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STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

Changes in the IR Spectra of Aqueous Solutions of Alkali Metal Chlorides during Crystallization

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Abstract—The IR spectra of aqueous solutions of sodium chloride and rubidium chloride with the same concentration of 0.1 M upon freezing are studied in the middle IR region. The changes that occur in the absorption bands of the bending ν_2, compound $\nu_2 + \nu_L$, and stretching (ν_1, $2\nu_2$, and ν_3) vibrations of water molecules with gradual crystallization of the solutions are studied. The obtained spectra of crystallized solutions are compared to the IR spectrum of ice Ih. Analysis allows conclusions about the structure of the investigated frozen crystallized solutions.

Keywords: IR spectra, solutions of alkali metal halogenides, freezing of aqueous solutions

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INTRODUCTION

Halogenides of alkali metals are contained in the waters of oceans and seas and play a crucial role in the vital activity of humans and animals. Aqueous solutions of salts are therefore an important object of study. Adding salt into water changes its properties and structural features. For example, the freezing point is lowered. The subcooling of aqueous solutions of alkali metal halides results in structural rearrangements [1]. The freezing of aqueous solutions of alkali metal halides proceeds gradually in a certain temperature range. When the temperature falls, water first freezes with increasing concentration of the remaining liquid solution. As the temperature falls, the water continues to freeze. The concentration of the remaining liquid solution grows to the eutectic temperature at which the solution completely freezes. It is of great interest to study structural features of the intermediate states of a solution during its freezing. Changes in the structure of aqueous solutions are registered via IR spectroscopy, since it can provide information on the rearrangements at the molecular level that cannot be obtained by macroscopic means. In this work, we used IR spectroscopy to study the stages of freezing of an aqueous solution of sodium chloride with a concentration of 0.1 M and an aqueous solution of rubidium chloride at a concentration of 0.1 M.

EXPERIMENTAL

IR spectra were obtained by means of ATR with multiple reflection of the beam (10 times) using a MIDAC M4000 IR Fourier spectrometer (MIDAC Corporation, United States). The possibility of using ATR was provided by a special HATR device and a cell for holding the sample under study (Pike Technologies, United States). The cell was installed on the HATR device. A cell with a germanium (Ge) crystal was used. Solutions were cooled with a thermostatting brass block placed on the cell. The temperature of the block was changed by passing refrigerant through it from a KRIO-VT-01 thermostat (Termeks, Russia) connected to the block by PVC hoses. The construction of the block allowed us to track the phase state of a sample in the cell. The temperature of the solution was measured using a noncontact Kelvin-IKS IR thermometer with an indicator (ZAO Evromiks, Russia). The measurement error was 0.5 K. Distilled water obtained using a DE-4 distiller (ZAO Zavod EMO, Russia) and salts of "chemically pure" grade (Labtekh, Russia) were used to prepare the solutions. Spectra were obtained with a resolution of 8 cm^{-1}. A detailed description of the experimental setup was given in [2, 3]. The accuracy of determining the wave number was ±2 cm^{-1}.

RESULTS AND DISCUSSION

The IR spectra of an aqueous solution of sodium chloride with a concentration of 0.1 M and an aqueous solution of rubidium chloride at a concentration of 0.1 M when frozen were studied in the region of absorption bands of bending ν_2, compound $\nu_2 + \nu_L$, and stretching (ν_1, $2\nu_2$, and ν_3) vibrations. In [4], IR

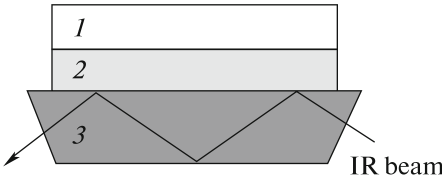

Fig. 1. Liquid interlayer between a germanium crystal of the cell and the frozen crystallized part of the solution: *1* is the frozen crystallized part of the solution, *2* is the liquid interlayer, *3* is the germanium crystal of the cell. The figure schematically shows two reflections of the light beam, when there were in fact 10 reflections.

spectra in the region of the absorption band of the stretching vibrations of water molecules for an aqueous solution of sodium chloride with a concentration of 0.1 M were studied when melted from the crystallized state. The location of the absorption band of the stretching vibrations, its shape, and the wave number of the maximum for the aqueous solution of sodium chloride, which can be seen in the IR spectra presented here, at all stages of solution freezing coincided with the results in [4]. The results obtained for the first time in this work include the changes in the shapes and wave numbers of maxima of the absorption bands of bending and compound vibrations of water molecules for an aqueous solution of sodium chloride with a concentration of 0.1 M upon freezing. Moreover for the first time a similar analysis was performed for the absorption bands of bending, compound, and stretching vibrations of water molecules for an aqueous solution of rubidium chloride with a concentration of 0.1 M upon lowering the temperature until it completely froze. Based on the changes in the wave numbers of the maxima and shapes of the absorption bands, structural changes were found to occur in aqueous solutions of sodium chloride and rubidium chloride, based on literature data from computer simulations [4–6].

It is known that freezing points for solutions are lower than for distilled water; the greater the concentration of the solution, the lower the freezing point. Upon freezing, the transition of the solution from the liquid phase to the solid phase state is extended in the temperature range.

In our experiment, the temperature of the solution in the cell was lowered gradually, beginning with the temperatures at which the solution was still liquid (−3°C for the RbCl solution and −1.5°C for the NaCl solution), and the spectrum typical of the liquid solution was observed. At a certain negative temperature (−6°C for the solution of RbCl and −5.5°C for the NaCl solution), there was a sharp change in the spectrum corresponding to the onset of crystallization of the liquid solution. The spectrometer recorded the spectrum of the remaining liquid interlayer between the cell crystal and the frozen crystallized part of the solution (Fig. 1).

The concentration of this liquid layer was higher than that of the original solution, since water initially begins to freeze from the solution. In the spectrum, this is reflected by a shift of the absorption band of stretching vibrations of a water molecule to the region of higher wave numbers (from 3344 to 3370 cm^{-1} for the 0.1 M solution of rubidium chloride and from 3332 to 3370 cm^{-1} for the 0.1 M solution of sodium chloride), a shift of the absorption band of compound vibration to the region of lower wave numbers (from 2114 to 2079 cm^{-1} for the 0.1 M solution of rubidium chloride and from 2106 to 2090 cm^{-1} for the 0.1 M solution of sodium chloride), and a shift of the absorption band of bending vibration also to the region of lower wave numbers, but not as great as for the band of compound vibration (from 1643 to 1639 cm^{-1} for both the 0.1 M solutions of rubidium chloride and sodium chloride). As the temperature fell, the absorption bands gradually shifted in these directions, due to the increase in the concentration of the solution. At a certain temperature (−9°C for a solution of RbCl and −8°C for a solution of NaCl), the entire solution transitioned to the solid phase, and the spectrometer recorded the spectrum of the completely crystallized solution. The spectrum of the completely frozen crystallized solution differed greatly from that of the solution in the liquid phase. When the solution was completely frozen, the absorption band of stretching vibrations of water molecules shifted to the region of lower wave numbers (compared to the initial liquid solution: from 3344 to 3248 cm^{-1} for the 0.1 M solution of rubidium chloride and from 3332 to 3248 cm^{-1} for the 0.1 M solution of sodium chloride) and the emergence of a characteristic shoulder was observed. Its intensity grew substantially in comparison to the spectrum of the liquid state. The absorption band of the compound vibration of a water molecule shifted to the region of higher wave numbers (compared to the original liquid solution: from 2114 to 2190 cm^{-1} for the 0.1 M solution of rubidium chloride and from 2106 to 2187 cm^{-1} for the 0.1 M solution of sodium chloride) and broadened. The absorption band of the bending vibration of a water molecule shifted slightly to the region of lower wave numbers (compared to the initial liquid solution: from 1643 to 1639 cm^{-1} for both the 0.1 M solutions of rubidium chloride and sodium chloride). It also changed its shape, broadening considerably in the region of lower wave numbers, as in the spectrum of ice Ih (Fig. 2).

The obtained spectra of crystallized solutions of sodium chloride and rubidium chloride when completely frozen have similarities with the spectrum of ice Ih. When distilled water freezes, the absorption band of the stretching vibrations of a water molecule also shifts to the region of lower wave numbers (3232 cm^{-1}) to reach a value similar to that of the

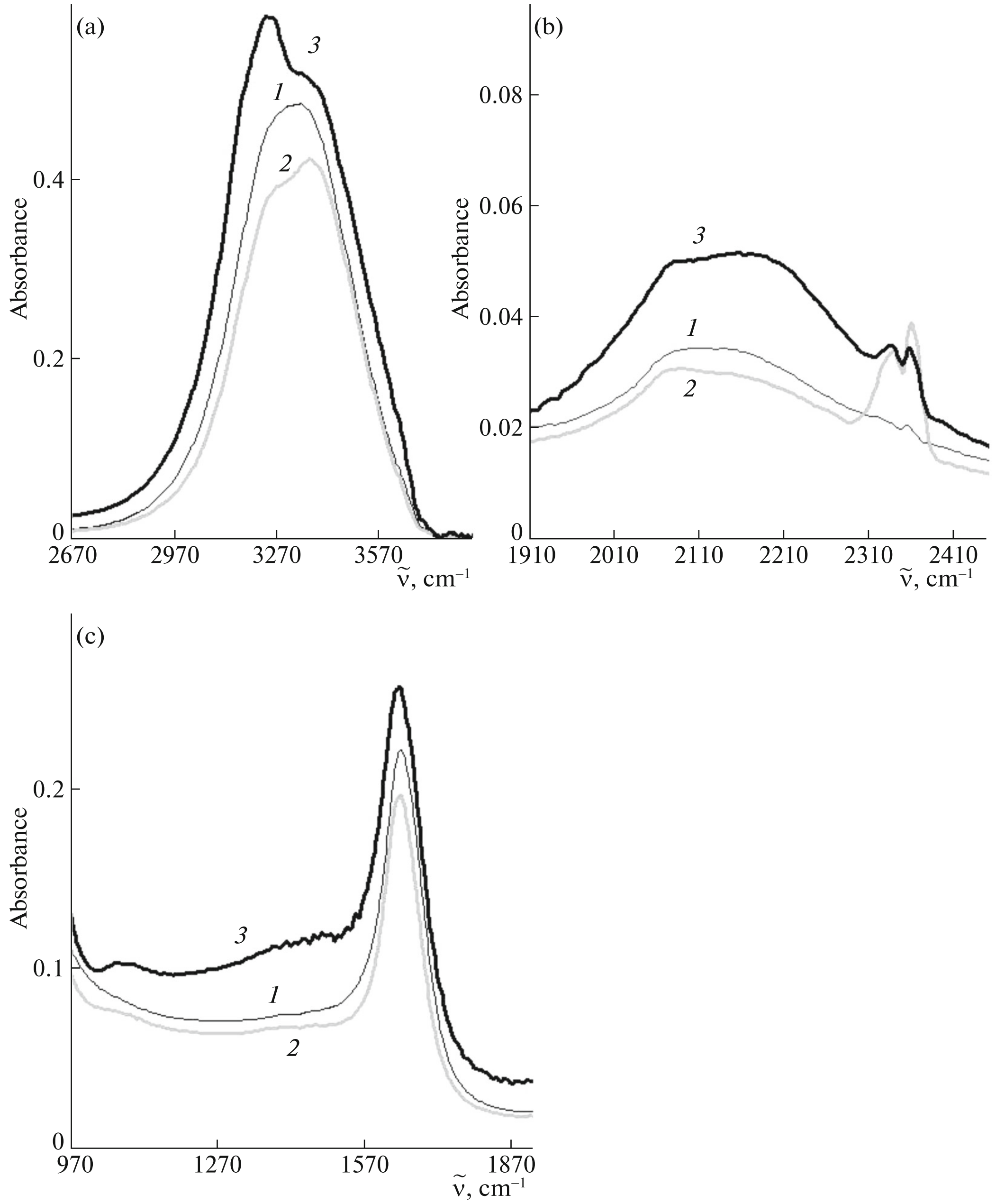

Fig. 2. IR spectra of the gradual freezing of a 0.1 M solution of RbCl: (a) the absorption band of stretching vibrations, (b) the absorption band of compound vibration, and (c) the absorption band of bending vibration; *1* is a liquid solution at −3°C, *2* is a liquid solution at −6°C, and *3* is a crystallized solution at −12°C; $\tilde{\nu}$ is the wave number.

absorption band of stretching vibrations of a water molecule of the crystallized solution (3248 cm^{-1} for the 0.1 M solution of rubidium chloride). However, the absorption band of stretching vibrations of a water molecule for ice Ih does not have the characteristic shoulder in the region of higher wave numbers that is present in the absorption band of stretching vibrations of a water molecule of the salt solution in the solid phase. The absorption band of the compound vibration for distilled water when freezing also shifts to the region of greater wave numbers (2210 cm^{-1}) to a value close to the wave number of the absorption band of the analogous vibration of a water molecule of the crystallized solution (2190 cm^{-1} for the 0.1 M solution of rubidium chloride). In contrast to the spectrum of the crystallized solution, however, no widening of the absorption band of compound vibration is observed in the ice spectrum. When distilled water freezes, the absorption band of bending vibration also shifts slightly to the region of lower wave numbers

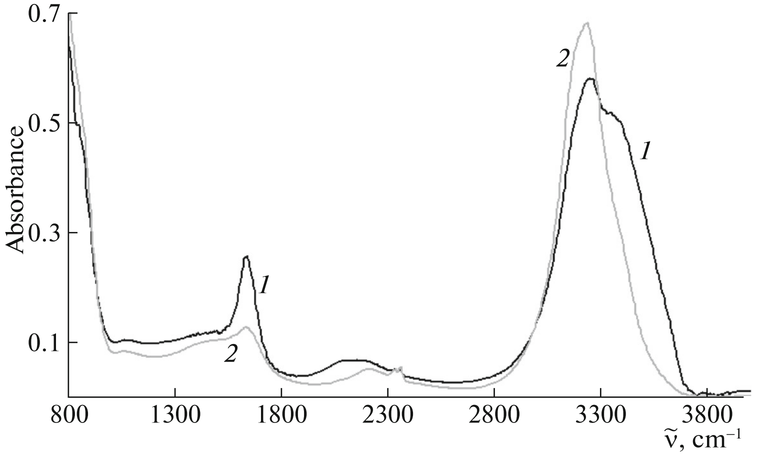

Fig. 3. IR spectra of a crystallized 0.1 M solution of (*1*) RbCl and (*2*) ice Ih at a temperature of −12°C.

(1635 cm^{-1}), virtually to the same wave number as the absorption band of the bending vibration of a water molecule of the frozen salt solution (1639 cm^{-1} for the 0.1 M solution of rubidium chloride). In addition, the absorption band of bending vibration for both ice Ih and the completely frozen solution broadens in comparison to the spectrum of the liquid state of the considered compound in the region of lower wave numbers (Fig. 3).

In [4], the change in the absorption band of stretching vibrations of a water molecule in the IR spectrum of an aqueous solution of NaCl with a concentration of 0.1 M was studied as it melted from a completely frozen crystallized state. The position of the absorption band of stretching vibrations of a water molecule of the crystallized solution and its shift relative to this band in the spectrum of the solution in the liquid state (before and after the onset of crystallization) found here coincide with the results in [4]. In both this work and [4], a shoulder at higher wave numbers was observed in the absorption band of stretching vibrations of a water molecule of the completely frozen solution. Based on the results from the computer simulation the authors of [4] explain the emergence of this shoulder by the presence of clusters built of sodium and chlorine ions with several water molecules in the solution. In accordance with the results in [4], we assume that the shoulder obtained in this work at higher wave numbers for the absorption band of stretching vibrations of a water molecule of the completely frozen solution was due to the presence of clusters formed by sodium and chlorine ions (or rubidium and chlorine ions) with several molecules of water in the solution.

It is possible that the widening of the absorption band of the compound vibration of a water molecule of the completely frozen solution can be explained by the formation of complexes of sodium, rubidium, and chlorine ions with water molecules.

The broadening of the absorption band of bending vibrations of water molecules of the solution in the solid phase resulted from the interaction between the intramolecular and intermolecular vibrations of water molecules, according to the results from the computer simulation in [5] obtained for the absorption band of bending vibration of ice Ih, for which widening is also observed.

The drop in the intensity of the absorption band of bending vibration of water molecules of the solution in the solid phase could be due to the strong anticorrelation between the constant dipole moment of a water molecule and the induced dipole moment of its acceptor molecule. Such anticorrelation in a liquid solution is less due to the disordering of the structure of the network of hydrogen bonds. We assume this in analogy with the results obtained in [6] for ice Ih, for which a drop in the intensity of the absorption band of bending vibration was also observed, compared to the spectrum of liquid water.

The rise in the intensity of the absorption band of stretching vibrations of a water molecule in the crystallized solution results from the positive correlation between the constant dipole moment of a water molecule and the induced dipole moment of its acceptor molecule observed for the absorption band of stretching vibrations. The ordered structure of hydrogen bonds in the crystallized solution increases the positive correlation in accordance with the results of [6] obtained for ice Ih, for which an increase in the intensity of the absorption band of stretching vibrations compared to the same band of water in the liquid state was also observed.

In addition to the experiments using a cell with a germanium (Ge) crystal, freezing experiments were performed using a cell with a crystal of zinc selenide (ZnSe) (for 0.1 M NaCl solution). Since the refractive index of zinc selenide is lower than that of germanium, the depth of penetration of the beam into the sample

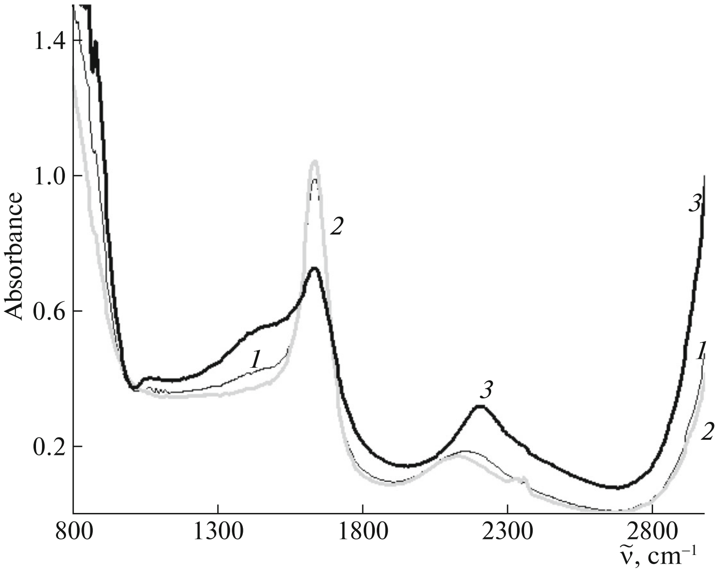

Fig. 4. IR spectra of the gradual freezing of a 0.1 M sodium chloride solution, obtained using the cell with the ZnSe crystal. For notations, see Fig. 2.

when using a cell with a ZnSe crystal is larger (at $\tilde{\nu}$ = 3300 cm^{-1}, the depth of penetration is 0.2 μm for a cell with a Ge crystal, while for a cell with a ZnSe crystal it is 0.5 μm). The total path length of the beam into the test compound for a cell with zinc selenide was therefore greater. The absorption of radiation by the sample was in this case more intense, and the absorption band of stretching vibrations of a water molecule was found to be scaled in intensity, while the absorption bands of bending and compound vibrations were more pronounced, resulting in stronger changes in these bands during crystallization of the solution (Fig. 4).

CONCLUSIONS

The IR spectra of frozen crystallized aqueous solutions of sodium chloride and rubidium chloride of a concentration of 0.1 M differ substantially from the spectra of these solutions in the liquid state. The IR spectrum of the crystallized solution was compared with the spectrum of ice Ih. There were similarities and differences between them. Our study of the IR spectra of crystallized solutions of sodium and rubidium chlorides and their comparison with the spectrum of ice Ih allowed conclusions regarding the structural features of frozen solutions. The similarity of the IR spectra of crystallized aqueous solutions of alkali metal chlorides upon their complete freezing with the Ih ice spectrum could indicate that like ice Ih, the solution in the solid phase had an ordered structure composed of tetrahedra formed by the hydrogen bonds of water molecules.

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