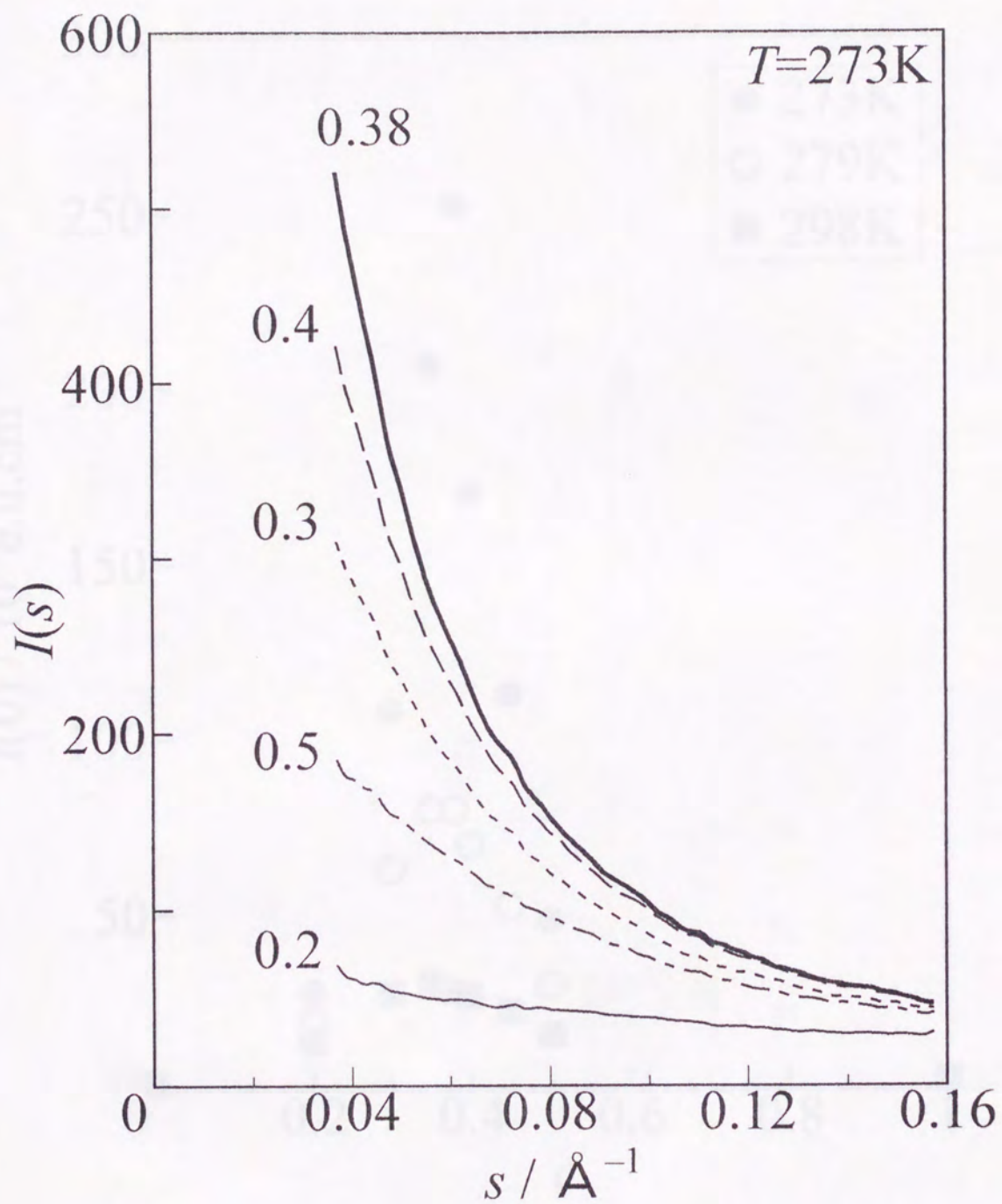


Fig1(c) Scattering intensities of aqueous acetonitrile solutions at 273K

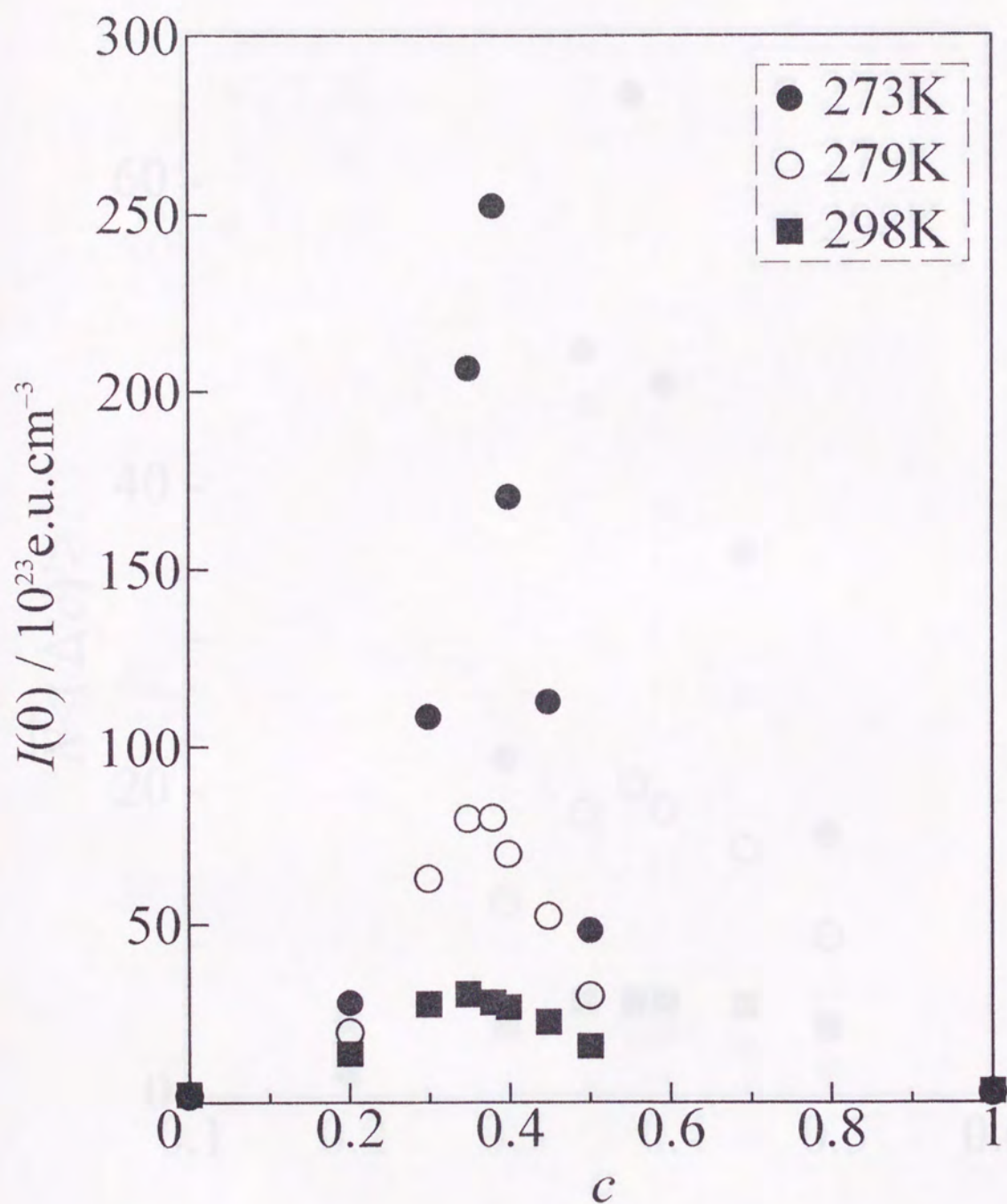


Fig2 Zero-angle X-ray scattering intensities of aqueous acetonitrile solutions against the mole fraction of acetonitrile(c).

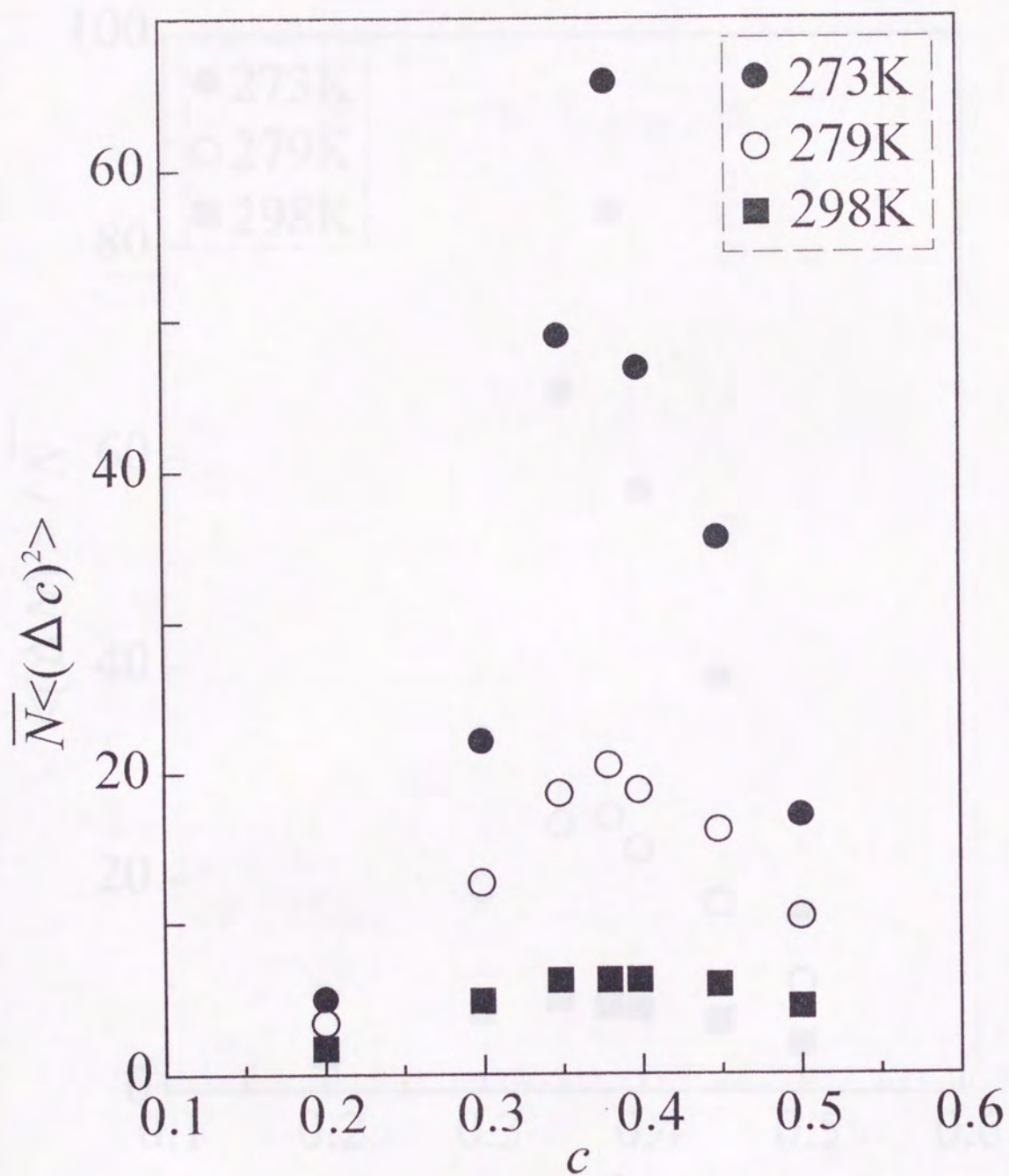


Fig3(a) Concentration fluctuation of aqueous acetonitrile solutions.

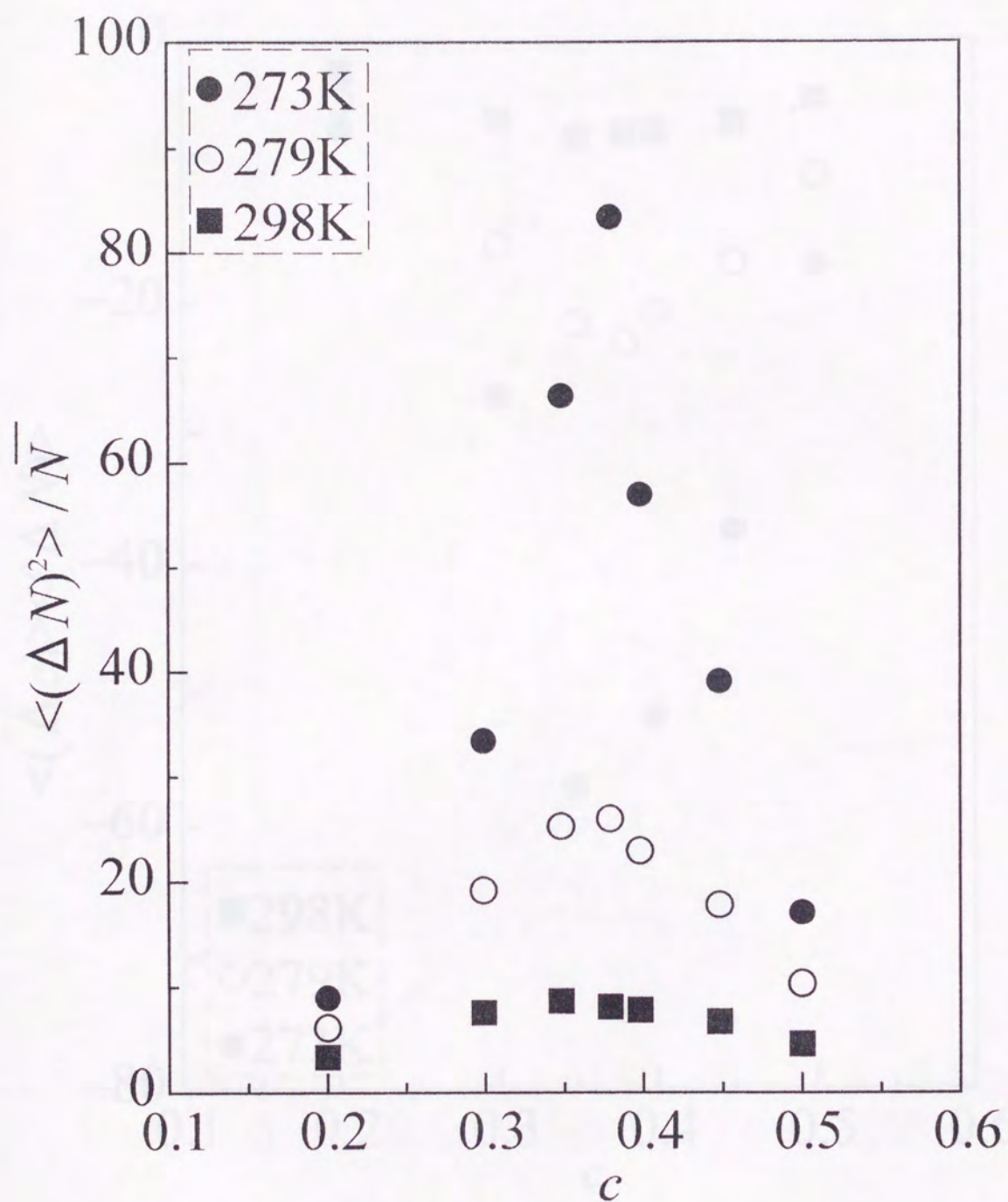


Fig3(b) Density fluctuation of aqueous acetonitrile solutions.

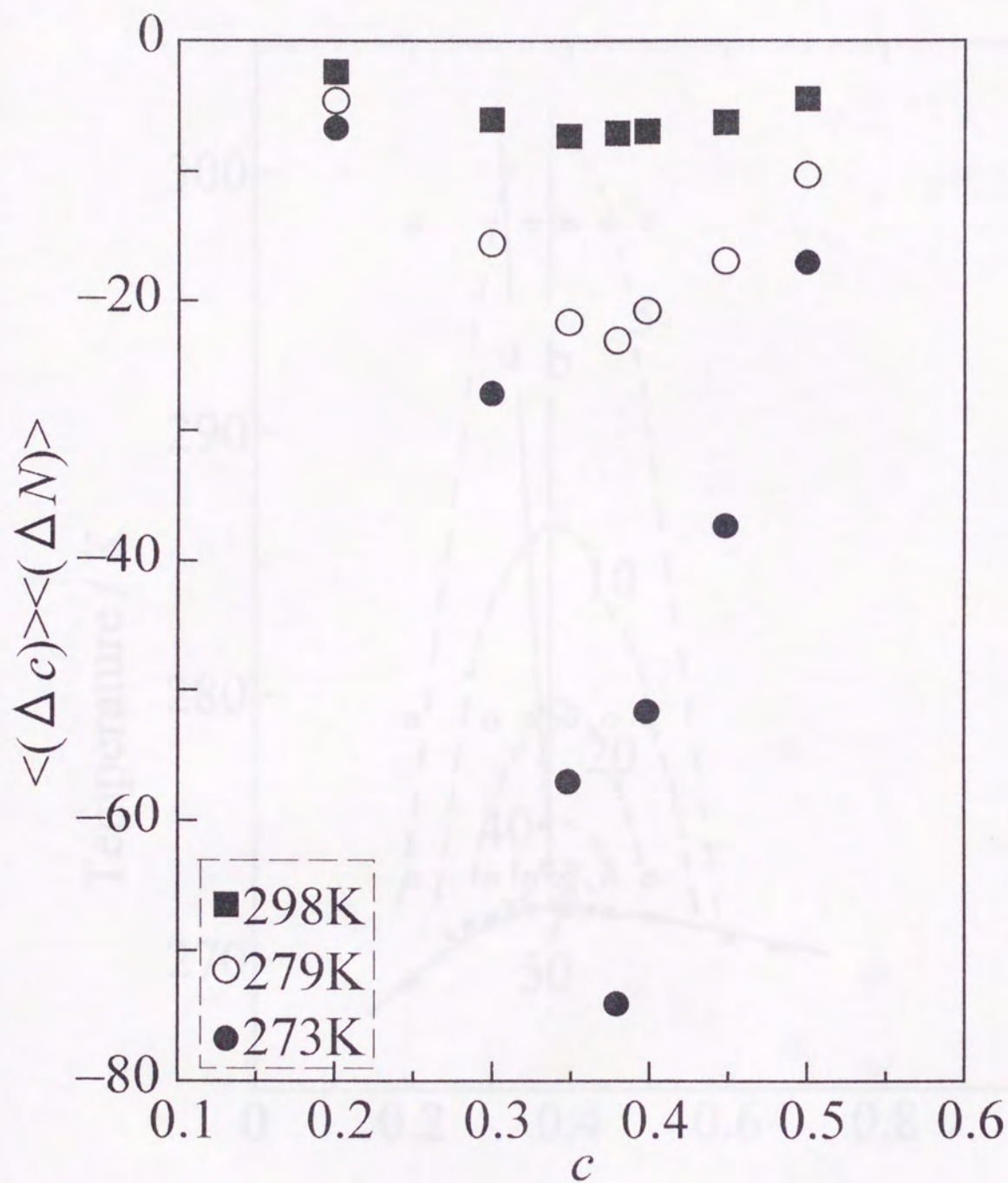


Fig3(c) Cross term of aqueous acetonitrile solutions.

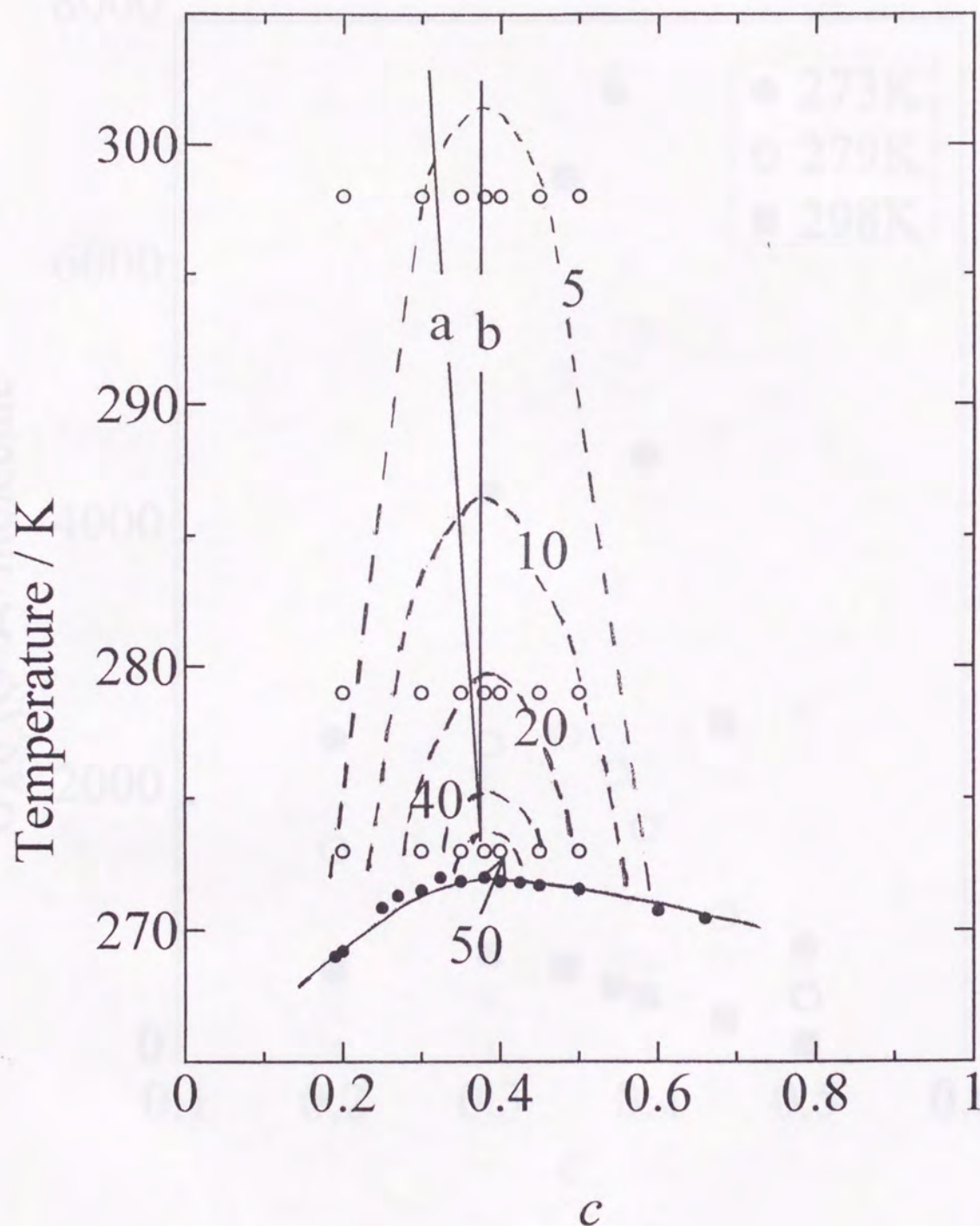


Fig4 Contour curve (broken curves) of the concentration fluctuation of aqueous acetonitrile solutions. The numbers on the curve show the values of the concentration fluctuation. Solid curve refers to the miscibility curve²⁾. Open circles are the measured points of the present study. The solid line **a** refers to the locus of the maxima in the isotherms for the density fluctuation of acetonitrile and the line **b** refers to the loci for the ones of water and of undistinguished particles. The dotted region shows the Orstein-Zernike region.

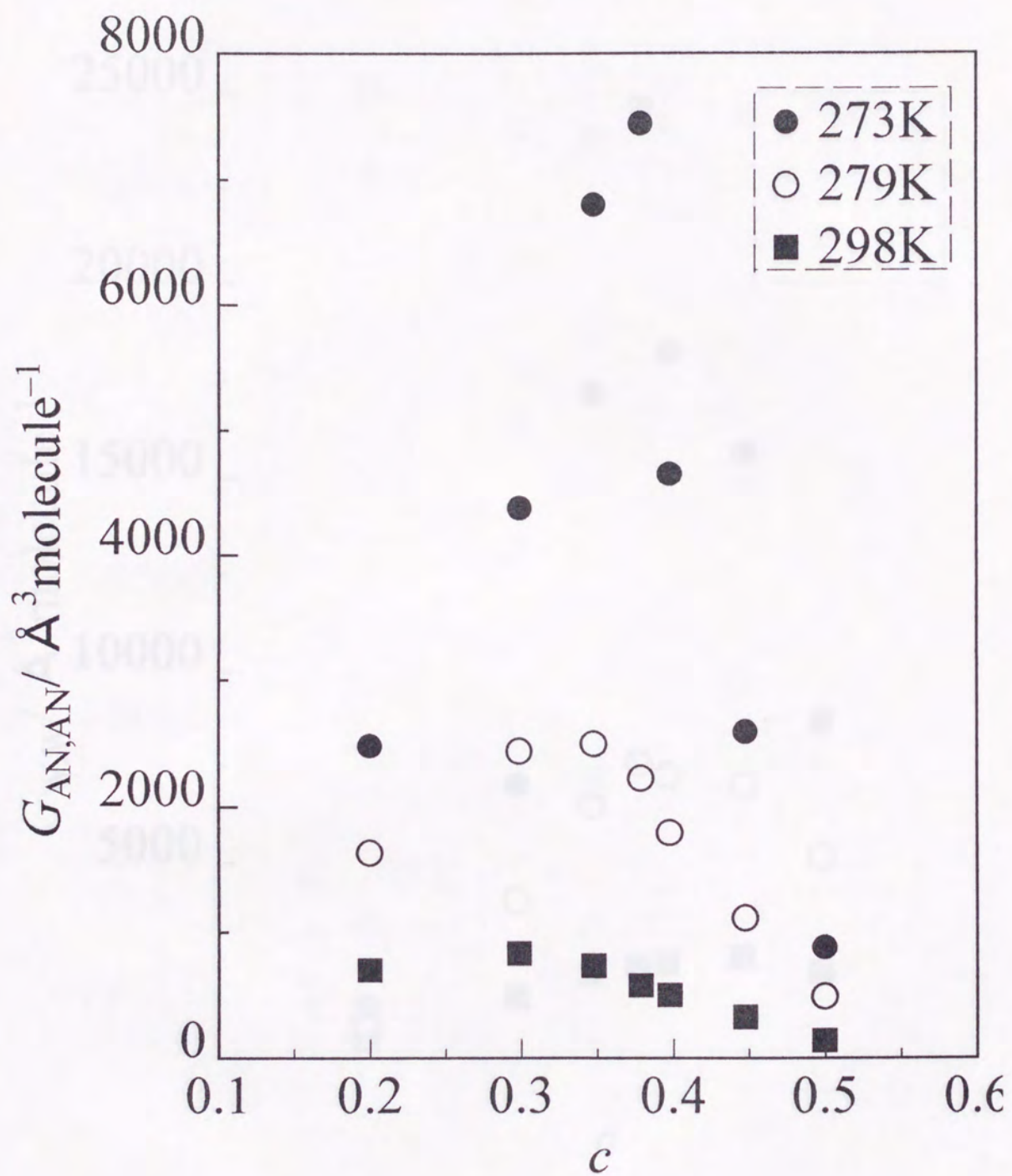


Fig5(a) The Kirkwood-Buff parameters ($G_{AN,AN}$) of aqueous acetonitrile solutions.

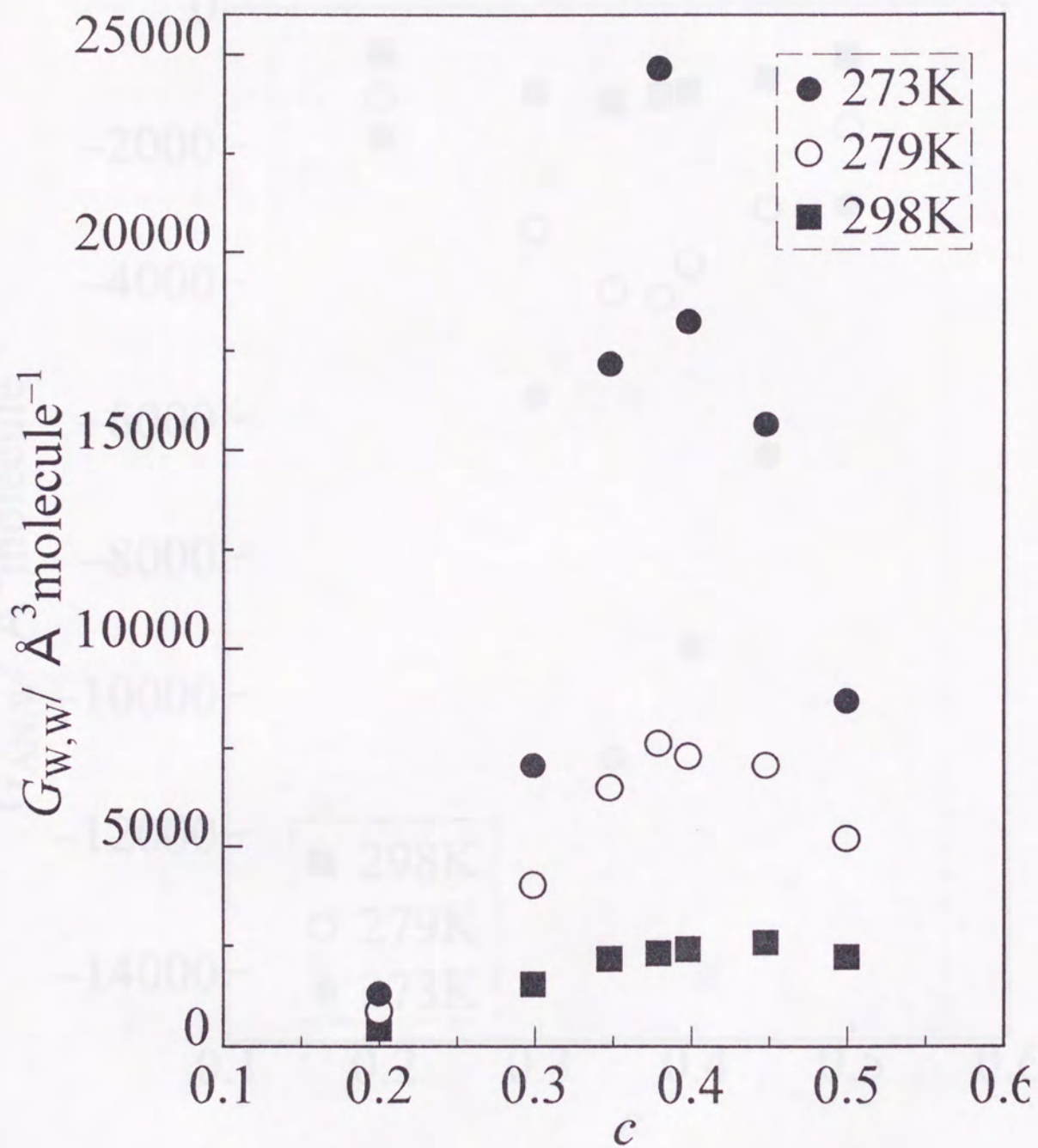


Fig5(b) The Kirkwood-Buff parameters ($G_{w,w}$) of aqueous acetonitrile solutions.

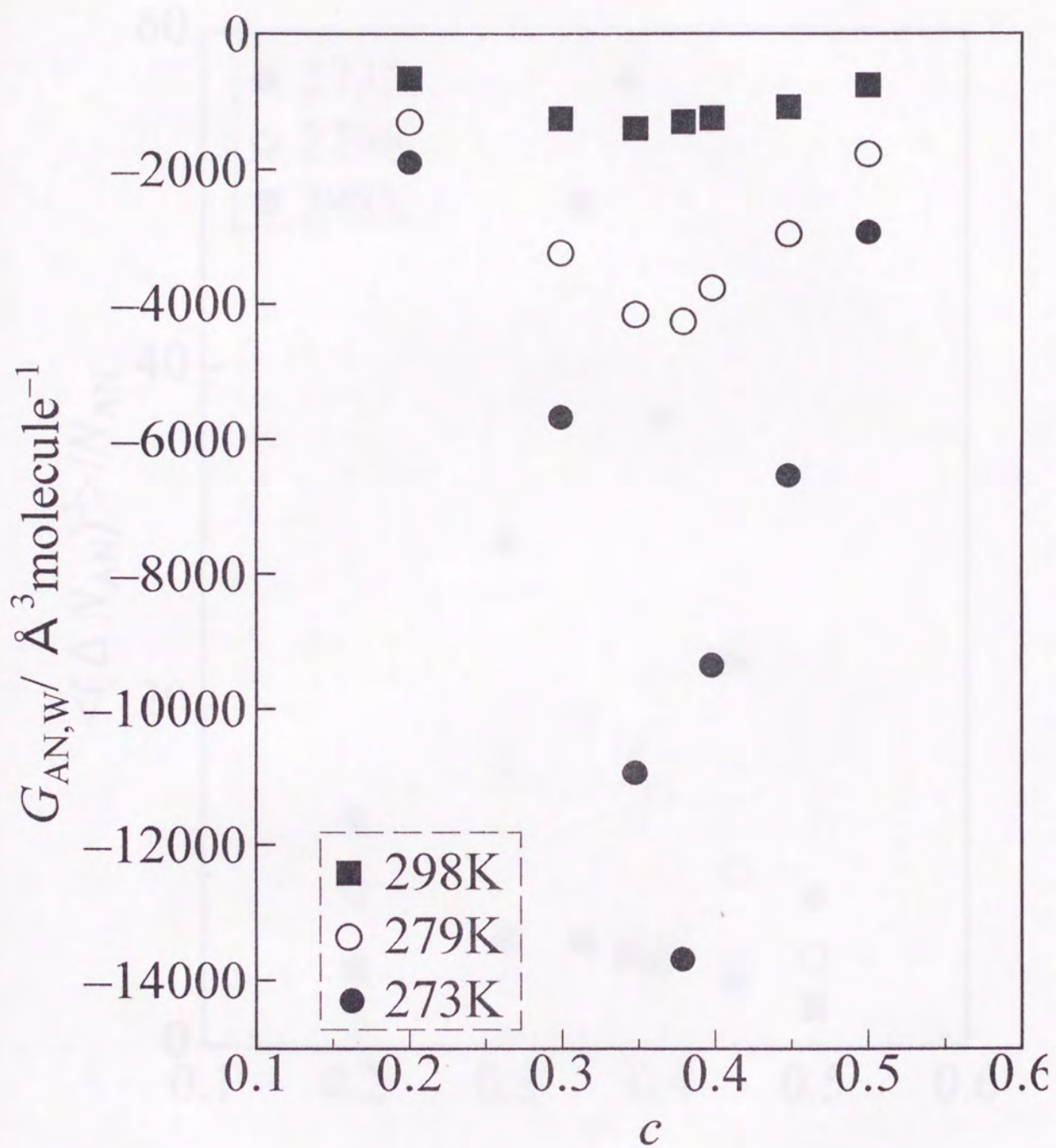


Fig5(c) The Kirkwood-Buff parameters ($G_{AN,w}$) of aqueous acetonitrile solutions.

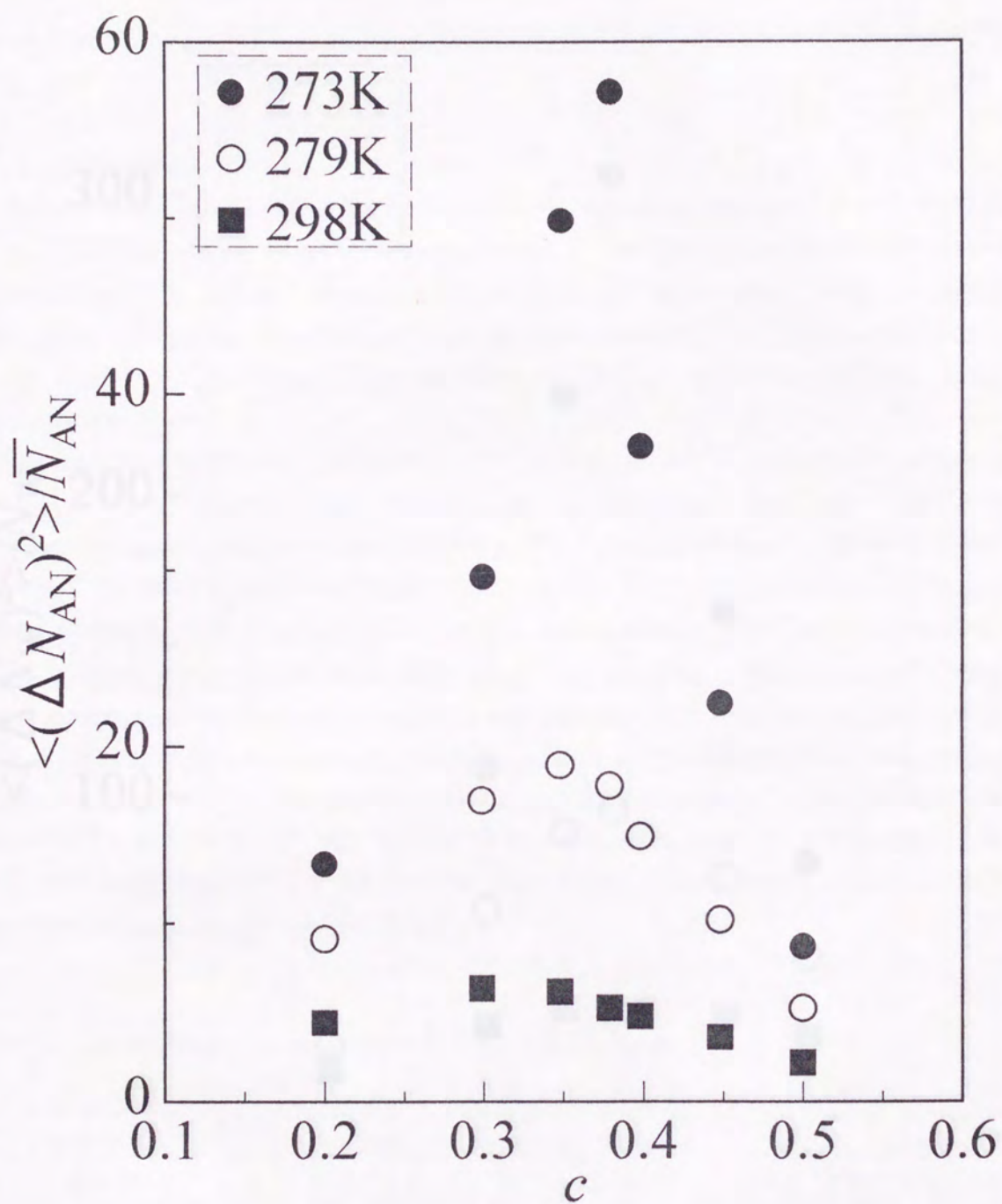


Fig6(a) Density fluctuations of each component of aqueous acetonitrile solutions.
(a) acetonitrile.

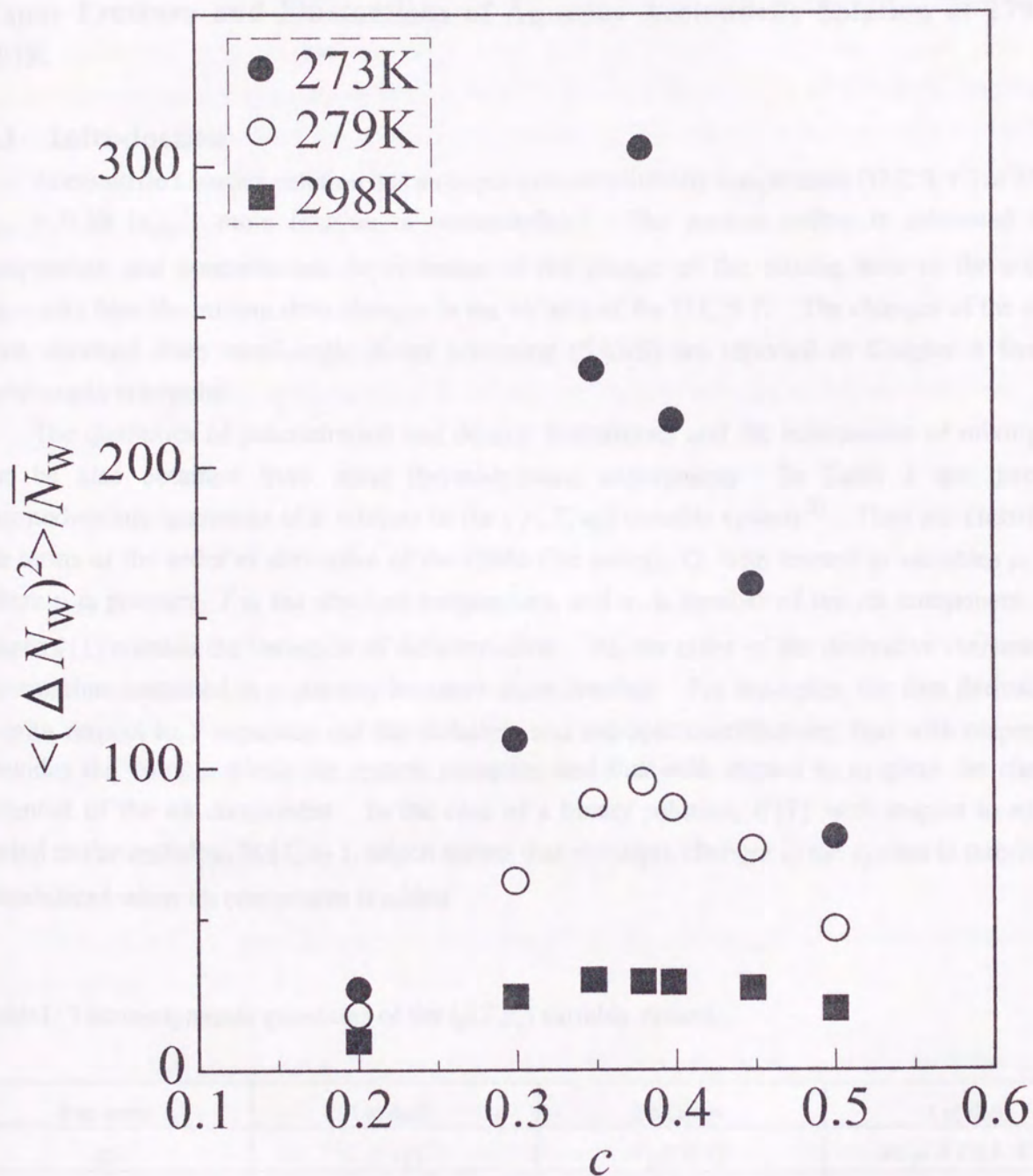


Fig6(b) Density fluctuations of each component of aqueous acetonitrile solutions. (b) water.

Chapter 5

Vapor Pressure and Fluctuations of Aqueous Acetonitrile Solution at 279 and 293K

5.1 Introduction

Acetonitrile aqueous solution has an upper critical solubility temperature (U.C.S.T.) at 272K at $x_{AN} = 0.38$ (x_{AN} : mole fraction of acetonitrile).¹⁾ The present author is interested in the temperature and concentration dependences of the change of the mixing state in the solution; especially how the mixing state changes in the vicinity of the U.C.S.T. The changes of the mixing state obtained from small-angle X-ray scattering (SAXS) are reported in Chapter 4 from the mesoscopic viewpoint.

The quantities of concentration and density fluctuations and the information of mixing state can be also obtained from some thermodynamic experiments. In Table 1 are listed the thermodynamic quantities of a mixture in the (p, T, n_i) variable system.²⁾ They are classified in the terms of the order of derivative of the Gibbs free energy, G , with respect to variables p, T, n_i , where p is pressure, T is the absolute temperature, and n_i is number of the i th component. The braces $\{\}$ contain the variables of differentiation. As the order of the derivative increases, the information contained in a quantity becomes more detailed. For examples, the first derivative of G with respect to T separates out the enthalpic and entropic contributions; that with respect to p provides the volume which the system occupies, and that with respect to n_i gives the chemical potential of the i th component. In the case of a binary solution, $H\{T\}$ with respect to n_i gives partial molar enthalpy, $H_i\{T, n_i\}$, which means that enthalpic changes in the system is stabilized or unstabilized when i th component is added.

Table1: Thermodynamic quantities of the (p, T, n_i) variable system.

0 th deriv.	1 st deriv.	2 nd deriv.	3 rd deriv
G	$H_i\{T\}$	$C_{p,i}\{T, T\}$	$\partial C_{p,i} / \partial T; \{T, T, T\}$
	$S_i\{T\}$	$H_i\{T, n_i\}$	$\partial C_{p,i} / \partial p; \{T, T, p\}$
	$V_i\{p\}$	$S_i\{T, n_i\}$	.
	$\mu_i\{n_i\}$	$V_i\{p, n_i\}$	.
		$\kappa_T\{p, p\}$	.
		$\alpha_{p,i}\{p, T\}$	.
		$N\langle(\Delta x_i)^2\rangle; \{n_i, n_i\}$	.

Koga *et al.* have discussed mixing states in some aqueous solutions by using various quantities obtained from thermodynamic experiments.²⁻⁷⁾

Though there are various thermodynamic quantities as shown in Table 1, a vapor pressure measurement for solution systems is one of the most suitable methods which give direct information on the mixing state of the solutions. The partial pressures of the each component in the binary solution are obtained by the measurement of the pressure of the gas phase which is in equilibrium to the liquid phase. This procedure is repeated for the samples whose concentrations are changed slightly. The concentration fluctuation of the solution, $N\langle(\Delta x_i)^2\rangle$, is obtained by differentiation of the partial pressure by concentration, which is classified to the second derivative of Gibbs' free energy.

The purpose of the present study is to obtain the fluctuation of acetonitrile aqueous solutions by the thermodynamic experiment and to compare them with those obtained by the SAXS experiment.

5.2 Experimental

A small amount of water in acetonitrile was removed by molecular sieves (4A) which was dried in oven for 24 hours.

The schematic diagram of the apparatus is shown in Fig. 1. The vapor pressures of acetonitrile, water and acetonitrile-water solution were measured by the static method. In the following section, the experimentation of the static method is introduced briefly.⁷⁾

5.2.1 Static method

For example, the procedure of transferring water in the sample cell for pure water (**D** in Fig. 1) into the sample cell **A** is explained.

1. Open the all valves, except **Vb**, **Vc** and **Vf**. The stainless pipes and two balloons **E** and **F** are vacuumed to 10^{-6} Torr with using a diffusion pump.
2. Shut the valves, **Va**, **Vg** and **Vh**, and measure the pressure of the pipes and both balloons by a pressure gauge.
3. Open the valve **Vb** connected to the pure water cell **D**, introduce pure water into the pipes and balloons as gaseous state, and then shut the valve **Vb**.
4. Measure the vapor pressure of water in the pipes and two balloons, when the whole system gets to equilibrium state after shutting off the valve **Vb**. The volumes of pipes between the valves and two balloons were obtained accurately, namely the volumes of each part **M**, **L**, **R**, **E** and **F** in Fig. 1 are 11.2, 5.9, 43.0, 500 and 5000 ml, respectively.

The volume of the other pipes in the system is neglected because those are so small. These parts are settled in a temperature-controlled box at 42 °C. The amount of the added sample into the balloons and pipes can be obtained from measuring temperature and pressure. The amount is defined as the one of initially added sample.

5. Cool the sample cell **A** by soaking with liquid nitrogen.
6. Open the valve **Vf**, and transfer the sample in the pipes and balloons into the cooled sample cell **A** by solidification. After the valve **Vf** is shut, the sample cell **A** is soaked in the water bath.
7. Measure the vapor pressure of water in the pipes and two balloons when the whole system was equilibrium after shutting off the valve **Vf**. The amount of sample obtained from vapor pressure in the system corresponds to the lost amount of the sample, which is so small. In this method, it is possible to transfer almost all samples into the sample cell **A**.
8. Actually, the total amount of added sample in the sample cell **A** corresponds to differential between initial added and lost amounts of the sample.
9. Some pure water was transferred into the sample cell **A** after repeating these ways. Wait until temperature of the sample becomes constant after soaking the sample cell **A** into the water bath.
10. Vacuum the whole system opening valves **Va** and **Vg**, and then close those valves.
11. Close the valves **Ve** and **Vg** in order to minimize the volume between the sample cell **A** and the pressure gauge **G**. Start to measure the vapor pressure when the system is in a equilibrium state after opening valve **Vf**.

The same handling mentioned above is made for the case of transferring a small amount of acetonitrile.

Most gaseous sample in the pipes and balloons is not lost and is transferred easily to sample cell, because gaseous sample cell is cooled by liquid nitrogen. The cell is soaked quickly into water bath.

5.3 Data Analysis

The obtained vapor pressures of pure acetonitrile, pure water and the aqueous solutions were corrected by the Boissonnas method for concentration and the Gibbs-Konovalow method for temperature.

The obtained total and partial vapor pressure for the aqueous solution and acetonitrile is shown in Fig. 2 at 293.15 K and 279.15 K. In briefly, I will explain those analyses, the Boissonnas method and the Gibbs-Konovalow method.

5.3.1 The Boissonnas Method (concentration correction)

Let consider the following Gibbs free energy system with pressure (p), temperature (T) and numbers of acetonitrile and water molecules (n_{AN} and n_W),

$$G = G(p, T, n_{AN}, n_W).$$

The differential formula is given by

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T, n_{AN}, n_W} \cdot dp + \left(\frac{\partial G}{\partial T}\right)_{p, n_{AN}, n_W} \cdot dT + \left(\frac{\partial G}{\partial n_{AN}}\right)_{p, T, n_W} \cdot dn_{AN} + \left(\frac{\partial G}{\partial n_W}\right)_{p, T, n_{AN}} \cdot dn_W \quad (1)$$

By substitution of the following equation into eq. (1),

$$V = \left(\frac{\partial G}{\partial p}\right)_{T, n_{AN}, n_W},$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{p, n_{AN}, n_W},$$

$$\mu_{AN} = \left(\frac{\partial G}{\partial n_{AN}}\right)_{T, p, n_W},$$

and

$$\mu_W = \left(\frac{\partial G}{\partial n_W}\right)_{T, p, n_{AN}},$$

we obtain the following equation

$$dG = V \cdot dp - S \cdot dT + \mu_{AN} \cdot dn_{AN} + \mu_W \cdot dn_W.$$

In the conditions of $dp = 0$ and $dT = 0$,

$$dG = \mu_{AN} \cdot dn_{AN} + \mu_W \cdot dn_W. \quad (2)$$

The Gibbs function, G , is represented by,

$$G = \mu_{AN} \cdot n_{AN} + \mu_W \cdot n_W. \quad (3)$$

By differentiating eq. (3),

$$dG = \mu_{AN} \cdot dn_{AN} + \mu_W \cdot dn_W + d\mu_{AN} \cdot n_{AN} + d\mu_W \cdot n_W. \quad (4)$$

From eqs. (2) and (4), we obtain the following relation

$$d\mu_{AN} \cdot n_{AN} + d\mu_W \cdot n_W = 0. \quad (5)$$

Equation (5) is called the Gibbs-Duhem relation.

The mole fraction of acetonitrile is given by

$$x_{AN} = n_{AN} / N \quad (6)$$

where N is total number of particles in the whole system.

The Gibbs-Duhem relation is also represented by,

$$d\mu_{AN} \cdot x_{AN} + d\mu_W \cdot x_W = 0 \quad (7)$$

Because

$$d\mu_i = RT(dp_i/p_i) \quad (8)$$

eq.(7) becomes

$$(dp_{AN}/p_{AN}) \cdot x_{AN} + (dp_W/p_W) \cdot x_W = 0 \quad (9)$$

and

$$dp_{AN} = 1/(1 - (x_{AN}p_W/x_Wp_{AN})) \times dp \quad (10)$$

When we describe the partial vapor pressure of acetonitrile in the measurement point k and $k+1$ as $p_{AN}^{(k)}$ and $p_{AN}^{(k+1)}$ respectively, the following relation is obtained,

$$p_{AN}^{(k+1)} = p_{AN}^{(k)} + dp_{AN}$$

or

$$dp_{AN} = p_{AN}^{(k+1)} - p_{AN}^{(k)}$$

The partial vapor pressure of water is shown as follows,

$$p_W^{(2)} = (1 - x_{AN}^{(2)}) \cdot p_W^{(1)}$$

when $x_{AN}^{(1)} = 0$.

and

$$p_W^{(1)} = p_W^{(0)}$$

where $p_W^{(0)}$ is vapor pressure of pure water. From these relations, we obtain

$$p_{AN}^{(2)} = p^{(2)} - p_W^{(2)}$$

The deviations dp can be given from substituting the obtained $p_{AN}^{(2)}$ and $p_W^{(2)}$ into the equation (10). The $p_{AN}^{(k)}$ and $p_W^{(k)}$ can be obtained in a sequence, by repeating those operations.

After the measurement, the valve **Vf** in Fig. 1 was closed. The part of **R** was pumped out, because a small amount of the sample as gaseous state remained in the part of **R**. By the procedure, the concentration of the solution in the cell shifts. Then the concentration correction was repeated until the deviation of the concentration before and after the calculation became nearly zero. The partial vapor pressure was obtained by using the corrected concentration mentioned above.

5.3.2 The Gibbs-Konovalow relation (correction for temperature)

It takes a few days to measure a series of the samples at a constant temperature. Although the temperature fluctuation of the water bath and the sample is within ± 0.01 K, it is too large to be neglected for the present study. Therefore, it is necessary to correct the temperature fluctuation. The Gibbs-Konovalow relation was adopted; namely

$$p^{total}(corrected) = p^{total}(measured) + (\partial p / \partial T)_{x_{AN}} \times (T - T^0). \quad (11)$$

The standard temperature, T^0 , refers to the graduation of a Beckmann's thermometer for the

measurement of the vapor pressure of pure water. T is temperature at measuring vapor pressure at a concentration. $(\partial p / \partial T)_{x_{AN}}$ is given by

$$(\partial p / \partial T)_{x_{AN}} = (p_{AN} \Delta h_{AN} + p_W \Delta h_W) / RT^2$$

where Δh_{AN} , Δh_W in eq.(11) are given by

$$\Delta h_{AN} = \Delta h^{vap}(AN) - H_m^E(AN)$$

$$\Delta h_W = \Delta h^{vap}(W) - H_m^E(W).$$

$H_m^E(i)$ and $\Delta h^{vap}(i)$ are excess partial molar enthalpy and vaporization enthalpy of i -th component in the solution.

5.3.3 Concentration Fluctuation

The fluctuation in the solution, as a quantity of the second derivative of Gibbs' free energy, can be obtained by taking derivative of partial vapor pressure with respect to composition. To do so, it is demanded that each data is accurate and the increment in the concentration is very small. The differentiation of data, if they include some errors, gives fatal influence on the analysis.

Accordingly, the partial vapor pressures are read out from graph, and they should be read up to 2 digits. The regression curve function ($F(x_{AN})$) for p_{AN} vs. x_{AN} was obtained from the measured values. The function was used for the derivation, because the derivation by use of raw data is apt to cause large errors. The residual between partial vapor pressure and the function at a composition is shown in Fig. 3. The read increments of concentration are following,

x_{AN}	increment(x_{an})	number of points
0~0.16	0.01	16
0.16~0.2	0.02	2
0.2~0.8	0.04	15

The second derivative of Gibbs' free energy in respect to composition is obtained as the concentration fluctuation, $N\langle(\Delta x_i)^2\rangle$.

5.4 Results and Discussion

The obtained values of $N\langle(\Delta x_i)^2\rangle$ are shown in Fig. 4, with ones by SAXS for comparison. The concentration fluctuation is expressed by

$$N\langle(\Delta x_i)^2\rangle = (1-x)RT / (\partial^2 G / \partial x^2)_{T,P,N}.$$

The absolute values of the concentration fluctuation obtained from the present measurement have a maximum near $x_{AN}=0.38$ and shows the same tendency as those obtained from SAXS at 279K. The fluctuation obtained from present measurement for 293K is between 279 and 298K for the SAXS measurements.

In the concentration fluctuation, the present results are qualitatively in agreement with SAXS one.; namely the present concentration fluctuations in the solutions are increasing with decreasing temperature such as SAXS result. Those behaviors mean that some clusters exhibit in the solution and that the cluster size is growing up with closing critical temperature.

However the present data are not quantitative because the data was obtained by taking twice derivatives of Gibbs' free energy with respect to composition. And the size of cluster is not possible to be obtained from vapor pressure measurement. In conclusion, the present study in the macroscopic viewpoint will support the SAXS study. However the present information is not sufficient to discuss mixing state in the solution. If experiments to obtain the enthalpy of the solution will be carried out, the entropy can be given. Moreover, partial molar enthalpy and entropy are obtained by taking derivatives of these values with respect to concentration. These informations are enthalpic and entropic changes between molecules of the solution. The combination of the macroscopic information from the thermodynamic analyses and semimicroscopic information from SAXS will prompt the detailed discussion on the mixing scheme of the solution, which is left for the future studies.

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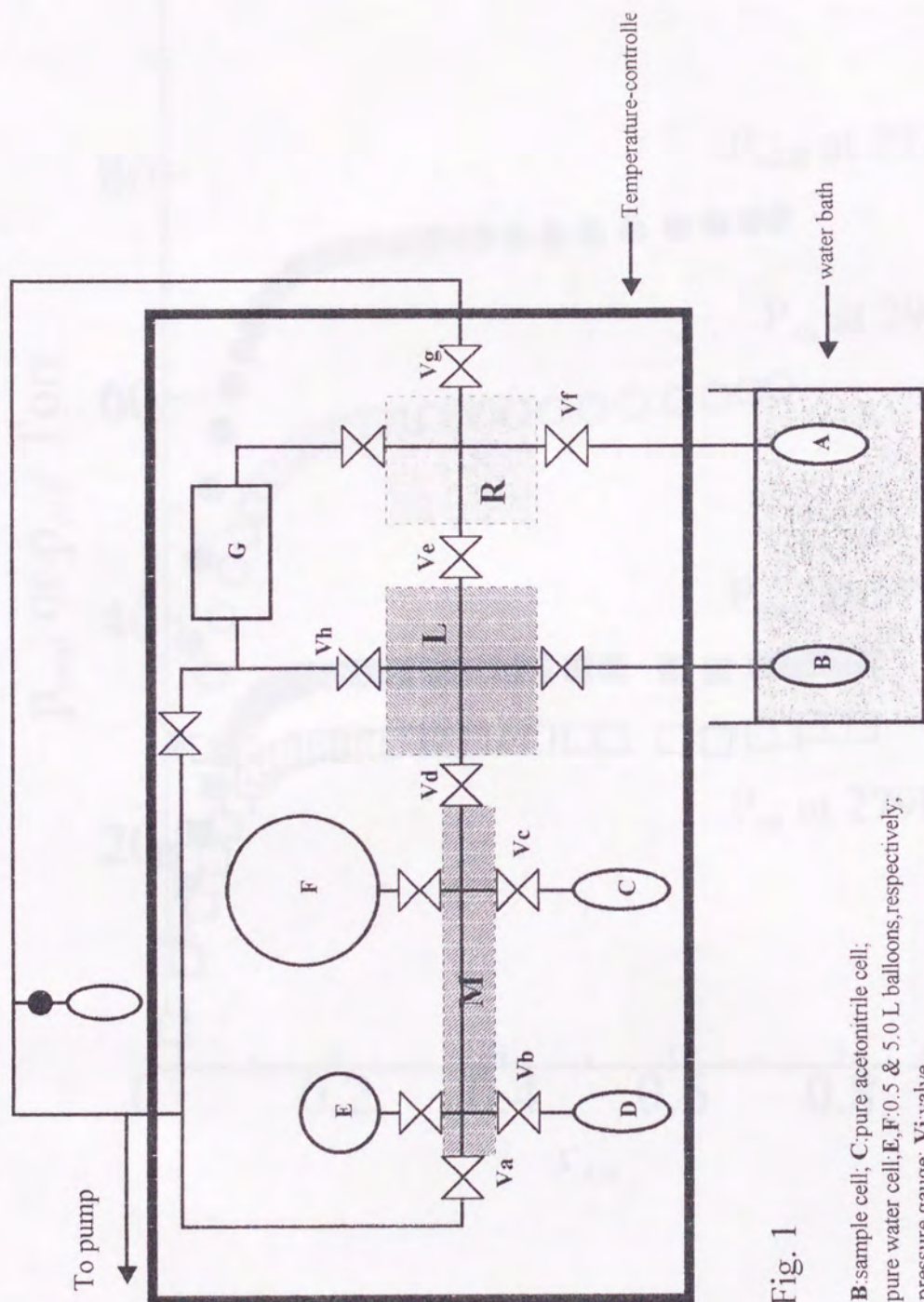


Fig. 1

A, B: sample cell; C: pure acetonitrile cell;
 D: pure water cell; E, F: 0.5 & 5.0 L balloons, respectively;
 G: pressure gauge; V_i: valve

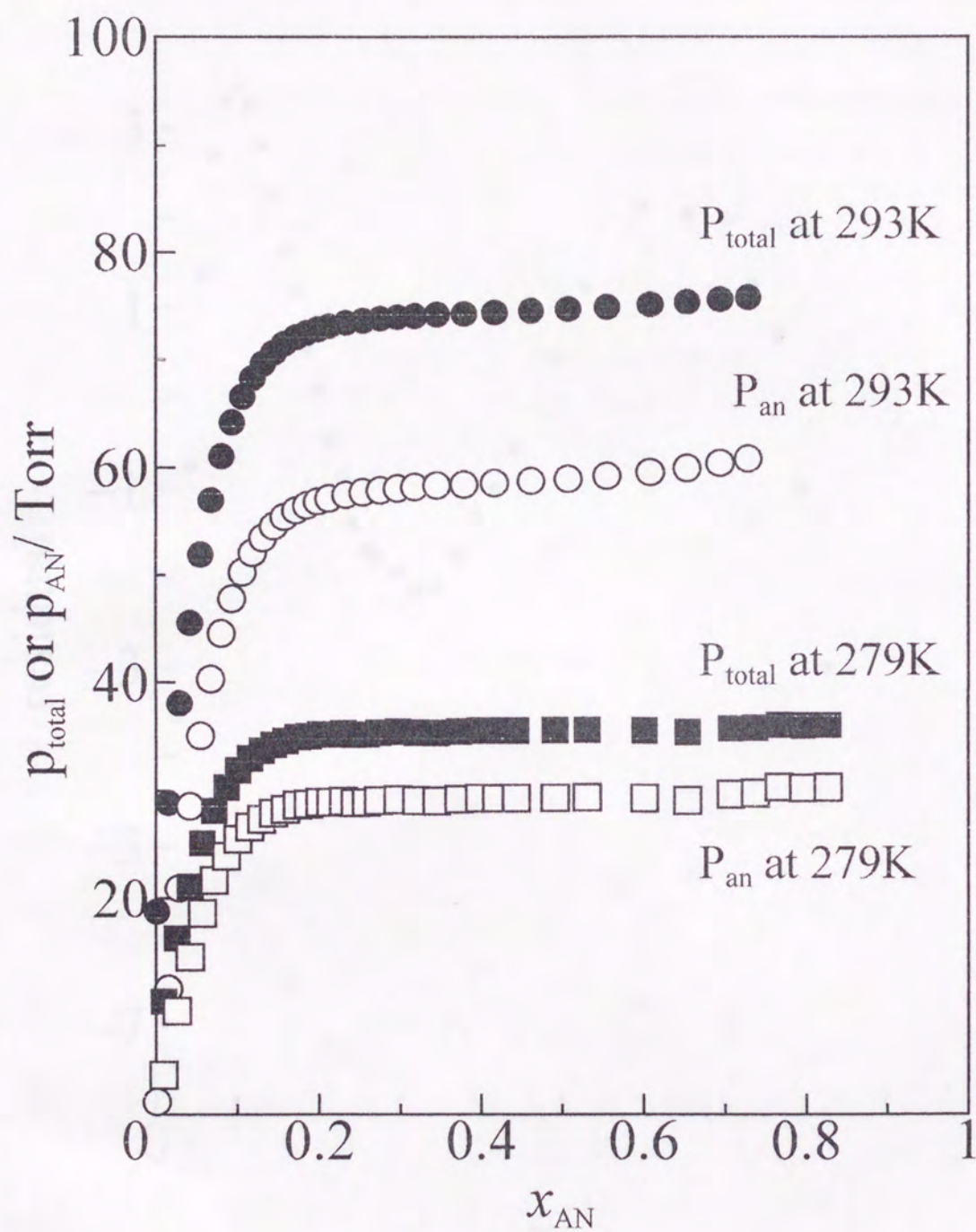


Fig.2 Total vapor pressure(p_{total}) and Partial vapor pressure(p_{AN}) at 279 K and 298K

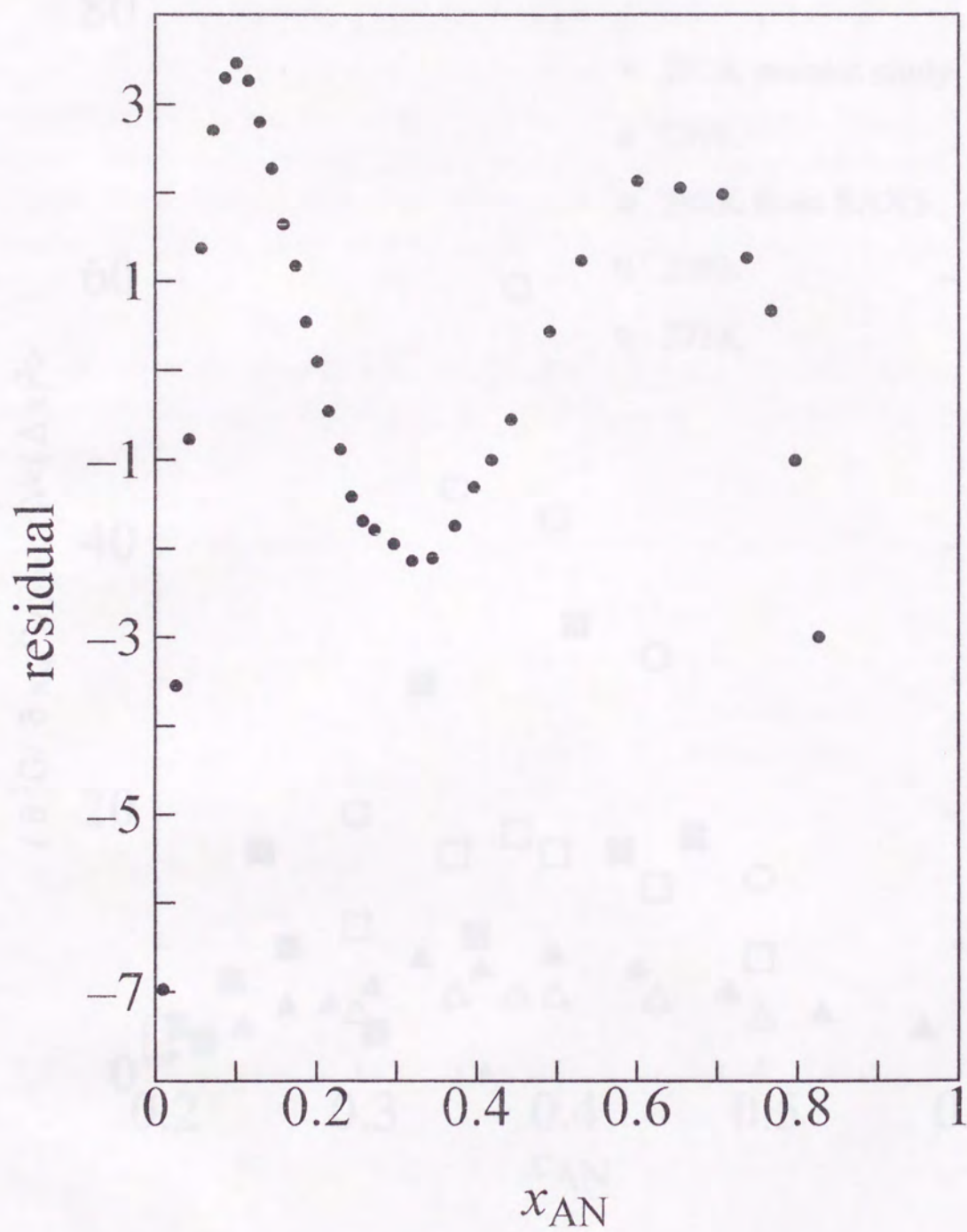


Fig.3 The residual between partial vapor pressure and the function, $F(x_{AN})$, at a composition.

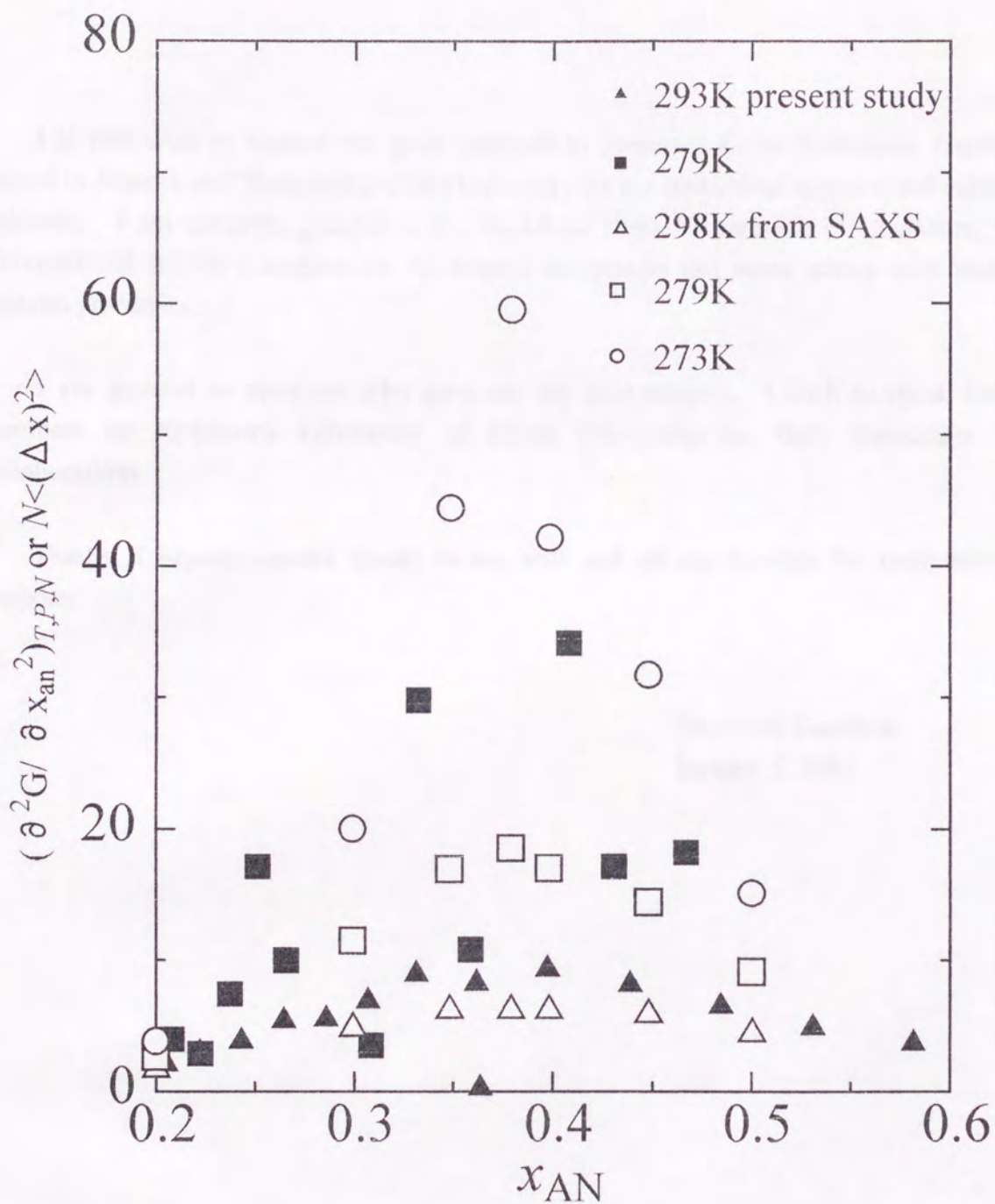


Fig.4 Comparison of the concentration fluctuation from SAXS measurements. Closed symbols are the concentration fluctuation of the present study. Opened symbols are that of SAXS measurements.

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