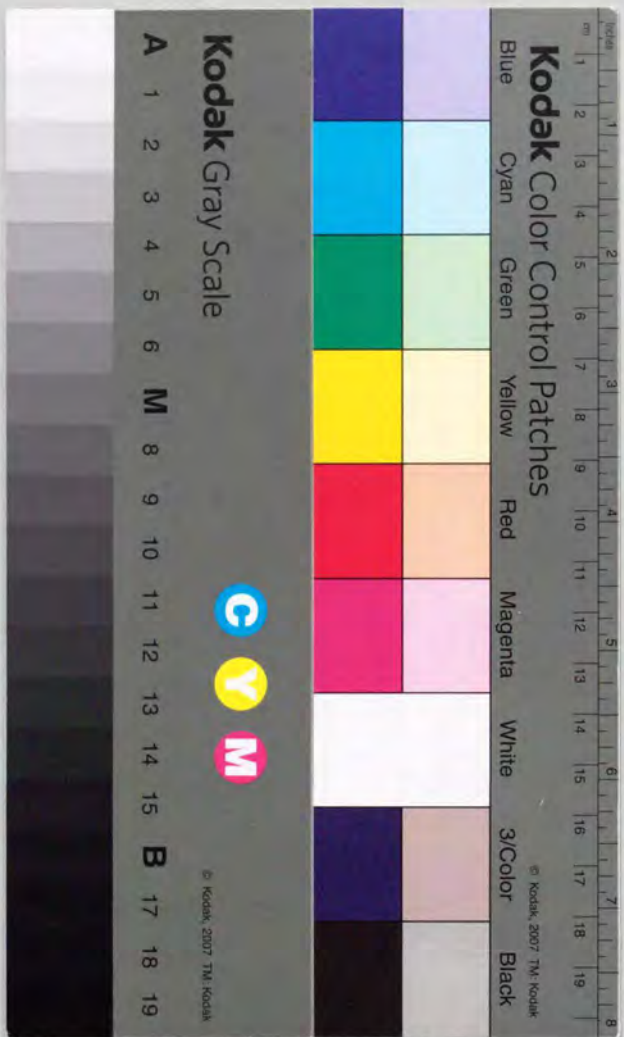


Specific Solute-Solvent Interaction of Aqueous Sodium
Chloride Solution at the Low Concentration.

(塩化ナトリウム低濃度水溶液における特異的溶質-溶媒間
相互作用の研究)

西本 右子



①

Specific Solute-Solvent Interaction of Aqueous Sodium
Chloride Solution at the Low Concentration.

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A Thesis
Submitted to The University of Tokyo
in Fulfillment of the Requirements
for the Degree of
Doctor of Science
(Rigaku Hakushi)

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Introduction

Electrolyte solutions, especially the aqueous sodium chloride solutions, play essential roles in the chemical processes in nature. Because, both almost surface on the earth and about seventy percent of all animal body consist of aqueous sodium chloride solutions. Therefore, extensive efforts have been made for a long time for the elucidation of the structure of such solutions or for the determination of the entities that make up the properties of these solutions. However, most of the experimental and theoretical investigations on aqueous solutions have been studied in the sufficiently dilute or the very concentrated range.

Spectroscopic and thermal investigations have led to the conclusion that the solutions may be classified into two phases; one in which each solute behaves as an individual independent of the others, and the other where all solutes behave as a united body with mutual interaction. Some elucidation is needed on the significance of the salt concentration of the sea water and the human blood as well as on the role of the dissolved oxygen.

The first law of thermodynamics attributes the conservation of the energy which is held by a chemical system, and the second its constitution as it is formed of two phases, of entropy and internal energy. At a constant temperature, the entropy and the internal energy are convertible to each other within the system when the system is in equilibrium with the surroundings.

It is essential that those two laws can hold only in the case where the system is in equilibrium. In other words, the laws of

thermodynamics do not tell much about a system composed of two subsystems which are not in equilibrium to each other or to the outside. Then a question arises on the energy flow between those two subsystems, whether they keep themselves thermally inert or not.

Spectroscopic investigations on the structural change of the aqueous electrolyte solutions suggest the presence of a critical concentration at which the solution behaves as an interface of two subsystems as cited above. The value of the critical concentration varies depending on the electrolytes as well as on the mechanism of the interface. The present investigation describes first what evidence the experiments offer for the presence of a critical concentration, i.e., that of the interface, and then the thermodynamical behavior of the solution of the specific concentration. It has been shown also that the oxygen dissolved in the solution plays a significant role in the flow of the thermal energy of the system. Furthermore, it has been found that the eutectic compound of sodium chloride and water forms adduct with oxygen at around the concentration of physiological salinity, and the two phases of eutectic compound, the pure and the oxygen adduct, coexist in the sample as being not mixed with each other. In concern with this, it has been investigated that the thermoenergetic difference of the enantiomeric isomers of amino acids under a certain condition of the solution that the concentration of the salt is lower than the physiological salinity and oxygen coexist.

Chapter 1

Preliminary spectroscopic investigation on the solute-solvent interactions in the binary component aqueous solutions.¹⁾

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Abstract

It has been supposed that the structure of binary solution may change depending on the molar ratio of solute to solvent. And it has been shown that the presence of some critical concentrations which solute-solvent interactions change. The spectroscopic investigations on aqueous solutions of propylene carbonate and alkali chlorides have really shown presence of critical concentrations. Furthermore, it has been shown that this critical concentration of the aqueous alkali chloride solutions has relationship to the reactivity of iodide ions added to the solutions.

Introduction

Vaslow observed discontinuity in molal volumes of alkali halide aqueous solutions²⁾. This report is valuable in showing experimental evidence for discontinuous property of aqueous solutions, however, as it remains qualitative in nature, further investigation on aqueous solutions by molecular spectroscopy seems necessary and useful.

This investigation revealed with respect to the discontinuous change has been spectroscopic properties of aqueous solutions of propylene carbonate, PC, 4-methyl-1,3-dioxolane-2-one, and of alkali halides. Concerning the solute-solvent interactions, the basic idea of present investigation is to see the composition of solution, R, the molar ratio of solute to solvent. The interactions in sample solutions were investigated by NMR, UV, IR and by the reactivity of iodide ions which are added to aqueous alkali chloride solutions. It is assumed here that if R is small, some of the solvent molecules are left free, being not bound to the solute, whereas, when R gets large, the number of free solvent molecules is reduced and finally becomes zero at some critical concentrations.

In this situation, all solvent molecules may be taken as associated with solutes either by direct or indirect solvation. At or beyond this condition of R, the solute-solvent interactions are assumed to occur among solvated solutes or between solvent and solvated solutions. Thus, critical concentration, C_{cr} , can be defined as the concentration which shows the critical R described above. The concrete values of C_{cr} 's have been reported for various systems.

Experimental section

A PC-H₂O system

The investigation has been carried out by UV and C-13NMR measurements with respect to the binary solutions of propylene carbonate, PC, and water.

Reagent:

PC, which was purchased from Wako Pure Chemical Industries, Ltd. was allowed to stand for 24 hours in contact with molecular sieve of Kanto Chemical Co., Inc. Cicasorv Z type 420, and then distilled twice under nitrogen atmosphere of about 20 mmHg. Only the middle fraction of distillate was used for the experiment. The water content of this PC was determined as about 100 ppm. This fraction of PC will be referred to hereafter as purified PC. The PC samples of different amount of water were prepared by adding water to purified PC. Water contents of all samples were determined by Karl Fisher titration.

Water was used the one obtained from Millipor Milli-Q SP system.

Apparatus:

The water content of PC was determined by Aquatest SS-202 of Shibayama Scientific Co., Ltd. made. The C-13 NMR was measured by JEOL JNM-FX-270 in Pulsed Fourier Transform mode at the JEOL Research Laboratory, Akishima. The UV spectra were measured

with Shimadzu double beam spectrometer UV-200 with Shimadzu Recorder U-125 MU.

Results:

The UV spectra are shown in Figure 1, where the isosbestic points are observed at 243 nm and 275 nm, 248 nm and 275 nm. This fact supports the PC-H₂O system is formed of two phases, X and Y, which are in equilibrium with each other. Phase X refers to the composition of H₂O less than 0.5 mol/l and Y with H₂O more than 0.5 mol/l.

Propylene carbonate has relatively inert groups of -CH₃ and >CH₂ and fairly hydrophilic groups of >CH and >C=O. A more detailed inside view of the mixtures can be obtained by C-13 NMR. The chemical shifts of C-13 NMR in Figure 2 and Table 1 show that in the solutions of low concentration of H₂O, 0.010 or 0.067 mol/l H₂O, the resonant positions of C-13 NMR for all functional groups are the same as those of the neat PC, whereas, in the mixture of 0.330 mol/l H₂O. The resonant positions of all the groups shift uniformly by the same amount without any specific shifts among each other. However, in the mixture of 0.670 mol/l H₂O, the radicals of >CH₂ and -CH₃ still remain in the same positions as in the solution of 0.330 mol/l H₂O, but those of >CH and >C=O are equally shifted from the former positions of the solution of 0.330 mol/l H₂O. These results suggest that the PC molecules in the solutions of lower water concentration behave uniformly and accordingly producing no function-dependent chemical shift on carbons. However, in the higher concentration range, PC molecules interact with the water

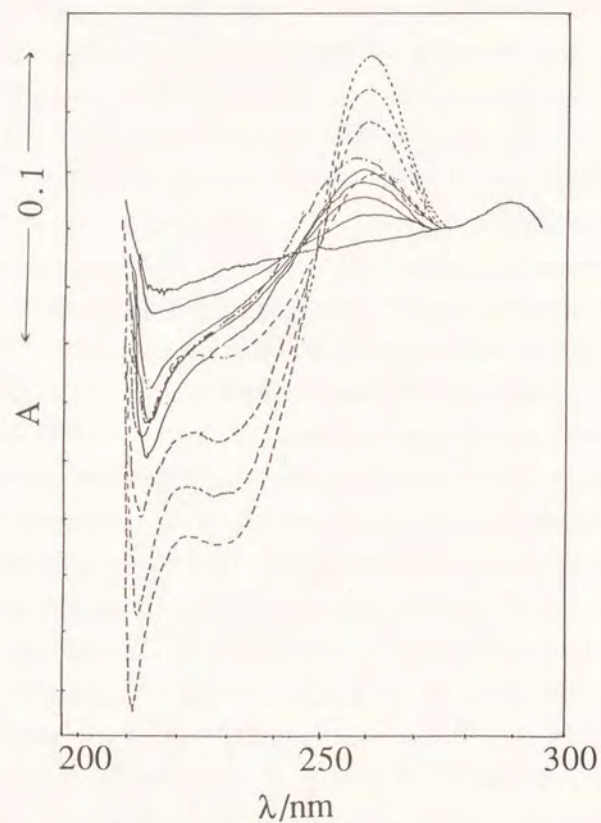


Figure 1 UV spectra of the binary solutions of propylene carbonate and water.

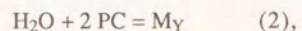
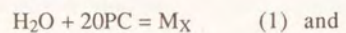
- : 0 ~ 0.43 mol/l H₂O (phase X)
- - - : 0.53 mol/l H₂O
- · - · : 0.67 ~ 2.20 mol/l H₂O (Phase Y)

molecules specifically, resulting in chemical shifts among different groups. Accordingly, one can estimate the presence of critical concentration in PC-H₂O system. Taking the results of the UV measurements into consideration, 0.5 mol/l H₂O is the critical concentration for the system of H₂O-PC. The aforementioned results may be interpreted as follows. The PC molecules in the purified sample are assumed to be associated with each other as the result of high dielectric constant of molecule. As H₂O molecules are introduced into PC, association among PC molecules are destructed partially and interaction between PC and H₂O starts. The PC-H₂O interaction is first isotropic so far as R is small, not specific with respect to the functional groups of PC. Specific bonding between PC and H₂O is formed when H₂O gets more than 0.5 mol/l, forming a kind of compound between PC and H₂O. In the samples with H₂O more than 0.5 mol/l this compound is assumed to behave as new solute in PC. The scheme cited above does not deny the possibility of the exchange of water molecules among PC molecules. Figure 3 presents a schematic diagram of the interactions between PC and H₂O, where (a) shows to the non-elastic mixture of PC and H₂O, (b) a solution of H₂O in PC where a weak and isotropic interaction works and (c) a system where compounds of PC with H₂O are formed and embedded in the media of PC.

Table 1 C-13 NMR chemical shift (ppm) for propylene carbonate

H ₂ O (mol)	C=O	CH	CH ₂	CH ₃
0.010	136.861	55.583	52.316	0.000
0.067	136.861	55.583	52.316	0.000
0.330	136.909	55.631	52.365	0.048
0.670	136.958	55.680	52.365	0.048

It is possible to estimate that about twenty molecules of PC interact with one H₂O molecule when scheme (b) starts, because isotropic shift of PC starts at around 0.10 mol/l H₂O. While in scheme (c), two PC molecules interact with one H₂O, because the range of (c) starts at 0.5 mol/l H₂O. Thus, equations (1) and (2) may hold for (b) and (c), respectively.



where, M_X and M_Y denote the chemical species of compounds of PC and H₂O in the X phase and Y phase, respectively. With the data of Table 1, equilibrium constants for (1) and (2) have been calculated as 2×10^{-23} and 10^{-3} or -2 , respectively.

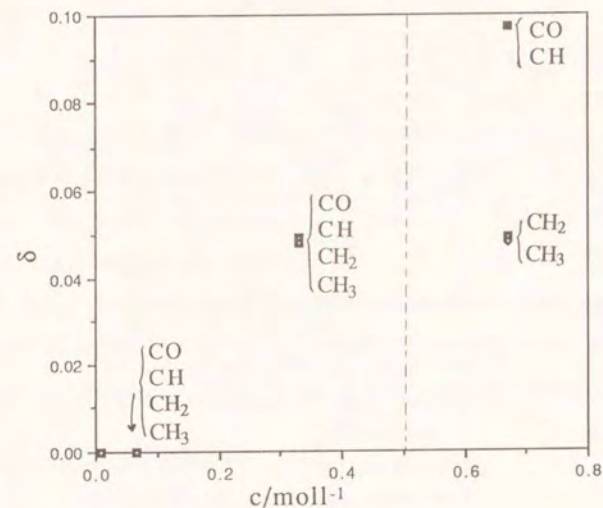


Figure 2 C-13 NMR shift (ppm) for mixture of PC and water.

The abscissa refers to the concentration of water added to PC and the ordinate to the shift of each functional group from the value of neat PC.

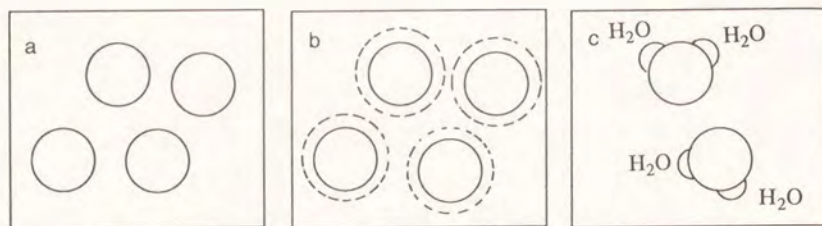


Figure 3 Schematic model of PC-H₂O after C-13 NMR measurement.
 Round circle shows PC molecule.
 a) PC and H₂O < 0.1 mol/l, where PC-H₂O interaction is non-elastic.
 b) PC and H₂O = 0.1 ~ 0.5 mol/l, where PC-H₂O interaction is elastic, but isotropic.
 c) PC and H₂O > 0.5 mol/l, where PC-H₂O interaction forms a compound.

B Aqueous alkali chloride solutions

This investigation has been carried out by UV and IR measurements of aqueous alkali chloride solutions.

Reagent:

Extra pure grade alkali chlorides were purchased from Wako Pure Chemical Industries, Ltd. and used without any further purification. The purity of sodium chloride was 99.99%, and that of the other alkali chlorides was 99.9%.

Same water as described in the experiment A was also used in the present experiment. Sample solutions were subjected to the experiment after one day or at least several hours after preparation.

Apparatus:

The UV spectra were measured with the same Shimadzu spectrometer UV-200 with Shimadzu Recorder U-125MU as described in the experiment A. The IR measurements were made by Digilab FTS-20 C/D Fourier transform infrared spectrometer at the Central Research Laboratory of Kuraray Company.

Results:

The features of the IR spectra are same to each other among all kinds of alkali chloride solutions examined, as exemplified in Figure 4. The band at ca. 3500 cm⁻¹ may be attributed to OH stretching of H₂O. It will be referred to the OH band hereafter. The intensity of

the OH band has shown a remarkable concentration dependence. It decreases with the increase of salt concentration until the concentration reaches a value of about 0.5 mol/l NaCl. Beyond the concentration, it levels off. Hence, the results of IR measurements suggest that 0.5 mol/l NaCl may be the C_{cr} for sodium chloride solution. All other salts have shown similar features, but different values of C_{cr} 's, as 0.2, 0.4, 0.05 or 0.1 and 0.3 or 0.4 mol/l for LiCl, KCl, CsCl and $(NH_4)_2SO_4$, respectively. Further evidence for the discontinuous properties of the alkali halide solutions has also been noticed with respect to the refractive indices of the solutions, which will be discussed to later.

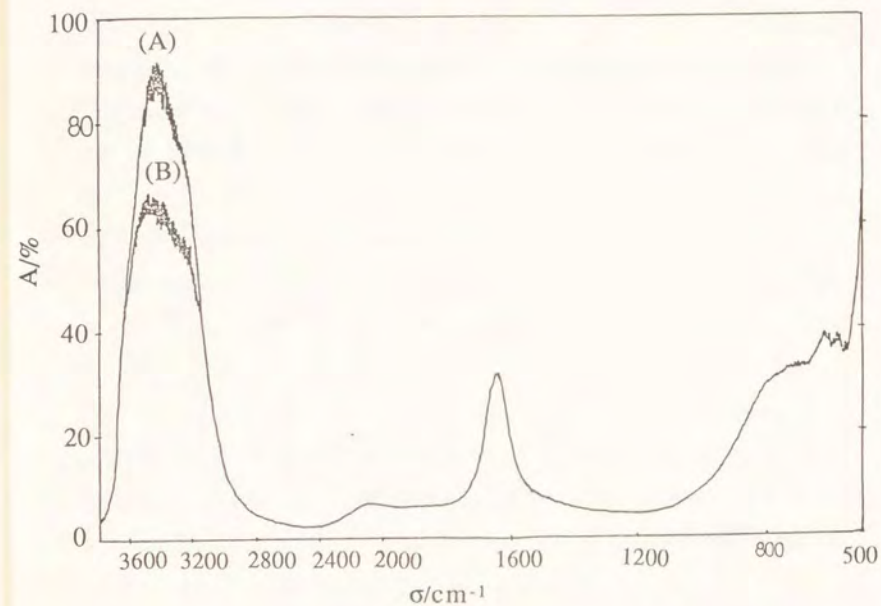


Figure 4 IR spectra of aqueous alkali chloride solutions.

- (A) : 0 ~ 0.4 mol/l NaCl, KCl
0 ~ 0.05 mol/l CsCl
- (B) : 0.5 mol/l ~ NaCl, KCl
0.1 mol/l ~ CsCl

C Salt effect on the redox reaction of iodide ions.

Reagent:

Extra pure grade KI, KNO₃, CH₃COOH and CCl₄ were purchased from Wako Pure Chemical Industries, Ltd. and used without any further purification. The same alkali chlorides as described in the experiment B were also used.

Same water as described in the experiment A was also used in the present experiment. Sample solutions were put to experiment after one day or at least several hours after preparation.

Apparatus:

The UV spectra were measured with the same spectrometer Shimadzu UV-200 with Shimadzu Recorder U-125MU as described in the experiment A.

Results:

It has long been known that the iodide ions in sea water cannot be determined directly by solvent extraction. Accordingly, a laborious indirect method has been adopted³⁾. A detailed investigation on the salt effect for the solvent extraction of I⁻ ions has been carried out, and found that the effect deeply relates to the critical concentration cited above. The I⁻ ions in the aqueous acidic media can be oxidized by nitrous acid according to equation (3), and extracted by carbon tetrachloride.

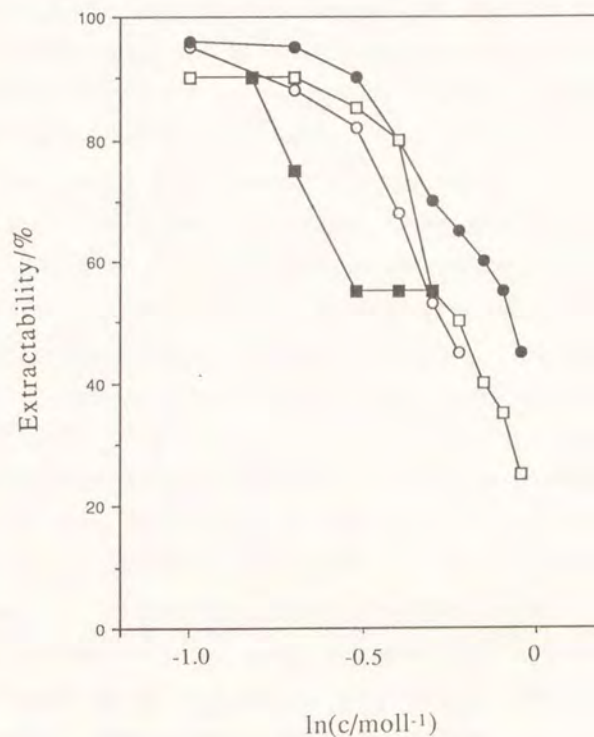
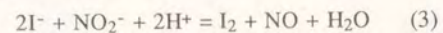


Figure 5 Extractability of iodide ion as the function of salts concentration.

The abscissa shows the logarithmic concentration of alkali chloride.

The ordinate shows relative extractability as measured by the absorbance of iodide ion extracted in carbon tetra chloride.

□ : LiCl, ○ : NaCl, ● : KCl, ■ : RbCl

However, the reaction (3) is heavily interfered with the presence of sodium chloride. Figure 5 shows the salt effect on extractability of I^- ions. Actual procedure of experiment is following. Iodide ions in 30 ml of 10^{-5} mol/l KI solutions with different amount of sodium chloride were extracted into 10 ml CCl_4 after reaction (3). As seen in the figure, an almost 100% recovery is attainable for the solutions with sodium chloride below 0.3 mol/l. The recovery drops markedly with sodium chloride over 0.4 mol/l, and becomes almost zero at 0.6 mol/l. The similar effect of salt has been observed for lithium chloride and potassium chloride, too. It is very remarkable that the concentrations of salts which show the interference are 0.2 and 0.4 mol/l for LiCl and KCl, respectively, and consistent with the concentrations at which have shown characteristic change of the OH band intensities occur.

In accordance with this findings, it has noticed that the reaction (3) can proceed in parallel with the appearance of a specific band of UV spectrum at 250 nm. Figure 6 presents the UV spectra for simple aqueous sodium chloride solutions of various salt concentrations. The absorption bands in figure may be assigned from the lower frequency side to higher one as the charge transfer (CT) band at ca. 200 nm (scaled over), and the $n-\pi^*$ excitation band at 225 nm. All solutions of other alkali chlorides, lithium chloride, potassium chloride, rubidium chloride and cesium chloride, show the similar spectra. As I^- ions are added to the solutions, a new band appears at 250 nm as shown in Figure 7. Molar absorption coefficient for this band is determined as 1.0 for sodium chloride solutions. The intensity of 250 nm band is heavily dependent on the

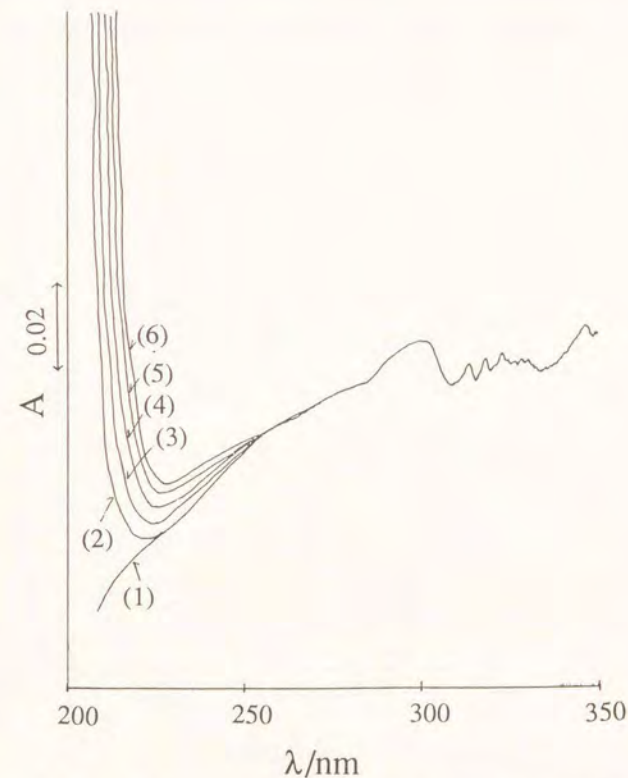


Figure 6 UV spectra of aqueous sodium chloride solutions without potassium chloride. Numbers in the figure from (2) to (6) show to the concentrations of sodium chloride, 0.1, 0.3, 0.4, 0.5, 0.6 mol/l respectively, and (1), baseline.

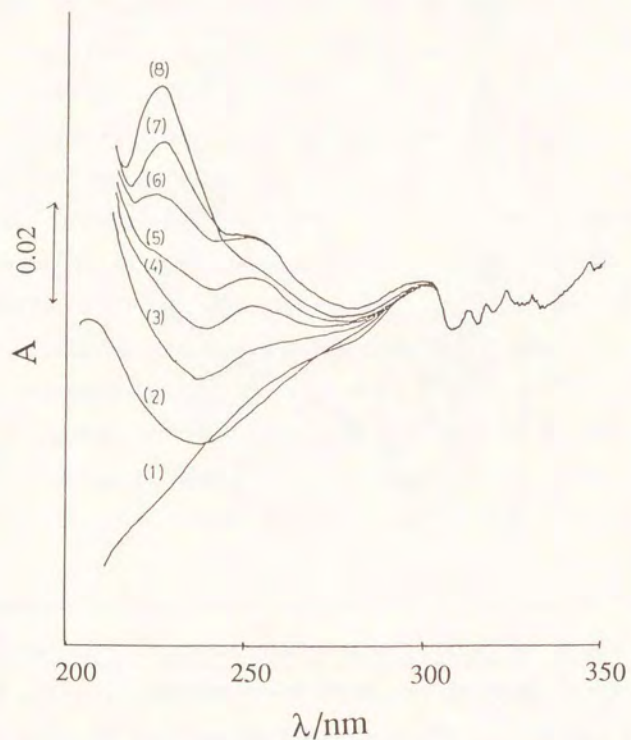


Figure 7 UV spectra of various aqueous sodium chloride solutions with 10^{-5} mol/l potassium chloride. Numbers in the figure from (2) to (8) show to the concentrations of sodium chloride, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 mol/l respectively, and (1), baseline. Intensity of 250 nm band is highest for (7) and gets lower for (8).

concentration of the salt. (cf. Figure 8) It increases with the concentration of the salt until the concentration reaches the characteristic one at which the I^- extraction is interfered. Beyond this concentration, the intensity of 250 nm band decreases. Thus, the 250 nm band is a keyband for the redox reaction of I^- ions.

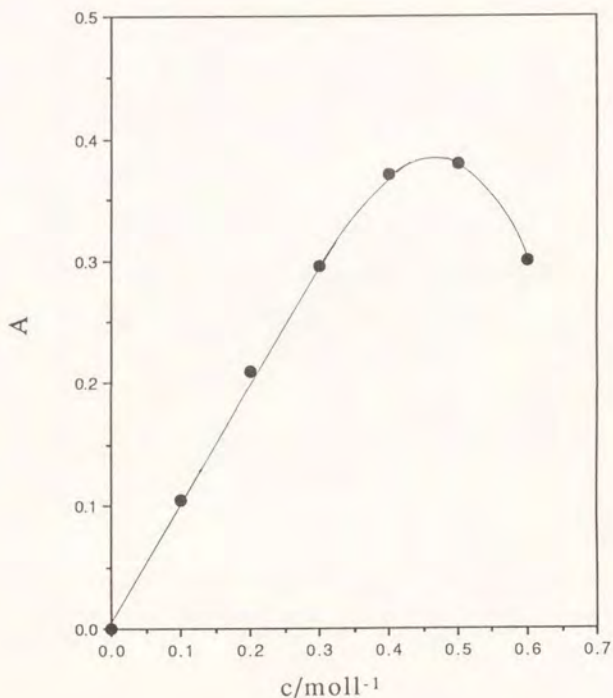


Figure 8 Absorbance of 250nm band as the function of the concentration of sodium chloride.

Discussion

All results of the spectroscopic investigations shown above seem consistently to support the presence of C_{cr} 's in aqueous solutions, and to suggest a discontinuity in the solution structure. The structure discontinuity may support, furthermore, to the discontinuous change of the electronic properties of the solution.

The 250 nm band, which has been noticed as the key band for the redox reaction of I^- ions, sites beside the CT band at 200 nm and the $n-\pi^*$ band at 225 nm. This fact may suggest that the solutions which give the 250 nm band carry the electrons more labile than CT or $n-\pi^*$ excitations. Namely, very labile electrons are formed in specific structure of solutions.

The other reports about the 250 nm band, it seems to show the relationship to the labile electrons. Atomic absorption has been observed at 250 nm with mercury in the condensed phase.⁴⁾ This absorption certainly refers to the excitation of the 6s electron. Another case of observation of 250 nm band has been reported with respect to thallium embedded in solid sodium chloride.⁵⁾ This band apparently shows the assistance of sodium chloride matrix for the electronic excitation of thallium. In this chapter, 250 nm band has examined salt effect on other system which apparently seem to hold labile electrons. The UV absorption bands have been measured for the aqueous solutions of alkali halides to which copper ions or tetraphenyl borate ions, BPh_4^- have been added. Figure 9a shows the spectra of aqueous potassium chloride solutions added with copper chloride and Figure 9b shows the those with BPh_4^- ions. The

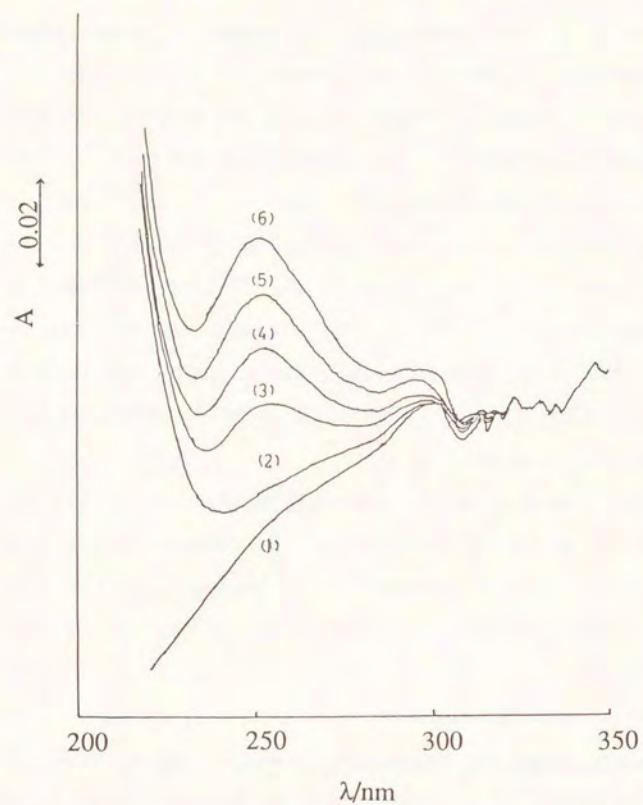


Figure 9a Observation of 250nm band in the aqueous potassium chloride solution of Cu^{2+} and BPh_4^- ions.
 a) KCl and CuCl_2
 Numbers in the figure refer to the concentrations of KCl, from (2) to (7), 0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 respectively, and (1), baseline.
 The concentration of CuCl_2 is 10^{-4} mol/l.

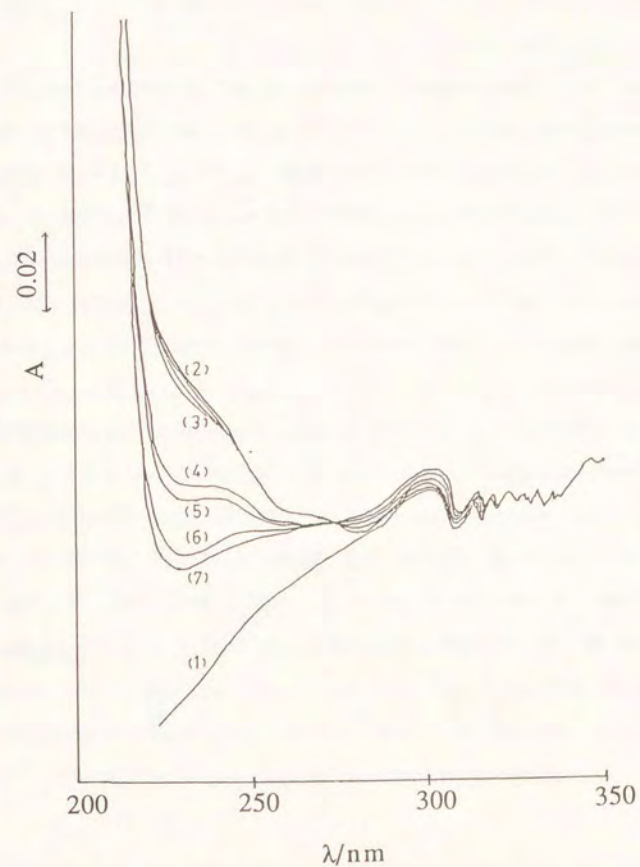


Figure 9b Observation of 250nm band in the aqueous potassium chloride solution of Cu^{2+} and BPh_4^- ions.
 b) KCl and BPh_4^-
 Numbers in the figure refer to the concentrations of KCl, from (2) to (7), 0.2, 0.5, 0.6, 0.7, 0.8 and 0.9 respectively, and (1), baseline.
 The concentration of BPh_4^- is 4×10^{-6} mol/l.

250 nm band is observed also in both cases. As it has been mentioned already, simple aqueous solution of potassium chloride does not show this band.

Thus, the solute-solvent interactions are strongly affected by the solute ions, so these interactions are classified each other depending on the condition of the solution either below or beyond the critical concentration. It should be noticed, furthermore, that the difference shows the relationship between the solution and its reactivity. This finding will be the first observation of the fact that structural change of solute-solvent interactions relates with the reactivity of solution.

In addition to the results of the spectroscopic investigations cited above, the data of the heats of the infinite dilution and the quantum chemically calculation of the solvation number of sodium and chloride ions in the aqueous sodium chloride solutions have cited nature of the concentration of ca. 0.5 mol/l NaCl. It will be introduced in the Appendix following.

Appendix 1 Heats of infinite dilution of aqueous sodium chloride solutions

The data of the heats of infinite dilution of the solutions of sodium chloride also present a clear cut critical concentration.⁶⁾ Figure 10 reproduces the data of the concentration dependence of the heats of infinite dilution $\Delta H_{inf.dil.}$ for the aqueous sodium chloride solutions. The data in Figure 10 suggest that the solutions can be divided into two phases. The data for the solutions of the concentration lower than ca. 0.5 mol/l NaCl, $\Delta H_{inf.dil.}$'s are positive and concentration independent, whereas those in the higher are negative and concentration dependent. The fact that the $\Delta H_{inf.dil.}$ values are positive and concentration independent may be interpreted in terms of the fact that the ions are dispersed in the media of the solution, being independent from each other; this results in a positive value of $\Delta H_{inf.dil.}$'s due to the dispersion entropy. The fact that the $\Delta H_{inf.dil.}$ values are constant can be interpreted in the same way. The fact that the values in the higher concentration range are negative and concentration dependent can be interpreted as being due to the ion-ion interactions.

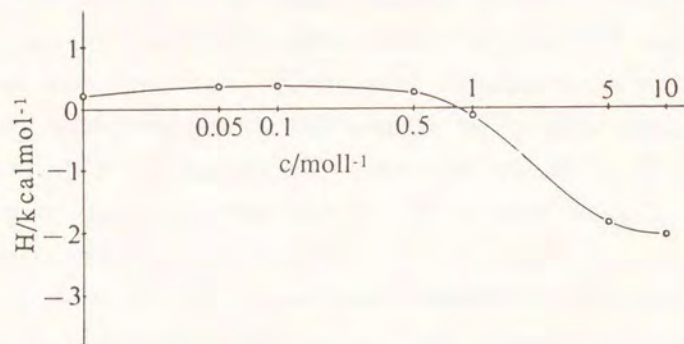


Figure 10 Heats of infinite dilution of aqueous sodium chloride solutions.
The abscissa shows the logarithmic concentration of sodium chloride

Appendix 2 Quantum chemical calculation on solvation number

Experimental studies by various spectroscopic methods⁷⁾ such as X-ray, NMR or neutron diffraction have led to more knowledge about solutions particularly with respect to the solvation number evaluation for the ions. However, they also led to new questions, due to problems inherent in these experimental techniques.

Especially, solvation (=solvent coordination) numbers for ions depend strongly on the methods being used for their determination (e.g., vapor pressure measurements, conductivity methods and NMR techniques) and have to be based, in addition, on an arbitrary separation of anionic and cationic contributions to the overall-effect being measured. X-ray diffraction data seem to yield the most well-defined results⁸⁾ in this field, but the results are confined to the first coordination shell. Furthermore, the limitations of the capability of this method cannot be denied with respect to the complexities of the system being investigated and the impact of energy exerted during the measurement by the X-rays, in comparison with the interaction energies determining the formation of structural units in solutions.

Theoretical approaches based on quantum chemically evaluated ab-initio interaction potentials and their use in Monte Carlo molecular dynamics simulations of solutions have made a new powerful tool available for this field of research. They allow us not only to evaluate solvation numbers and solute-solvent distances from computed radial distribution functions, but also give access to data not available from any experimental technique so far as for

example an analysis of the percent contribution of various coordination numbers in average solution of the ion or solvent molecules.

Thus, a series of calculations has been performed with the focus on Monte Carlo simulations of aqueous sodium chloride solution to find the the distribution of coordination numbers and the angular distribution in the first solvation shell of the ions.⁹⁾

Table 2 gives the first and second shell solvation numbers of ions and solvent molecules at different concentrations. Figure 11 shows the distribution of the coordination numbers for Na⁺ and Cl⁻. Data of Table 2 suggest that a fully solvated sodium ion requires 23 water molecules, a fully solvated chloride ion 7~8 water molecules and that "complete" bulk water units consist of a minimum amount of approximately 26 solvent molecules.

Table 2 Solvation numbers from radial distribution functions for Na⁺·····O, Cl⁻·····O and O·····O distances at various concentrations.

System	Na ⁺		Cl ⁻		H ₂ O	
	1st shell	2nd shell	1st shell	2nd shell	1st shell	2nd shell
Infinite dilution	6.0	-	7.4	-	-	-
0.55	6.1	17	7.1	0	5.5	20.2
3.5	5.4	0	11.8	0	10.0	0

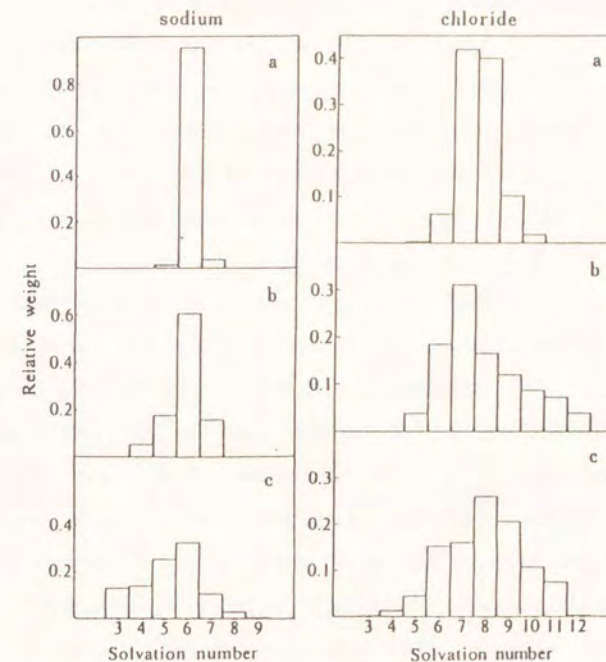


Figure 11 Distribution of coordination numbers for sodium and chloride ions.
a: infinite dilution
b: 0.55 mol/l
c: 3.5 mol/l.

On the basis of those data, it has been calculated that in 0.5 mol/l solution about half of the solvent available is used up for ion solvation. In this sense, lower concentrations can be considered as "bulk solvent dominated", whereas concentrations of more than 0.5 mol/l sodium chloride have to be rather designated as "solvation shell water dominated". This peculiarity of 0.5 mol/l sodium chloride solution is assumed to refer to the critical concentration cited above. Figure 11 illustrates how the average first shell solvation numbers of sodium are made up statistically of varying concentrations. It can be seen that, with increasing salt concentration, the variation of coordination numbers becomes successively larger, indicating not only a wider variability of structural units, but also a "sharing" of solvation shell waters by more than one ion.

The results of the quantum chemical calculation also suggested that 0.5 mol/l solution is the start of the ion-pair formation. The point of this calculation is that from around 0.5 mol/l ion-pairs can be formed, where the solvent molecules are not separated but rather correspond to the formation of ion-pairs, the so-called "contact ion pairs". This develops a rather concise picture of the structural units of highly concentrated sodium chloride solution as containing almost no independent solvated ions, but rather such contact ion-pairs, imbedded in a network of other ion-pairs at nearly the statistical distance, and water molecules, whose orientation is influenced more by the sodium ions than by the chloride ions.

The quantum chemical calculation suggests the same calculation as that obtained before by the experiments, that from above 0.5

mol/l concentration, the composition of the solution is characterized by the formation of ion-pairs which are not solvent separated, but rather correspond to so-called "contact ion-pairs", and that a larger structure unit containing another three counter ions is formed with a radius of 6.4 Å.

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Chapter 2

Fluctuation of refractive index of aqueous sodium chloride solution and oxygen effect.^{1) 2)}

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Abstract

Fluctuation of the refractive index in aqueous electrolyte solutions has been measured for the purpose of to see its concern with the internal structure of the solution. It is found that the fluctuation is anomalously enhanced at the specific concentration with the presence of oxygen. When oxygen is removed, enhancement dose not occur. The results obserbed suggest the presence of a critical concentration which divides the structure of the solution into two phases: in one, the bulk solvent molecules are dominant, and in the other, the solvated ones are dominant. It is considered that oxygen plays a catalytic function for the enhancement of the thermal flow in and out of the solution. The critical concentration for the sodium chloride solution was determined to be ca. 0.5 mol/l, which almost coincides with the concentration of salt in sea water. Significance of the present finding in nature was discussed as well as the usefulness of the measurements of fluctuation in analytical chemistry.

Introduction

Detection or analysis of dynamical properties of chemical substance is now one of the most important subjects to be investigated in analytical chemistry. Although the rigid structures of molecules have been fairly well elucidated, the dynamical ones, particularly those in solution, remain mostly unknown.

It has been shown in chapter 1, the spectroscopic features of aqueous electrolyte solutions, particularly those of the solvent water molecules, are markedly changed at specific concentrations. This chapter describes a further finding that this occurs only when oxygen is present. It will be shown that the specific concentration observed here corresponds to a critical concentration where the solute-solvent interactions change.

The structure of aqueous electrolyte solutions changes discontinuously as a function of the salt concentration. Thus the measurement of the fluctuation of refractive index is useful for the analysis of the dynamical characteristics of solution.

Fluctuations are usually taken as elements which disturb measurement. So, many experiments try to keep them as small as possible. However, on the contrary, it is being recognized that the fluctuations are a source of valuable information. They are being investigated in various fields, such as physics³⁾ and biochemistry⁴⁾. The present investigation will add one more example of a positive application of fluctuations.

The refractive index of a chemical substance is assumed to be dependent on its density and temperature. Thus, the fluctuation of

the refractive index is assumed to relate with the thermal condition of the sample.

The solute-solvent interaction in aqueous solution must vary depending on the concentration of the solution. So far as the concentration is low, the solute entities are assumed to be dispersed in the solvent, where the solute-solute interactions are negligible. However, as the concentration increases, the solute entities should interact with each other. A critical concentration should be encountered where a transition of the solution state occurs from the former phase to the latter.

One example has been obtained by the C-13 NMR measurement in the aqueous solutions of propylene carbonate as described in chapter 1. Although it is expected that the solute-solvent interactions in aqueous alkali halide solutions are isotropic, still one can assume that a kind of discontinuous change occurs as the concentration of the salt is changed. While the salt concentration is low, the solution is assumed to be formed of the solvated solutes and the bulk solvent molecules. Here, by bulk, we mean those solvent molecules which are not bound to the solutes by solvation. As the concentration increase, the number of the bulk solvent entities is assumed to decrease and finally to become zero at some critical concentration, C_{cr} . Beyond this concentration, the whole body of the solution may be taken as equal to pileup of the solvated balls, where the interactions among the solvated balls stabilize the solution. Thus, for the convenience of the discussion, the states of the solution may be divided into two different phases, below and above C_{cr} . It is noticed that those two phases must be

different from each other with respect to their thermodynamical aspects. In the solutions of the concentration below C_{cr} , the energy of the solution is assumed to be determined by the dispersion entropy of the solutes; in those above C_{cr} , by the interaction energy among the solvated solutes.

This situation has been verified by the data of the heat of infinite dilution of aqueous strong electrolyte, $\Delta H_{inf. dif}$. The $\Delta H_{inf. dif}$ values for the NaCl solutions below about 0.6 mol/l are positive and almost constant in comparison to pure water, whereas $\Delta H_{inf. dif}$ values for the solutions above C_{cr} are negative and concentration-dependent⁵⁾. Spectroscopic investigations on the solutions have been conducted of cupric ions and of spin-label compounds.^{6,7)} These have suggested the presence of some critical concentrations. A quantum chemical calculation has also shown⁸⁾ that the second shell solvation energy for sodium ions is about 9 kcal/mol, which is larger than the hydrogen bonding energy of pure water, whereas the third shell energy is less than the latter. It has been assumed, then, that the critical concentration may correspond to the concentration where water molecules are used up for the formation of the second hydration shell. The calculation which follows the present one has shown more clearly the presence of the critical concentration.⁹⁾ The concept of the critical concentration of the solution is considered to be important for several reasons. First, it classifies the solution into two thermodynamically different phases: one whose energy is entropy-determined and the other whose energy is determined by the interaction energy of the solute entities. If this classification is the case, the solution with the

concentration of C_{cr} must be unique in the sense that it is an interface of two chemical phases which have the same species of chemical components but are different from each other in their thermodynamics. Secondly, the concrete value of C_{cr} for sodium chloride solution, ca. 0.6 mol/l, which is obtained by the data of the heat of infinite dilution, or about 0.5 mol/l obtained by the present measurement of the refractive index, fall in the range of the concentration of the salt in sea water. Thus the sea is a solution of the salt concentration of C_{cr} , being an interface of two thermodynamically different phases as described above. The function of the sea water in nature may be interpreted in terms of this fact, which will be discussed more in detail later.

Experimental section

Reagent:

The same grade alkali chloride as described in chapter 1 was used in the experiment without further purification.

Same water was also used as described in chapter 1.

Apparatus:

Refractive index meter:

The refractive index meter which has been used in the present investigation is the one made by Showa Denko Ltd., Shodex RI SE31. The construction of the meter is shown Figure 1. A beam of tungsten light goes through the solution, and is compared with the light passed through the reference sample. Thus, the output of the meter is, as has been mentioned, the difference between the refractive indices of two solutions, $\Delta n = n_s - n_r$, where n_s and n_r are the indices of the sample and of the reference, respectively. The Δn value is presented in four digits. Measurements are done segmentally for separated concentration ranges. Namely, the Δn values are measured for a group of samples whose n_s values are close to each other as well as to the n_r value. As the value of n_s gets too far from n_r , the reference is changed to another one whose n_r value is closer to n_s 's of the new series of samples. The actual procedure of the measurement is as follows. The aqueous sodium chloride solutions of both the reference and the sample are fed into the box by polyethylene tubes. The box contains the lead tubes and other components of measurement. The diameter of the lead tube is

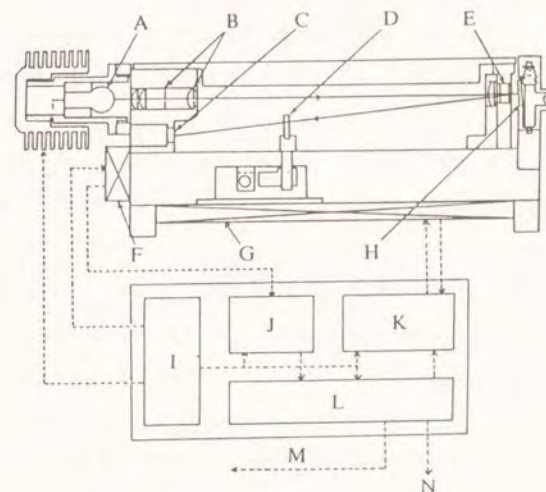


Figure 1 Diagram of the refractive index meter.
A, lamp; B, slit; C, photocell; D, adjust glass; E, flow cell for the sample and the reference solutions; F, preamp; G, heater; H, mirror; I, power stabilizer; J, amp; K, temperature controller; L, operation panel; M, output to the meter; N, output gate of the sample.

about 1 mm and the total length of the tubes inside of the box is about 20 cm. This value of the tube is the length from the inlet gate of the box to the measuring spot. The solutions in the tubes are held thermally constant in the box. Both the sample and the reference solutions are held in the reservoirs which are located outside of the box at the height of about 100 cm. The solutions flow down through the polyethylene tubes and are introduced to the measuring box. The temperature of the measurements has been set variously at 10, 25 and 35°C, mostly at 35°C. The temperature of measurement, namely, that of the sample within the box, is estimated to have an ambiguity of $\pm 0.1^\circ\text{C}$ at the set temperature. The actual procedure of the measurement of the refractive indices is, first, to allow both solutions to run through the tubes. Then, stop the flow of the sample solution by putting a stopper at the outlet gate of the tube. The values of Δn are sampled by the microcomputer, NEC PC-8801, at certain intervals. The values of the latter has been set at three different intervals of 0.1, 1 and 5 s. In the preliminary experiment, the digital values read on the meter were recorded at an interval of 20 s. The number of the data sampled by the computer is 720, 600 and 60 for the 0.1, 1 and 5 s of sampling interval, respectively, and that of the visual measurement is 20. In the case of the computer sampling, the standard deviation of the observed data has been calculated mechanically; in the visual case, this was done manually. As the sample flow is stopped, the sample must get a mechanical shock, and the reading of the output is assumed to be influenced. Therefore, the effect of stopping on the output of the meter has

been measured by the digital memoryscope, GMS-6430, of Iwatsu Elec. Co., where a sizable tumbling is observed in the output just after the stopping. However, the output reaches a stabilized level soon. Data sampling has made in the stabilized range (Figure 2).

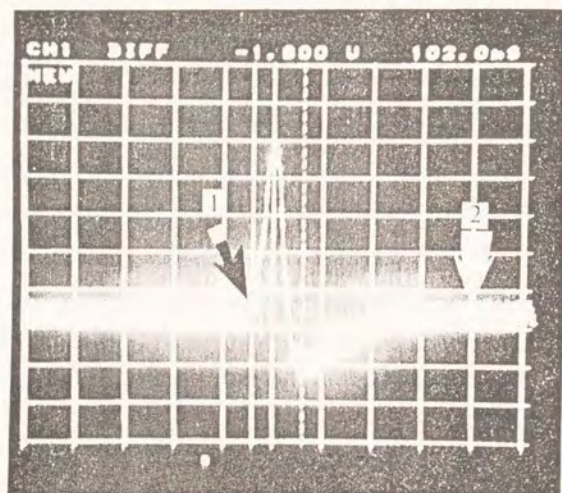


Figure 2 Transient record of output of refractive index meter, measured by the memory scope of BMS-6430, Iwatsu Elec. Co..
The ordinate shows the output of the meter and the abscissa, time. Arrow 1 shows the time when the flow is stopped and 2 to the range where the data are sampled.

Results and discussion

The observed values of the refractive indices of aqueous sodium chloride solutions are presented in Figure 3. They make a straight line as a function of the concentration of salt. The slopes of the lines for 10 and 25°C coincide well with each other as well as with that for the data in the literature¹⁰⁾. The data of the measurements at 35°C have also shown a straight line. However, the slope is different from that of the lower temperature data. Figure 4 shows the data of fluctuation, where σ/\bar{n}_s in the ordinate refer to the standard deviation of the measurements. The data in the figure show to the results of two different sampling times, of 1 and 20 s. Although some difference is observed in the value of the σ/\bar{n}_s peak concentration, it is obvious in the figure that the fluctuation is strongly enhanced in the solutions in the region between 0.4 and 0.5 mol/l. With respect to the different values of the σ/\bar{n}_s peak concentrations, it is not certain whether the effect is real or due to some experimental cause.

Figure 4 also shows to the effect of oxygen. The solid symbols in the figure are the data for the solutions which carry oxygen, while the open ones are those without oxygen. Oxygen was removed in the samples simply by introducing nitrogen into the reservoir of the sample solution. Hence, the presence of a small amount of oxygen in the solution cannot be denied. Even so, however, it is obvious from Figure 4 that the enhanced fluctuation which has been observed in the oxygen carrying solutions disappears when oxygen is removed. The height of the enhanced

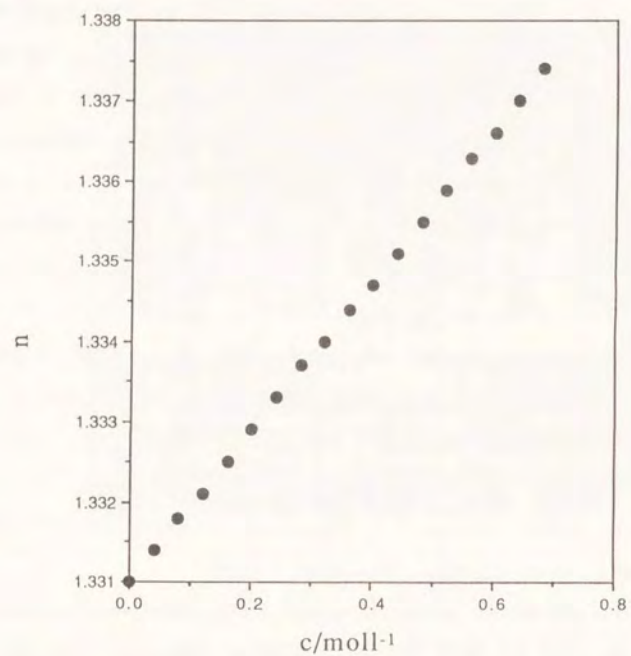


Figure 3 Linear relation of refractive indices of aqueous sodium chloride solutions as a function of the concentration of sodium chloride at 35°C.

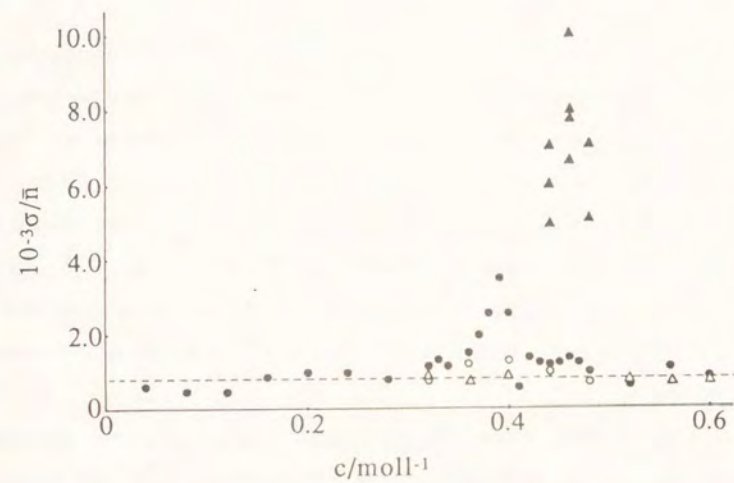


Figure 4 Fluctuation of refractive index of aqueous sodium chloride solutions. σ/n_s shows the standard deviation of refractive index, n_s , for solutions with oxygen (solid) and for those without oxygen (open). Sampling time for the data of $\blacktriangle, \triangle$, 20s and for \bullet, \circ , 1s.

fluctuation depends on the interval of the sampling time. As seen in Figure 5, the height depends on the sampling time, apparently with a logarithmic relation. The enhancement of fluctuation of n_s 's at C_{cr} 's have been found for the solutions of lithium chloride, potassium chloride, and caesium chloride at 0.2, 0.4 and 0.1 mol/l, respectively (Figure 6).

The point of interest are why the fluctuation is enhanced at a specific concentration, and why it occurs only when oxygen is present. As has been mentioned, the specific concentration, C_{cr} , is considered to be a kind of critical concentration which divides the solution into two phases. For the convenience of further discussion, solutions below C_{cr} will be called phase I and those above C_{cr} phase II. Independent quantum chemical calculations have also shown that the structure of the aqueous solution can be divided into two phases¹⁰).

Fluctuation of the refractive index can be taken as equivalent to that of the thermal energy of the sample. Thus, the observed values of σ must refer to the fluctuation of the uptake and withdrawal of thermal energy of the sample. The results of Figure 4 suggest that neither phase I nor phase II alone can have violent thermal fluctuation, regardless of the presence of oxygen, but that only the interface of I and II, which moreover carries oxygen, can show violent thermal fluctuations. One possible interpretation for this finding is that oxygen works as a kind of catalyzer to decrease the specific heat of the sample. For example, oxygen may work as a porter of energy between the two phases I and II. Oxygen is assumed to be able to form bonding with bulk water molecules via

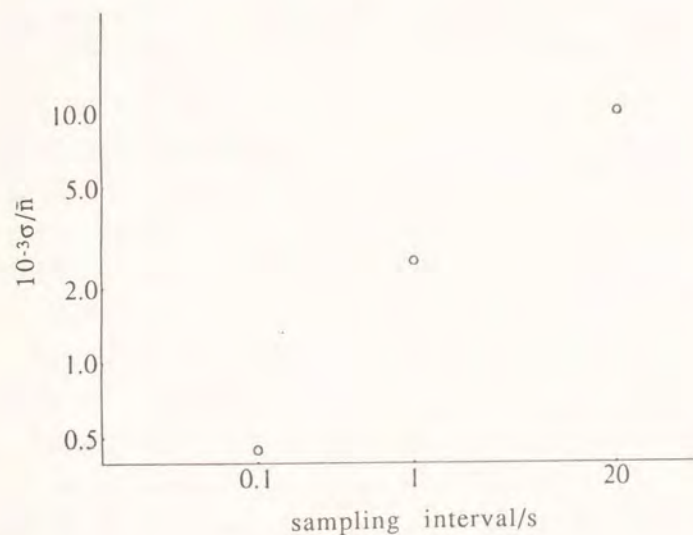


Figure 5 Logarithmic relation of the enhanced fluctuation with the interval of sampling time.

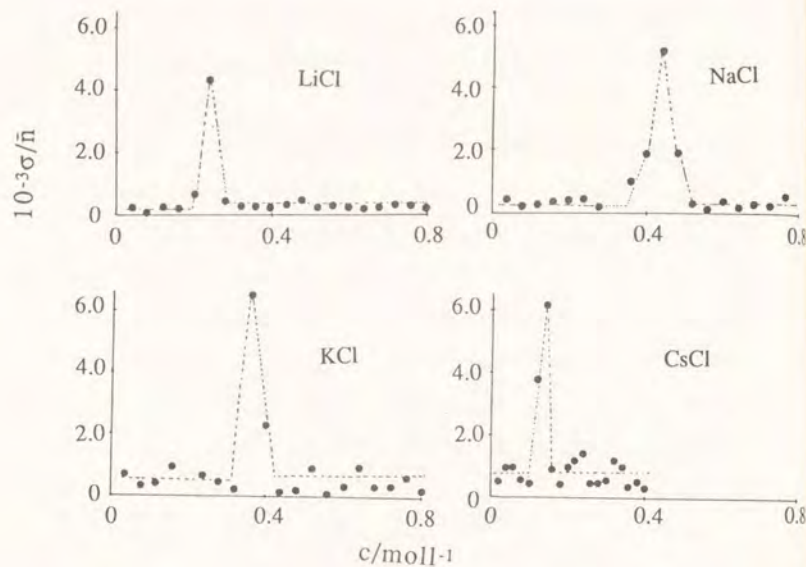


Figure 6 Fluctuation of refractive index of aqueous alkali chloride solutions. σ/\bar{n}_s shows the standard deviation of refractive index, n_s , for solutions with oxygen. Sampling time for the data of 20s.

lone-pair electrons (oxygen)-vacant π orbital (bulk water). It is supposed that in phase I alone, the entropy energy is dominant, hence, only the uptake of the thermal energy can occur and withdrawal cannot. However, if I and II are interfaced and oxygen is present, then, it is assumed that oxygen can form bonding with the bulk water in I, which later migrates or is exchanged with the water molecule in II, resulting in the energy transportation from I to II. Because the phase II the energy is dominated by the binding energy, energy exchange between the solution of II with the surrounding is possible. A reverse energy path from outside to I through II may also be possible with the work of oxygen.

The concentration of salt in sea water is usually assumed to be simply due to the equilibrium of the amount of water evaporating from the sea surface and that put into from rivers. However, the question remains why the evaporation does not go beyond the present salt concentration of sea water, and why sea water is so homogeneous all over the world, or at least, why and how the concentration of the present sea water became such as it is now. The experimental data of the heat of infinite dilution of aqueous sodium chloride solution have suggested that the value of the critical concentration, which divides the phase I and II, is around 0.6 mol/l. The present investigation on the fluctuation of the refractive index leads to a value of around 0.5 mol/l. Also, the quantum chemical calculation which gives the critical concentration with respect to the state of the bulk water molecules presents a value of 0.5 mol/l. All these values cited fall in a range around the concentration of salt in sea water. In another words, it seems quite

certain that the concentration of salt in sea water is a thermodynamically significant concentration.

The solution of the concentration of C_{cr} can get thermal energy from outside easily when oxygen is present. This fact may find an analogy in the function of the surface water of sea which holds the salt concentration in the range around C_{cr} and oxygen. We assume thus that by the nature of the phases of I and II, the salt concentration has arrived at its present value, and has come to take a value suitable for the reception of the solar energy at the surface of the sea.

Appendix Structure related anomalous fluctuation of refractive index and oxygen effect in human blood model saline water.¹¹⁾

The fluctuation of the refractive index has been measured in aqueous sodium chloride solutions of around 0.1 mol/l concentration, which is the salinity of the human blood. The aim of the measurements is to see if fluctuations of the refractive index can be observed in the human blood salinity solution, which is the other important saline solution in nature beside seawater. Because the solution of the seawater salinity has been evidenced to be an interface of two phases, one dominated by the dispersion entropy of the ions and the other by the inner energy of the mutually interacting solvated ions, it has been assumed that if similar fluctuation were observed with the solution of the salinity of 0.1 mol/l of sodium chloride, the result could be taken as the evidence for the fact that 0.1 mol/l is another interface of two different phases. In fact, the fluctuation has been observed and the specific concentration of 0.1 mol/l has been interpreted in terms of the break of hydrogen bonding.

Experimental section

The fluctuations of refractive index were measured in the same way as the that of the previous investigation except that the output of the refractive index meter was directly sampled and processed by a personal computer PC-9801, Nippon Electric Company. The output of the meter, which actually shows to the difference of the refractive indices of the sample and the reference solutions, is sampled for 1 min at an intervals of 1 ms. Six thousand data are thus obtained with one measurement run. They are then broken into groups of data of different sampling intervals. Group No.1 shows to the data with an interval of 1 ms, No.2 for the intervals of 2 ms, No.3 for those of 3 ms and so on. Statistical analysis of the data for each of the groups was carried out by the computer. The fluctuation, σ , has also been calculated for each group in the same way as that in the former investigation.

The aqueous sodium chloride solutions were prepared with a concentration difference of 0.01 mol/l.

We wanted to see how the hydrogen bonding influenced the structure of the electrolyte solution, so measurements of σ were also made on the mixtures of the heavy water and the normal water. We assumed that the hydrogen bonding in the normal water was controlled by the heavy water resulting in a change of the refractive index of the water. 2.5% by volume of heavy water was added to the normal water.

Results and discussion

The results of measurement for D_2O/H_2O are shown in Figure 7, where the concentration of D_2O is taken along the x axis, the sampling time interval along y and the fluctuation of the refractive index, σ , along z . The figure presents a lineup of σ 's of all groups of data. The front most line in the figure refers to the fluctuation of group No.1 for the data of 1 ms sampling interval, the next line to that of group No.2 and so on.

It is obvious in the figure that all lines show a peak at the concentration of 15% D_2O and fall to the ground level at 20%.

Figure 8 presents the results of the sodium chloride solutions which exhibit a drastic drop of σ at the concentration range from 0.03 to 0.10 and almost a zero value as the average for the higher concentration range. Again, the x axis in Figure 8 refers to the concentration of salt, y to the sampling time interval and z to the fluctuation, σ .

The results of Figure 7 on the D_2O/H_2O system suggest that an anomalously heavy fluctuation of the refractive index occurs in the system of 15-20% D_2O , which may imply the formula of the system of $D_2O(H_2O)_4$. Actually, a quantum chemical calculation has recently shown that the tetrahedral coordination is the most probable arrangement of the cluster structure of water¹²). Raman spectroscopists have reported that the cluster structure is one possible form for the interpretation of the spectra¹³).

These results suggest a possible basis for the interpretation of the fluctuations of the aqueous sodium chloride solutions. It is

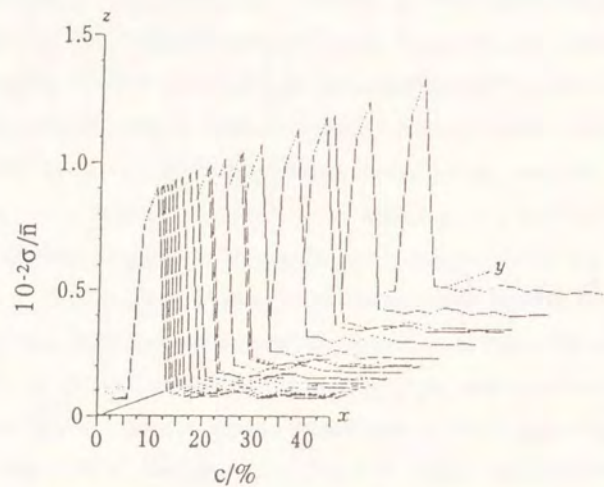


Figure 7 Fluctuation of refractive index, σ , of D_2O-H_2O mixtures. x , concentration of $D_2O\%$ /volume. y , interval of data sampling in ms. z , fluctuation. The front-most line of the data show σ for 1 ms of y , the next line for 2 ms, and so on.

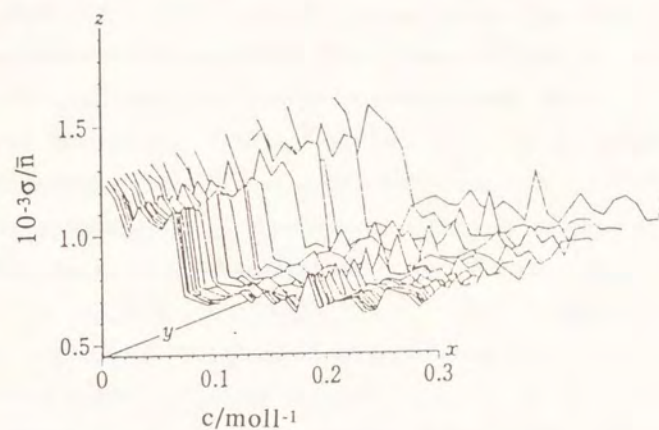


Figure 8 Fluctuation of the refractive index, σ , of the aqueous sodium chloride solution. x , concentration, mol^{-1} , y , interval of data sampling in ms, z , fluctuation.

normal that electrolytic ions which are dissolved in water break the hydrogen bonding of the water. The chemical shift of the proton NMR in polar liquid is usually interpreted in terms of the formation and destruction of the hydrogen bonding¹⁴). If this is the case with the aqueous sodium chloride solution, the hydrogen-bonded structure of water may be broken by the introduction of the ions, which must result in the formation of the cluster of water molecules. As in the case of the D₂O/H₂O system, the aqueous sodium chloride solution must start with the competition between the two phases of water, one dominated by the unified system of the hydrogen bonded water molecules and the other governed by the clusters.

The specific concentration of 0.1 mol/l NaCl may be the critical concentration for the competitive two phases, and accordingly, may cause the anomalous fluctuations of the refractive index. The situation would be just the same as that in the case of the seawater. The only difference between the two is that the key of the critical work for the seawater is the hydration of ions, whereas that for the human blood is the hydrogen bonding. Both cases may rely on the nature of the solution at the critical interface of the dispersion entropy of the solute individuals and the internal energy of the solution⁵). This remark must play an important role in the sea and in the human body.

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Chapter 3

The investigation of the eutectic compound of sodium chloride and water.¹⁾

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Abstract

The detailed investigation has been carried out with respect to the thermal behavior of the eutectic compound of sodium chloride and water. The result of the investigation has revealed a clear cut salt concentration dependence of the latent heat of melting of this compound, ΔH . Namely, the value of ΔH jumps at the specific salt concentration of the human blood and of the sea water, 0.1 and 0.5 mol/l NaCl, respectively.

Furthermore, it has been found that the eutectic compound of sodium chloride and water forms "adduct" with oxygen. This "adduct" means a kind of additional compound. The melting points of the pure and the adduct compound are -21.7°C and -22.3°C , respectively, and the value of the literature shows the melting of the oxygen adduct. Most characteristic point of this finding has been that the two phases of the eutectic compound, the one is without oxygen and the other is with oxygen. These two phases are not smeared out with each other under the molten condition when the salt concentration is as low as around 0.1 mol/l NaCl.

Introduction

As it has been shown in chapter 2, fluctuation of the refractive index in aqueous sodium chloride solutions is enhanced at the specific concentration with the presence of oxygen. This chapter describes a further finding about oxygen effect of aqueous sodium chloride solutions.

The eutectic compound of sodium chloride and water, $\text{NaCl}\cdot 2\text{H}_2\text{O}$, melts at -22.3°C in the literature.²⁾ In the aqueous sodium chloride solutions, if oxygen interacts the hydrated water, it is considered that there are any differences between the eutectic compounds of oxygen free and that of oxygen saturated solutions in the liquid phase. The investigation has been carried out by DSC and NMR, about this eutectic compound of both oxygen free and oxygen saturated aqueous sodium chloride solutions.

Experimental section

Reagent:

The same grade sodium chloride as described in chapter 1 was used in the experiment without further purification.

Same water was also used as described in chapter 1.

Apparatus:

Measurements have been made with the differential scanning calorimeter, DSC, made by Seiko Instruments Inc., model SSC5000 DSC100, and the nuclear magnetic resonance, NMR, made by JEOL, model EX90. The oxygen holding sample is actually the one in which are oxygen saturated and the sample of oxygen free is the solution from which oxygen was removed by the membrane deoxygenizer of the ERMA Inc. made. The oxygen content of the oxygen saturated sample was about $8.7\ \mu\text{g/ml}$ and that of oxygen free down to $0.7\ \mu\text{g/ml}$.

The DSC measurements have been made on the aqueous sodium chloride solutions with concentrations around $0.1\ \text{mol/l}$ NaCl . The sample solution was sealed in a silver metal container with the size of $6\text{mm}\phi\times 4\text{mm}$, and weighed $\pm 1\ \mu\text{g}$. After the sample solution was cooled down to -60°C and has kept 20 min at this temperature, the temperature of the sample was raised slowly at a rate of 1°C/min with the computer controlled program. As the reference of the DSC, a sapphire stone was used. Figure 1 shows the DSC melting curves of the eutectic compound. And Table 1 shows the results of reproducibility of melting of Indium metal

which is the usual standard of DSC. From these results, the reading of the temperature measurement of the sample is estimated to be within a range of $\pm 0.01^\circ\text{C}$.

Table.1 The results of reproducibility of DSC melting data of indium metal.

measurements	melting point/ $^\circ\text{C}$	melting $\Delta H/\text{J} \cdot \text{g}^{-1}$
No.1	156.39	28.44
No.2	156.39	28.38
No.3	156.40	28.45
No.4	156.39	28.42
No.5	156.40	28.41
No.6	156.39	28.43
No.7	156.39	28.39
No.8	156.41	28.41
No.9	156.39	28.44
No.10	156.39	28.36
\bar{x}	156.39	28.41
σ_{n-1}	0.007	0.029
cv%	0.005	0.10

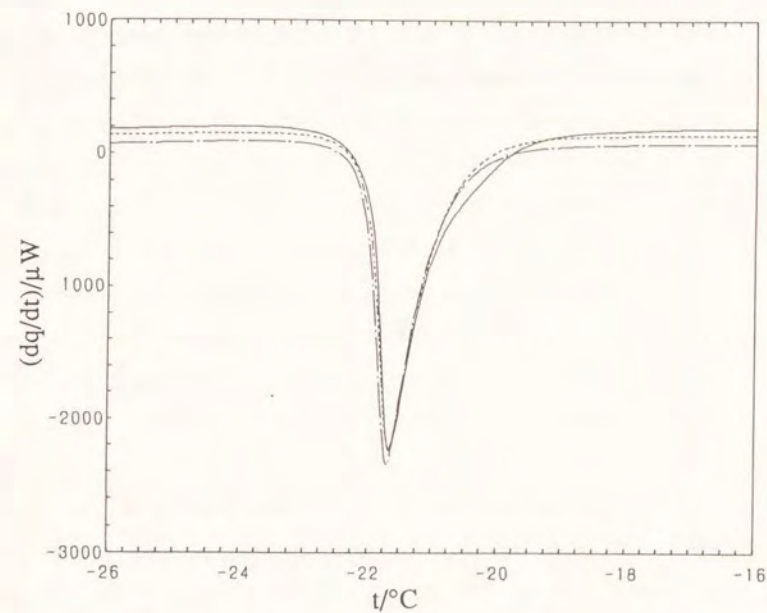


Figure 1 The DSC reproducibility of melting of eutectic compound of sodium chloride and water.

The NMR measurements have been made on the same samples as the DSC measurements. The sample was cooled down to -60°C and was kept for 20 min in this temperature, then brought up to -20°C . While the sample is kept at -20°C , the proton resonance measurement has been made.

Result and discussion

Figure 2 shows the DSC melting curve of frozen aqueous sodium chloride solution. The DSC records give a small peak of heat absorption at $-22.3^{\circ}\text{C}/-21.7^{\circ}\text{C}$ and a main peak at 0°C . The former peak is attributed to the melting of the eutectic compound and the latter to that of the ice. The detailed investigation has been carried out with respect to the thermal behavior of this eutectic compound. The result of this investigation has shown a clear cut salt concentration dependence of the latent heat of melting of this compound, ΔH . Figure 3 shows that the value of ΔH jumps at the specific salt concentrations of the human blood and of the sea water, 0.1 and 0.5 mol/l NaCl. It has been mentioned already in the chapter 1 and chapter 2 that these characteristic concentrations should have significant relationship to the structure of water, i.e., the hydrogen bonding of water and the hydrated ions. The present results should be taken as suggesting that the thermal behavior of the eutectic compound works as a sensitive probe of the structure of water.

The value of the melting point of -22.3°C is observed only the samples which hold oxygen. Whereas, when oxygen is removed from the sample in advance of measurement, the peak is shifted to -21.7°C . The record of the oxygen free sample is a clear cut single line. But the record of the oxygen carrying sample is a doublet which is formed of two component lines. Figure 4 shows the records. The relative intensity of each component of the doublet lines was measured from the record of DSC. In practice, the record

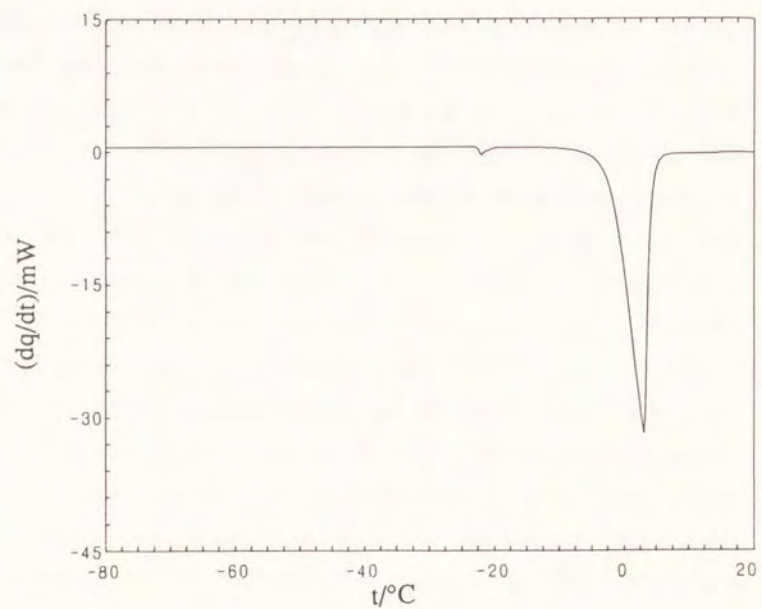


Figure 2 DSC record of melting of frozen sodium chloride aqueous solution.

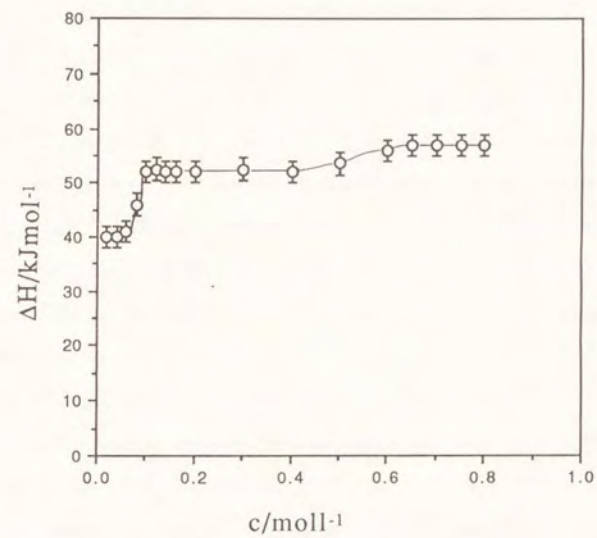


Figure 3 Salt concentration dependence of latent heat of eutectic compound.

paper was first enlarged and cut into component portions. These were weighed. Figure 5 presents the results for the relative intensity of -22.3°C . It reaches a maximum at 0.1 mol/l NaCl and disappears at around 0.2 mol/l NaCl . The ΔH value of the oxygen free sample at 0.1 mol/l NaCl concentration is 47 kJ/mol NaCl and that of the oxygen holding sample, as the total ΔH for the doublet, is about 5 kJ/mol NaCl higher.

To examine the relationship between the two forms of the eutectic compounds, one pure and the other adducted with oxygen, NMR measurements have been made on the samples. As seen in Figure 6 and Figure 7, the NMR record of oxygen free sample is a simple broad line with a half line width about 80 Hz . However, that of oxygen holding sample shows a signal which is an overlap of two broad lines. The relative intensity of the overlapped components is changed depending on the salt concentrations. The lower field component has been assigned to the oxygen adduct compound and the higher to the pure eutectic compound. This assignment was done after condition of the change of the relative intensities of the components. The chemical shift between the two components is about 10 Hz .

Particular attention should be called on the fact that the NMR records of the oxygen carrying samples give signals overlapping of two component lines, i.e., the eutectic compounds which are in the molten condition are not mixed with each other, but remain as separate phases. This fact suggests that the two phases of the eutectic compounds, one pure and the other the oxygen adduct, exist separately from each other. It is also to be noted that the

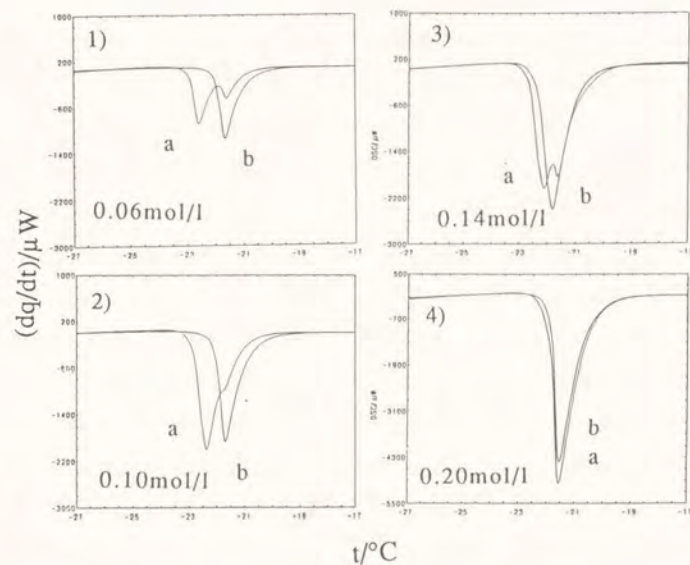


Figure 4 DSC records of melting of eutectic compounds in a) without oxygen and b) with oxygen aqueous sodium chloride solutions.
1) 0.06 , 2) 0.10 , 3) 0.14 and 4) 0.20 mol l^{-1} .

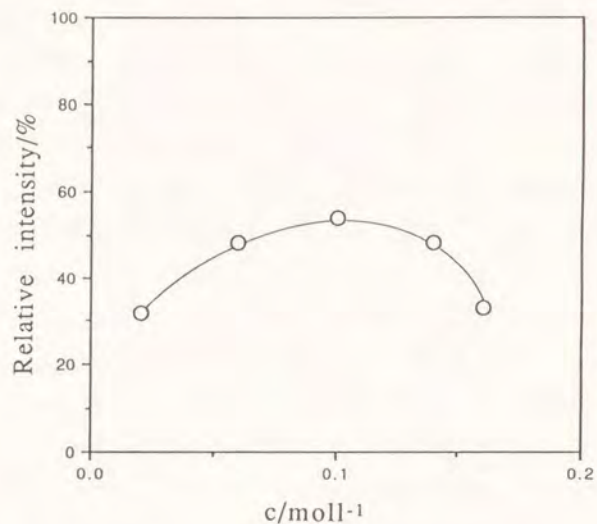


Figure 5 Concentration dependence of the relative intensity of DSC signal of oxygen adduct in eutectic compound phase of oxygen-carrying samples.

oxygen adduct compound more easily melts than the pure eutectic according to the results of the DSC measurement.

The results shown above will solve the problem which has been raised in chapter 2 with respect to the fluctuation of the refractive index of the aqueous sodium chloride solution.³⁾ In chapter 2, an anomalous fluctuation has been observed with the solutions of the concentrations around 0.1 mol/l NaCl, it has disappeared when oxygen is removed from the sample. If exchange of the two forms of the eutectic compound happens in the liquid phase, it may cause the fluctuation observed. Previously, S. Fujiwara has mentioned to the physicochemical and physiological significance with respect to the specific concentration of 0.1 mol/l NaCl before.⁴⁾ He pointed out that this concentration is a critical one where the interionic interaction among the paramagnetic ions starts. In other words, the ions in the solutions lower than this specific concentration can behave freely as the individual solute entities, each being away from the mutual interionic interactions. There, a critical volume of the solutions has been assigned to each solute entity as the free space. This free space was named the 'molecular space'. In practice, the molecular space is counted as equal to the quotient of the total volume of the solution divided by the number of the ions. The size of this specific volume has been estimated at about $10 \pm 5 \text{ \AA}$ and evidenced experimentally.⁵⁾ If the concept of the molecular space holds the present case, it will be taken as feasible that the results of the DSC and the NMR measurements which have showned two coexist-, but separated from each other- compounds of the pure and the oxygen adducted eutectic compounds.

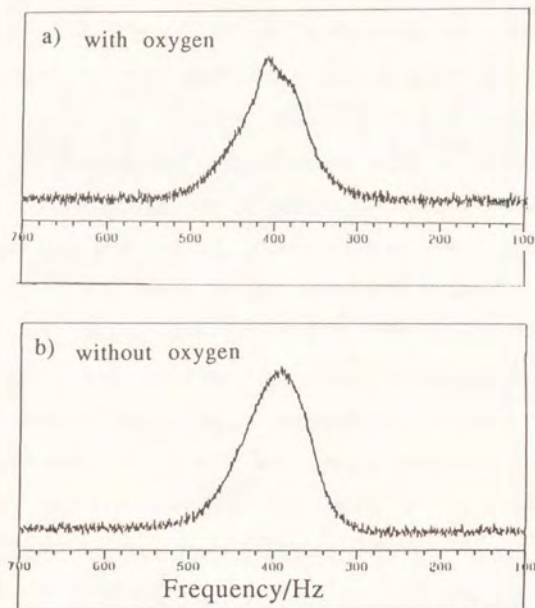


Figure 6 NMR records at -20°C for a) with oxygen and b) without oxygen aqueous sodium chloride solutions of 0.06 mol l^{-1} .

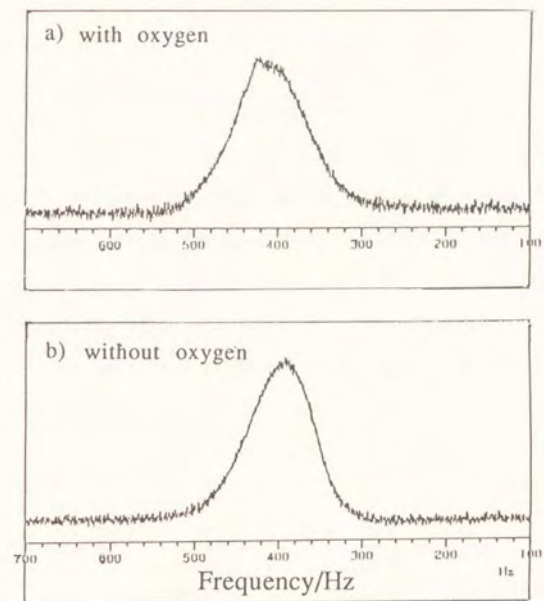


Figure 7 NMR records at -20°C for a) with oxygen and b) without oxygen aqueous sodium chloride solutions of 0.10 mol l^{-1} .

Application Thermoenergetic identification of enantiomeric isomers of amino acids.⁶⁾

Introduction

In relation to the finding of the eutectic compound, the interest has been taken if the enantiomeric isomers of amino acid behave differently from each other when they are in association with the eutectic compound which is confined in the 'molecular space'⁵⁾ of the salt ions. Actually, the motive of the interest lies on the facts that the critical concentration of the 'molecular space' is 0.1 mol/l, and almost equal to the salt concentration of the human blood and that of the physiological saline water for mammals.

Experimental

Reagent:

Same water and sodium chloride as described in the previous chapter were also used.

Threonine and aspartic acid purchased from SIGMA Chemical Company were used in the experiment without further purification.

Apparatus:

Same DSC, NMR and the membrane deoxygenizer as described already were used in the experiment.

The DSC and NMR measurements have been made on the aqueous sodium chloride solutions with concentrations around 0.1 mol/l NaCl to which about 2 mmol/l amino acid has been added.

Results and discussion

Figure 8 and Figure 9 show the DSC records of melting of eutectic compounds for the aqueous sodium chloride solutions of 0.10 mol/l holding 2 mmol/l L-amino acid (1) and D-amino acid (2). The results of the oxygen free samples are same as the amino acid free samples. However, in the oxygen saturated samples, the results are different from each other in the case of D-amino acid holding and L-amino acid holding samples. The DSC data of oxygen saturated and holding D-amino acid samples present a doublet line at -21.7°C and -22.3°C , same as amino acid free samples.

Figure 10, 11, 12 and 13 show the NMR data of aqueous sodium chloride solutions holding L or D-amino acid. The records of NMR of oxygen free and holding L or D-amino acid samples give a single line same as the amino acid free samples. The records of NMR of oxygen saturated and holding L-amino acid samples give a single line same as that of oxygen free samples. However, the record of oxygen saturated and holding D-amino acid samples give a signal with two lines overlapping.

Figure 14 shows the difference of the DSC data between with oxygen sample and without oxygen sample which carries 2 mmol/l L- or D-threonine. The same results have been obtained with aspartic acid (Figure 15).

Particular attention must be called to the NMR signal in which of two component lines overlap. The NMR spectrum reveals the fact that the two component species of compound with melting point of -22.3°C and -21.7°C are not mixed with each other, but remain as

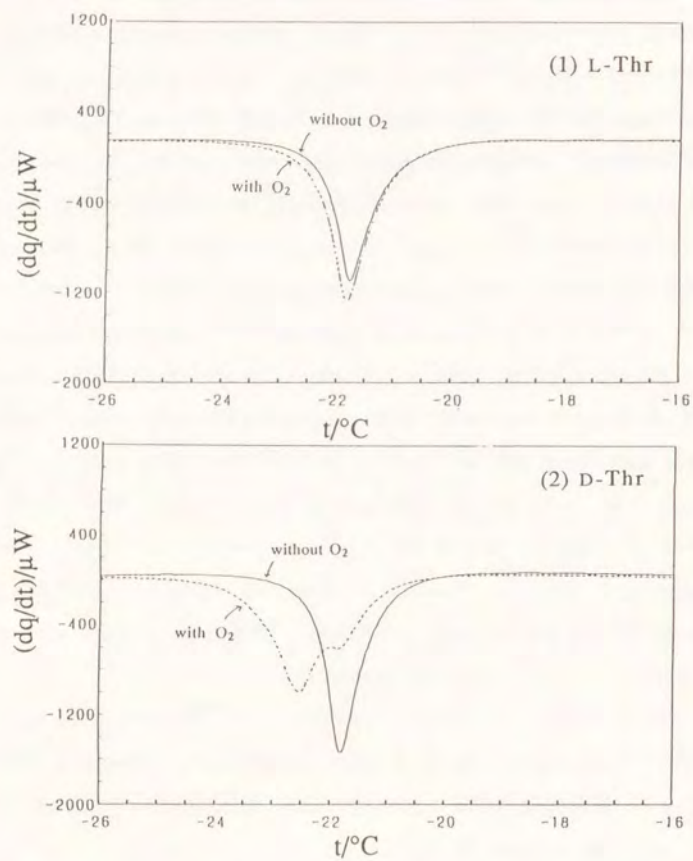


Figure 8 DSC records of melting of eutectic compounds for the sodium chloride solutions of 0.10 mol l^{-1} NaCl coexisting with 2 mmol l^{-1} L-threonine (1) and D-threonine (2).

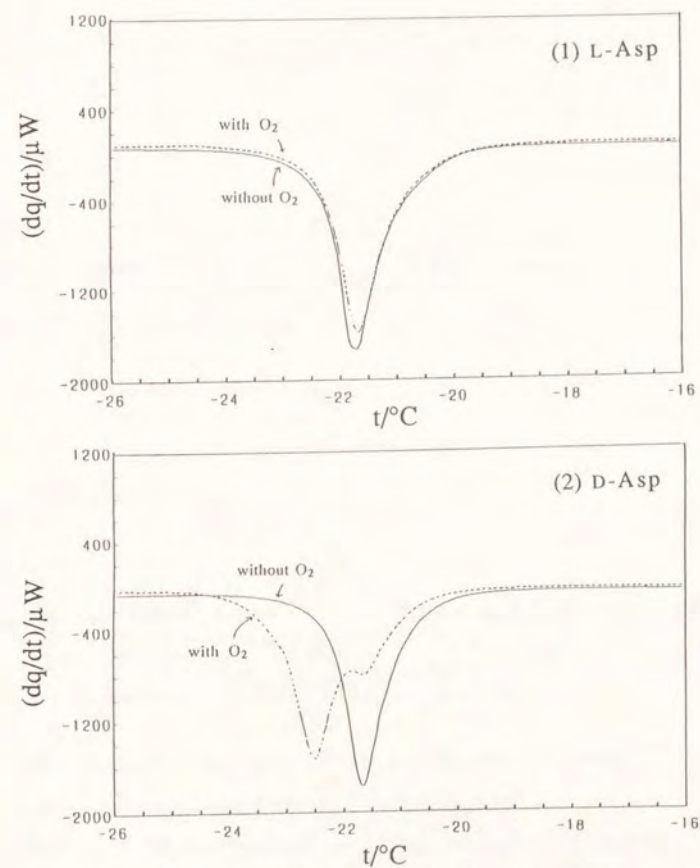


Figure 9 DSC records of melting of eutectic compounds for the sodium chloride solutions of 0.10 mol l^{-1} NaCl coexisting with 2 mmol l^{-1} L-aspartic acid (1) and D-aspartic acid (2).

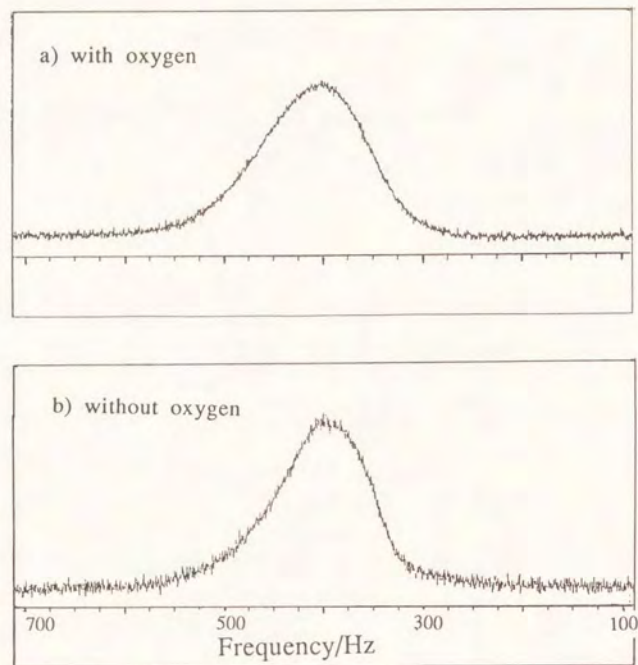


Figure 10 NMR records at -20°C for the sodium chloride solutions of $0.10\text{ mol}\cdot\text{l}^{-1}$ with $2\text{ mmol}\cdot\text{l}^{-1}$ L-threonine. a) with oxygen, b) without oxygen

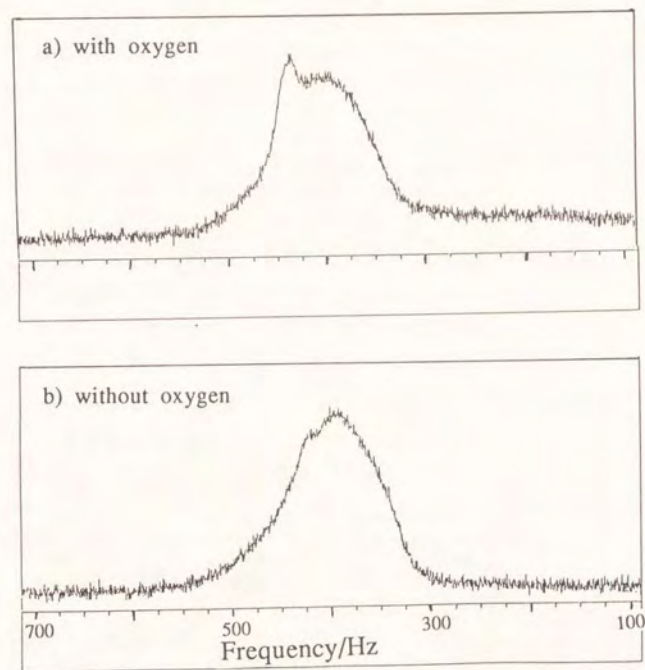


Figure 11 NMR records at -20°C for the sodium chloride solutions of $0.10\text{ mol}\cdot\text{l}^{-1}$ with $2\text{ mmol}\cdot\text{l}^{-1}$ D-threonine. a) with oxygen, b) without oxygen

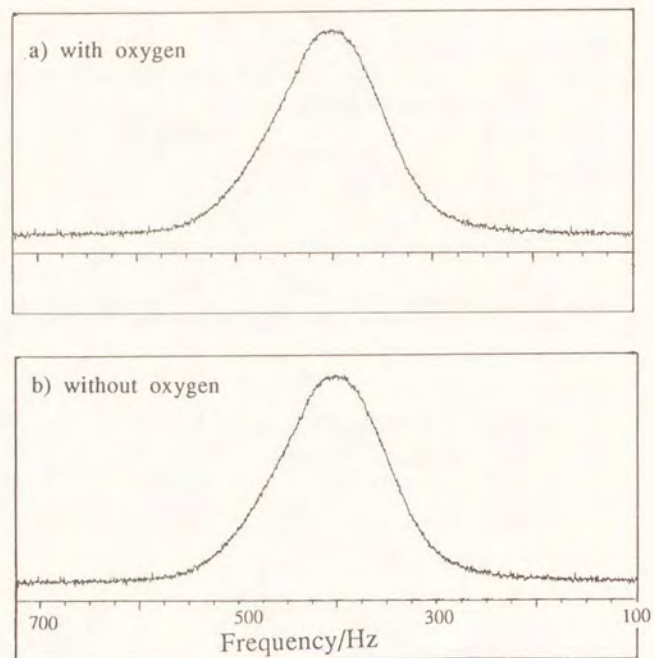


Figure 12 NMR records at -20°C for the sodium chloride solutions of $0.10\text{ mol}\cdot\text{l}^{-1}$ with $2\text{ mmol}\cdot\text{l}^{-1}$ L-aspartic acid. a) with oxygen, b) without oxygen

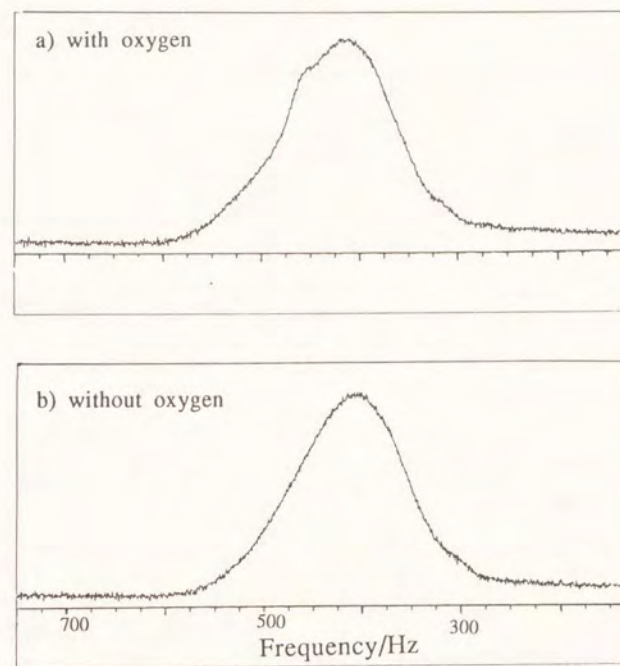


Figure 13 NMR records at -20°C for the sodium chloride solutions of $0.10\text{ mol}\cdot\text{l}^{-1}$ with $2\text{ mmol}\cdot\text{l}^{-1}$ D-aspartic acid. a) with oxygen, b) without oxygen

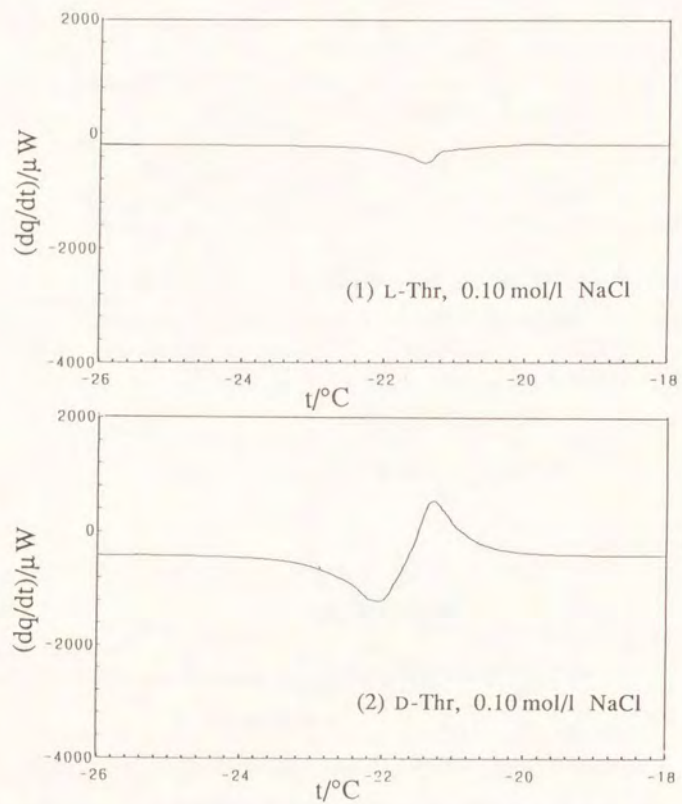


Figure 14 Difference of DSC data between with oxygen sample and without oxygen sample which carries 2 mmol l^{-1} L-threonine (1) and D-threonine (2).

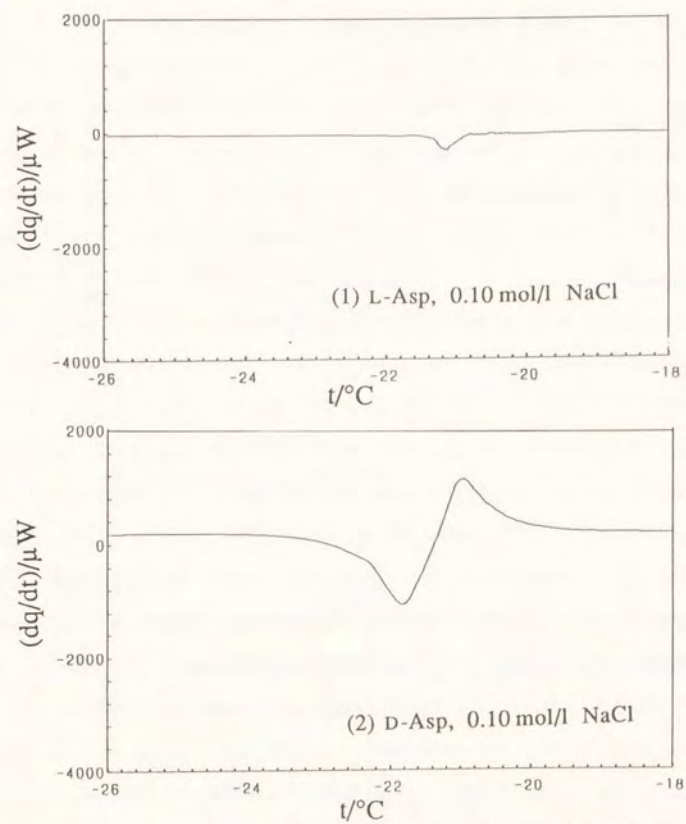


Figure 15 Difference of DSC data between with oxygen sample and without oxygen sample which carries 2 mmol l^{-1} L-aspartic acid (1) and D-aspartic acid (2).

separate phases in spite of the fact that they are in the molten condition. Since the discovery of the D and L enantiomeric isomers of tartarate by Pasteur, artificial synthetic method has ever succeeded to produce of either one of the isomers separately. The artificial method of preparation of amino acid produces only racemic compounds. This may be due to the fact that the artificial method of synthesis is not fine enough for identification of the thermoenergetic difference between the isomers. Hence it cannot control the individual reaction of each of the isomers separately.

Present results of the DSC measurements allow evaluation of the latent heat of melting, ΔH . The ΔH 's of the eutectic compound and oxygen adduct for 0.1 mol/l NaCl solution are measured as 47 and 52 kJ/mol NaCl, respectively. The ΔH for the sample which carries 2 mmol/l D-form threonine is 43 kJ/mol NaCl and that of L is 37. These values are the ΔH for the doublet signal of the oxygen adduct as a whole. Figure 16 shows the salt concentration dependence of the value of ΔH for the sample which carries 2 mmol/l D-threonine and L-threonine. These results suggest that about 6 kJ/mol NaCl difference exists between the ΔH 's for the 2 mmol/l solutions of D and L isomers which are in association with the oxygen adduct of the eutectic compound. This observed fact may explain why the peptides or the proteins in nature are mainly formed of the L-form amino acids. We consider that the intermolecular associations which work in the melt in the frozen samples still hold in the solutions at room temperature.

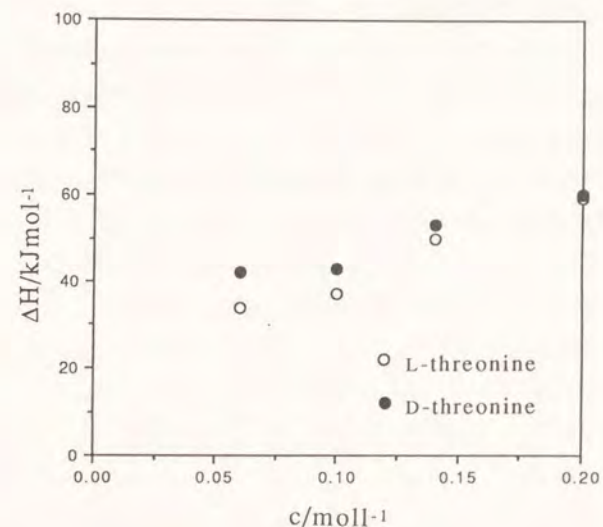


Figure 16 Salt concentration dependence of the value of ΔH for the sample which carries 2 mmol/l D-threonine (●) and L-threonine (○).

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Summary

Solute entities in solution are considered to take one of two phases depending on the concentrations. One can be seen in the lower concentration range, where each of the solute is considered to be in the solvent, the other in the heigher range, where the solutes interact with each other.

Spectroscopic investigations on aqueous solutions of propylene carbonate and alkali halides have shown presence of critical concentrations. Further, a remarkable fluctuation enhancement has observed with the refractive indices of the aqueous sodium chloride solutions at thiscritical concentrations, 0.1 mol/l and 0.5 mol/l. In addition, this enhanced fluctuation disappears when oxygen is removed from the sample solution. It has been found that the eutectic compound of sodium chloride and water forms an adduct with oxygen. The rate of oxygen adduct reaches a maximum at 0.1 mol/l. This concentration overlaps the concentration that a remarkable fluctuation enhancement observed. It is regarded that an exchange of the two forms of the eutectic compounds happens in the liquid phase, and it may cause the fluctuation. These critical concentrations correspond to the salinities of the human blood and the sea water.

The salinities of the human blood and the sea water were regarded as thermodynamically important concentrations. Oxygen plays an important role for the mammals and the earth.

List of publications

- Chapter 1 "Spectroscopic Investigation on Critical Concentration of Aqueous Electrolyte Solution."
S. Fujiwara and Y. Nishimoto,
Spectroscopy Letters, vol.17 (1984)
- Chapter 2 "Structure Related Fluctuation of Refractive Indices of Aqueous Strong Electrolyte Solution."
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- "Fluctuation of Refractive Index of Aqueous Sodium Chloride Solution and Oxygen Effect."
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Analytical Sciences, vol.1 (1985)
- Chapter 3 "Oxygen Adduct of Eutectic Compound of Sodium Chloride and Water."
S. Fujiwara and Y. Nishimoto,
Analytical Sciences, vol.6 (1990)
- "Thermoenergetic Identification of Enantiomeric Isomers of Amino Acids."
S. Fujiwara and Y. Nishimoto,
Analytical Sciences, vol.6 (1990)

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