

OPTICS AND SPECTROSCOPY.
LASER PHYSICS

Studying the Concentration Dependences of IR Spectra for Aqueous Solutions of Alkali Metal Chlorides at a Negative Temperature

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Abstract—In this work, the concentration dependences of IR spectra were studied for aqueous LiCl, NaCl, RbCl, and CsCl solutions within the range from 4 to 0.2 M and an aqueous KCl solution within the range from 3 to 0.2 M at a temperature of -3.5°C in the middle IR region. The wavenumbers of the absorption band maxima were determined for stretching (ν_1, ν_3), combined ($\nu_2 + \nu_L$), and bending ν_2 vibrations at these concentrations. The established trends of the shift in the considered absorption bands provided a basis to make several conclusions about the structural transformations of the studied solutions with a decrease in concentration within the studied range. The calculations demonstrated an increase in the energy of hydrogen bonds between water molecules and their reduction in length with decreasing concentration for all of the studied solutions.

Keywords: IR spectra, aqueous solutions of alkali metal chlorides, concentration dependence of spectra, hydrogen bond energy.

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INTRODUCTION

The interest in the study of aqueous salt solutions is caused by their application for medical purposes and the presence of salts in sea and oceanic water. The addition of a salt to water leads to the transformation of its structure. Moreover, the dissolution of a salt in water decreases its freezing temperature. In this case, the higher the concentration of a solution is, the more its crystallization temperature decreases. After the temperature of an aqueous solution of alkali metal halides decreases below 0°C , their structure experiences transformations. Using X-ray diffraction, it has been established that the overcooling of these solutions decreases the coordination number of cations and increases the coordination number of anions. This is due to the fact that the overcooling of these solutions initiates the structural strengthening of water, the restoration of hydrogen bonds, and the involvement of unbonded water molecules in the network of hydrogen bonds [1]. The study of aqueous solutions at negative temperatures is of interest due to a great number of abnormal properties exhibited by water in the overcooled region. The study of solutions of alkali metal halides at negative temperatures is important for cryobiology [2].

Previous studies [3–8] of the concentration dependences of IR spectra for aqueous solutions of alkali metal halides were performed only at positive temperatures. However, it is of interest to study the region of negative temperatures due to the above-described issues. In this work, the concentration dependences of IR spectra were studied for the first time for aqueous LiCl, NaCl, RbCl, and CsCl solutions within a range from 4 to 0.2 M and an aqueous KCl solution within a range from 3 to 0.2 M at a negative temperature of -3.5°C . All the studied solutions remained in the liquid phase at this temperature. These studies allowed conclusions about the structural transformations that occur in these solutions with decreasing concentration.

MATERIALS AND METHODS

Our experimental setup was described in [9, 10]. The IR spectra of solutions were recorded by the attenuated total reflection (ATR) method on a MIDAC M4000 IR Fourier-transform spectrometer (MIDAC Corporation, United States). This ATR method uses multiple reflection of radiation (ten times). This method uses a special HATR device and a cell (Pike Technologies, United States) for the studied

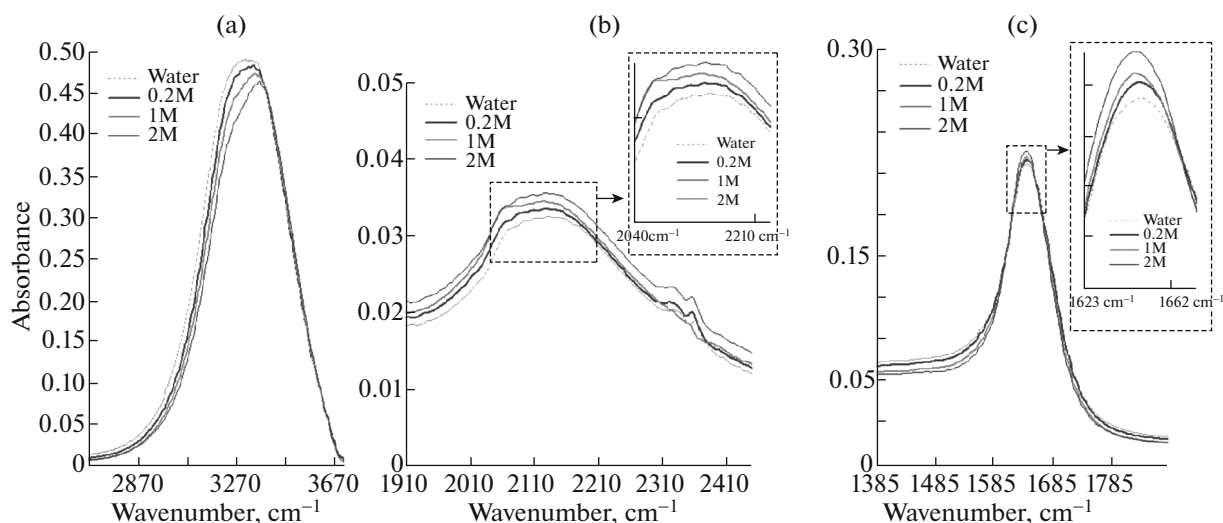


Fig. 1. The concentration dependence of the IR spectra of an aqueous LiCl solution for the absorption bands of (a) stretching (ν_1 , ν_3), (b) combined ($\nu_2 + \nu_L$), and (c) bending (ν_2) vibrations.

samples. A cell with a Ge crystal, for which the working region of this spectrometer lies within 780–4000 cm^{-1} , was used. The spectra were recorded with a resolution of 8 cm^{-1} . A temperature controlling metallic block was used to cool the solutions to the temperature of -3.5°C . It was cooled by a cold heat-transfer fluid that passed through it from a KRIO-VT-01 liquid low-temperature thermostat (Thermex, Russia). This block was installed on the cell designed for a sample. The temperature of the samples was measured using a Kelvin-IKS contactless IR thermometer (Evromiks, Russia) with a precision of 0.5°C . The solutions were prepared using distilled water obtained on a DE-4 distiller (Elektromedoborudovanie Plant, Russia). The salts were of chemically pure grade (Labtekh, Russia).

RESULTS AND DISCUSSION

In this work, the concentration dependences of IR spectra were studied for aqueous LiCl, NaCl, RbCl, and CsCl solutions within a range from 4 to 0.2 M and an aqueous KCl solution within a range from 3 to 0.2 M at a temperature of -3.5°C . The regularities of the shift with a change in concentration were determined for the absorption bands of bending ν_2 , combined $\nu_2 + \nu_L$, and stretching (ν_1 and ν_3) vibrations. For all the absorption bands, the wavenumbers of their maxima were determined at each concentration using created software [11, 12] with high precision. This software was also used to calculate the derivatives of all the bands. The wavenumber of an absorption band maximum was determined from the point of intersection between the derivative and the wavenumber axis. The precision for each wavenumber was $\pm 2 \text{ cm}^{-1}$. The precision for the concentration was $\pm 0.01 \text{ M}$.

Dissolution of a salt in water leads to weakening and destruction of the hydrogen bonds between water molecules due to the presence of salt ions. In this case, a shift of absorption bands occurs. The wavenumber of the stretching (ν_1 , ν_3) absorption band maximum for alkali metal chloride solutions increases in comparison with the IR spectrum of pure water, the wavenumber of the combined ($\nu_2 + \nu_L$) absorption band maximum decreases, and the wavenumber of the bending ν_2 absorption band maximum shifts slightly towards lower wavenumbers.

When the concentration of alkali metal chloride solutions is reduced within the studied range at a temperature of -3.5°C , the wavenumbers of the absorption band maxima are shifted in the same direction as in the case of a decrease in the temperature of these solutions of the same concentration [12] (Fig. 1).

When the concentration is reduced, the wavenumber of the stretching absorption band maximum decreases, the wavenumber of the combined absorption band maximum grows, and the wavenumber of the bending absorption band maximum increases slightly. The concentration dependences of their wavenumbers were fitted with linear functions found by the least-squares technique (Figs. 2–4).

The obtained dependences reflect the fact that a decrease in concentration leads to the strengthening of hydrogen bonds between water molecules (as well as a decrease in temperature) and reduces the number of cations and anions that destroy hydrogen bonds and the number of H_2O molecules involved in the coordination spheres of ions. The wavenumber of the stretching absorption band maximum for an LiCl solution (for each concentration) is lower than for the other alkali metal chloride solutions. The maximum decrease in the wavenumber of the stretching band maximum among all the studied solutions was

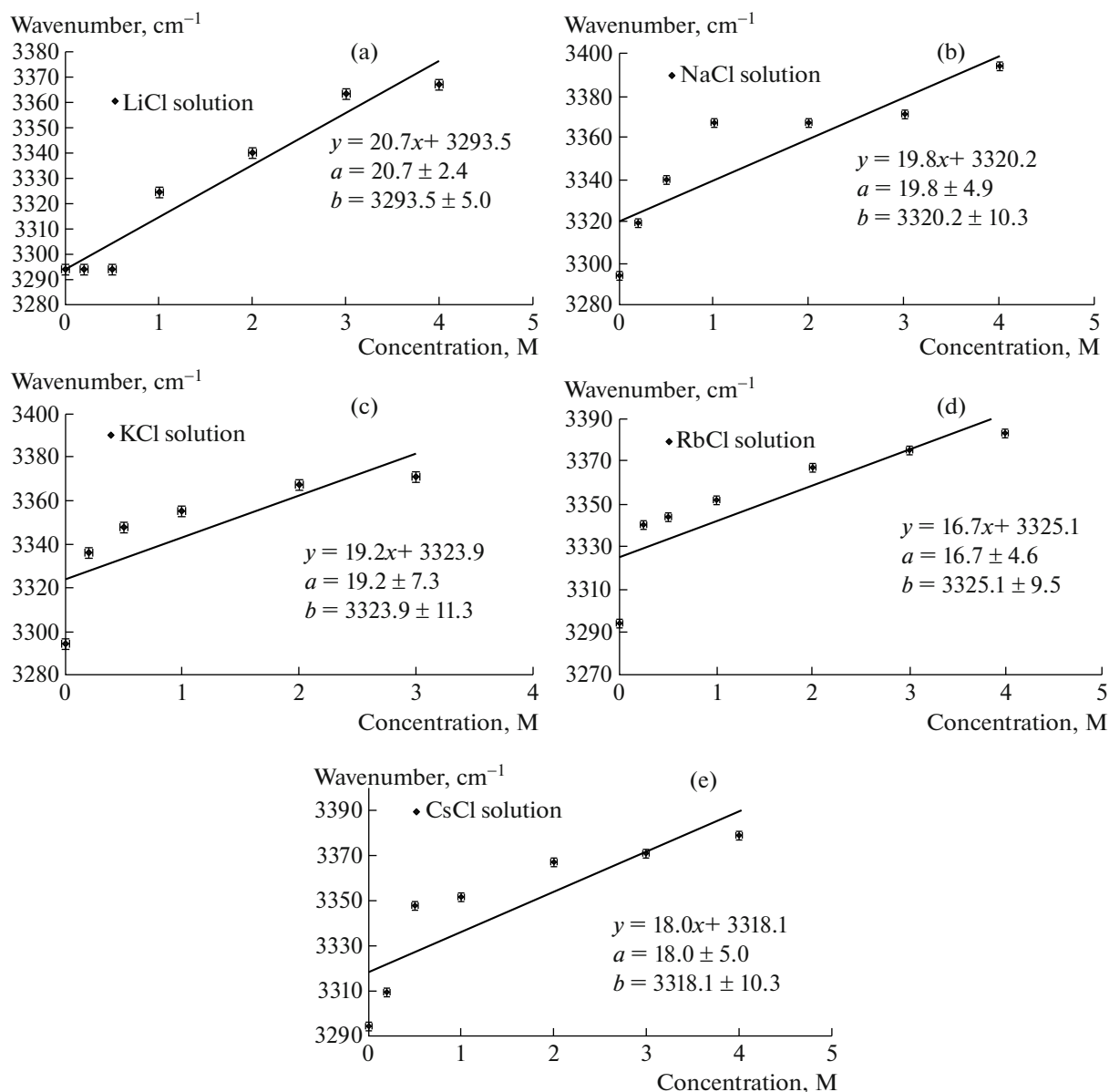


Fig. 2. The concentration dependence of the wavenumber of a stretching vibration-band maximum for an aqueous solution of (a) lithium chloride, (b) sodium chloride, (c) potassium chloride, (d) rubidium chloride, and (e) cesium chloride.

observed for the LiCl solution (3294 cm^{-1}) at a concentration of 0.2 M. This may be explained by the fact that the strength of hydrogen bonds in a lithium chloride solution is higher than in the other alkali metal chloride solutions. Since the lithium ion radius is smaller than the radii of the other alkali metal ions, it promotes the destruction of hydrogen bonds to a lesser degree. Moreover, the lithium ion is a kosmotrope, i.e., an ion that orders the structure of water, for which a greater strength of hydrogen bonds between water molecules in a solution is observed as a whole [13]. The wavenumber of the bending absorption band maximum for a LiCl solution is constant with a change in concentration within the studied range (1643 cm^{-1}).

This is due to the small radius of the lithium ion in comparison with the other alkali metal ions. For this reason, it destroys hydrogen bonds less readily, which has an effect on bending vibrations; a change in concentration almost does not lead to changes.

For each of the studied alkali metal chloride solutions, the energies and lengths of hydrogen bonds between water molecules were calculated at a decreasing concentration using the Johanssen formulas

$$-E_H = \frac{18\Delta v}{720 + \Delta v},$$

$$R_H = 2.44(-E_H)^{-0.2},$$

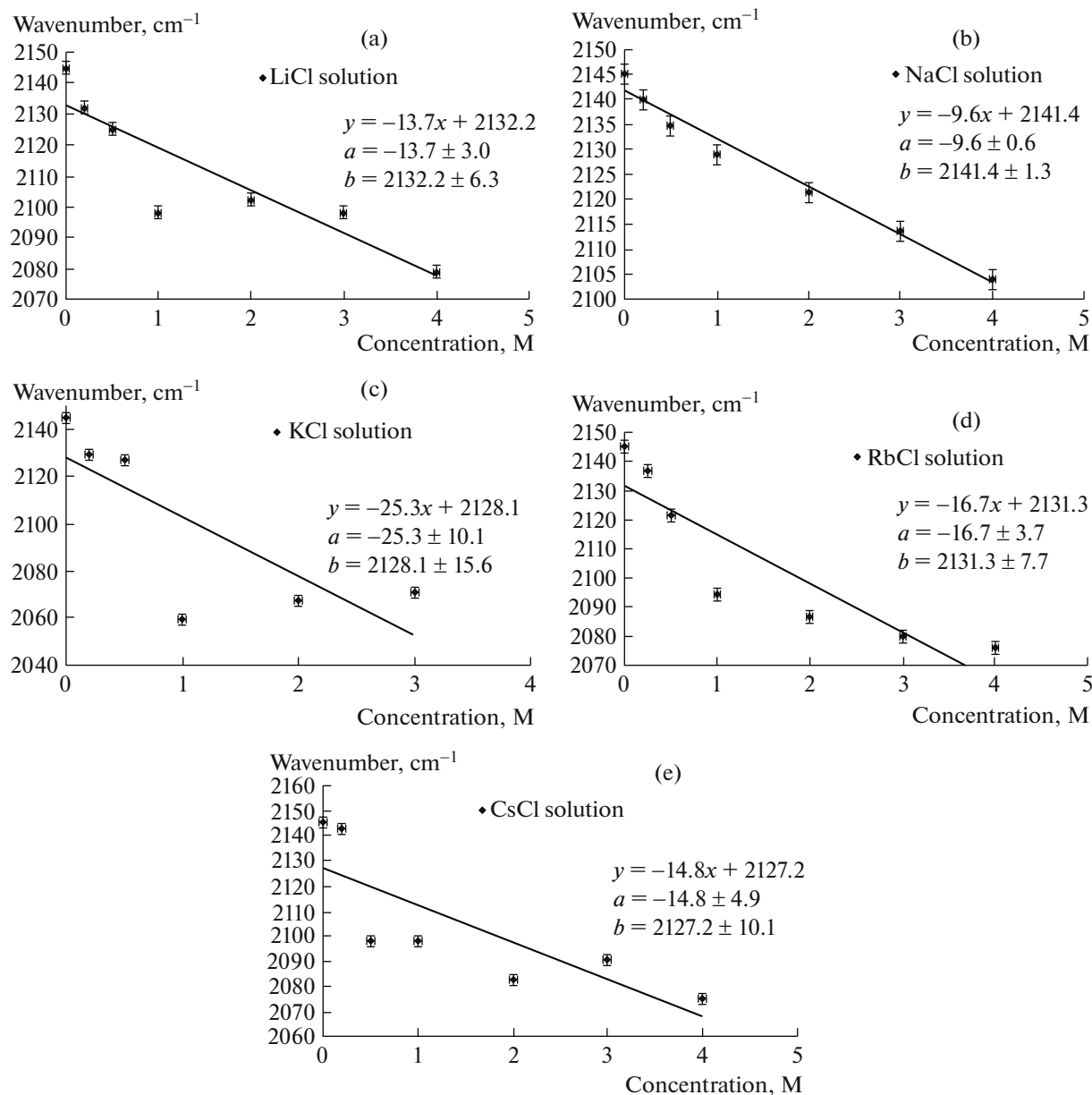


Fig. 3. The concentration dependence of the wavenumber of a combined vibration-band maximum for an aqueous solution of (a) lithium chloride, (b) sodium chloride, (c) potassium chloride, (d) rubidium chloride, and (e) cesium chloride.

where $\Delta\nu = \nu_0 - \nu$, ν is the frequency of bonded OH group vibrations, ν_0 is the frequency of free OH group vibrations [14], and $\nu_0 = 3600 \text{ cm}^{-1}$ [15].

As can be seen from Fig. 5, the energy of hydrogen bonds increases for all the studied solutions, while their length decreases with decreasing concentration.

CONCLUSIONS

A change in the concentration of aqueous LiCl, NaCl, RbCl, and CsCl from 4 to 0.2 M and an aqueous KCl solution from 3 to 0.2 M at a temperature of -3.5°C led to a shift in the wavenumbers of the absorp-

tion band maxima in an IR spectrum. The trend towards a shift in the wavenumbers of absorption band maxima with decreasing concentration is the same as in the case of a decrease in the temperature of these solutions with the same concentration. When the concentration is reduced, the wavenumber of the stretching (ν_1, ν_3) vibration band maximum shifts towards lower values, while the wavenumber of the combined ($\nu_2 + \nu_L$) vibration band maximum shifts towards higher values. The wavenumber of the bending (ν_2) vibration band maximum grows slightly. Such a trend in the changes in the wavenumbers of absorption band maxima is caused by the strengthening of hydrogen

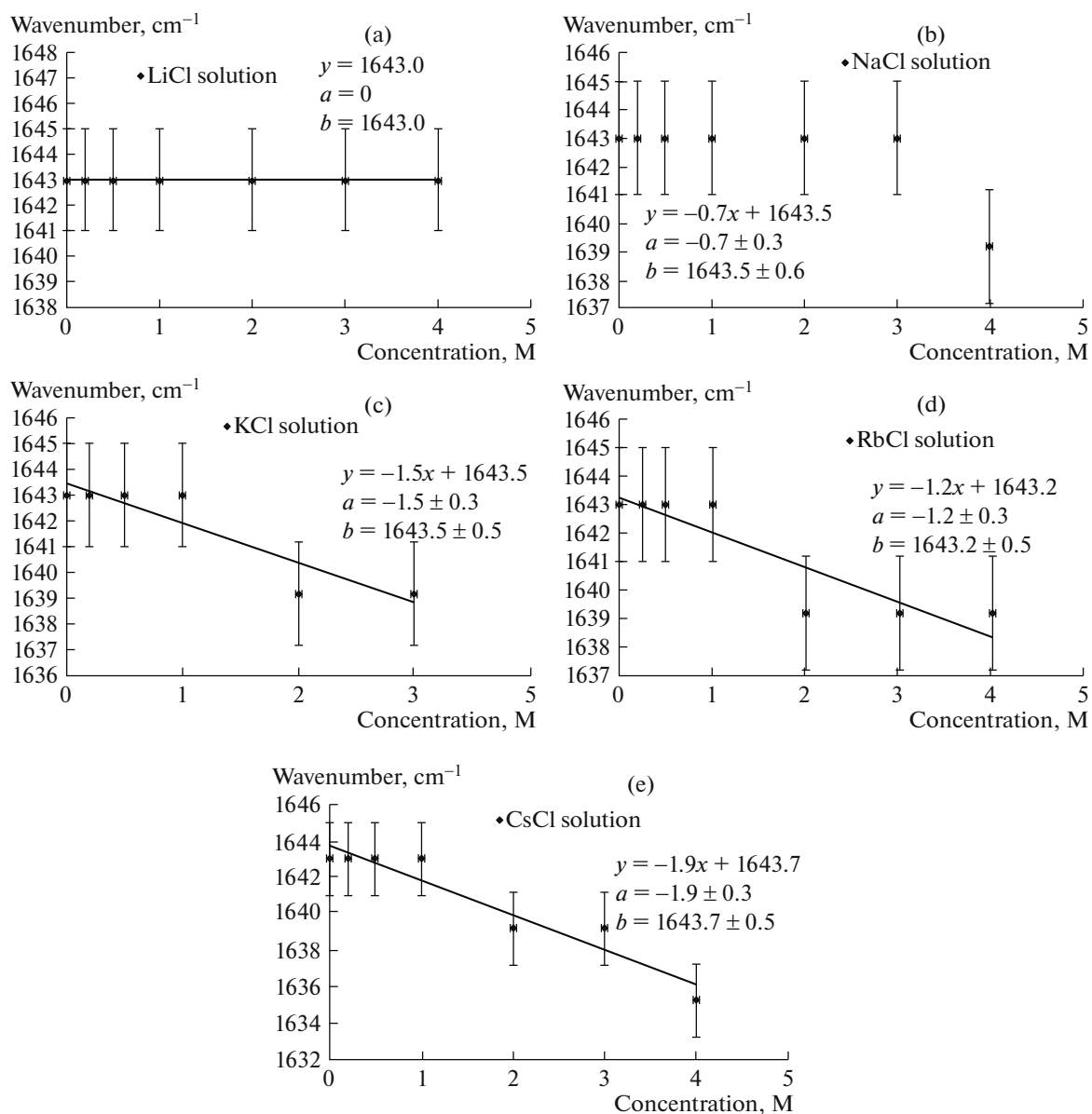


Fig. 4. The concentration dependence of the wavenumber of a bending vibration band maximum for an aqueous solution of (a) lithium chloride, (b) sodium chloride, (c) potassium chloride, (d) rubidium chloride, and (e) cesium chloride.

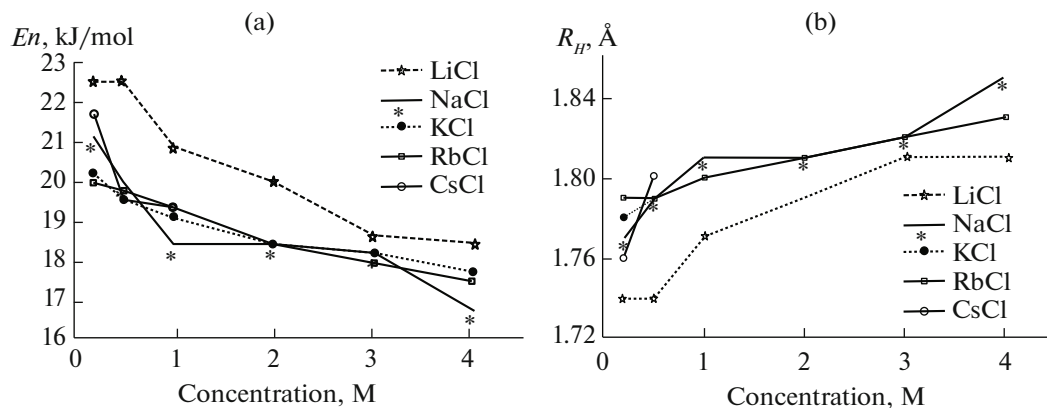


Fig. 5. (a) The energy of hydrogen bonds and (b) the length of hydrogen bonds between water molecules in alkali metal chloride solutions versus concentration at a temperature of -3.5°C .

bonds between water molecules with a decrease in the concentration of a solution.

REFERENCES

1. P. R. Smirnov and V. N. Trostin, *Structure of Aqueous Solutions of Inorganic Electrolytes in a Wide Range of Concentrations and Temperatures* (Inst. Khim. Rastvorov Ross. Akad. Nauk, Ivanovo, 2003).
2. *Water and Aqueous Solutions at Subzero Temperatures*, Ed. by F. Franks (Springer, 1982).
3. N. Yoshikawa, H. Sato, and H. Ohya, *Anal. Sci.* **14**, 803 (1998). doi 10.2116/analsci.14.803
4. J.-J. Max, S. Blois, A. Veilleux, and C. Chapados, *Can. J. Chem.* **79**, 13 (2001). doi 10.1139/v00-160
5. J.-J. Max, V. Gessinger, C. Driessche, P. Larouche, and C. Chapados, *J. Chem. Phys.* **126**, 184507 (2007). doi 10.1063/1.2717184
6. S. Park and M. D. Fayer, *Proc. Natl. Acad. Sci. U. S. A.* **104**, 16731 (2007). doi 10.1073/pnas.0707824104
7. C. H. Giammanco, D. B. Wong, and M. D. Fayer, *J. Phys. Chem. B* **116**, 13781 (2012). doi 10.1021/jp3095402
8. A. G. Davidian, A. G. Kudrev, L. A. Myund, O. S. Khlynova, and M. K. Khripun, *Russ. J. Gen. Chem.* **84**, 1877 (2014). doi 10.1134/S1070363214100028
9. A. V. Khakhalin, A. V. Koroleva, and Ya. N. Shirshov, in *Proc. Scientific-Practical Conf. "Fundamental and Applied Aspects of Innovative Projects of the Physical Faculty of the Moscow State University," Moscow, 2011*, p. 180.
10. A. V. Khakhalin, A. V. Koroleva, and Ya. N. Shirshov, *Instrum. Exp. Tech.* **56**, 749 (2013). doi 10.1134/S0020441213060183
11. A. V. Khakhalin, A. V. Koroleva, and R. F. Khamidullina, *Moscow Univ. Phys. Bull.* **70**, 397 (2015). doi 10.3103/S0027134915050069
12. A. V. Koroleva, Candidate's Dissertation in Mathematics and Physics (Moscow State Univ., Moscow, 2016).
13. http://www1.lsbu.ac.uk/water/kosmotropes_chaotropes.html.
14. N. D. Sokolov, *Hydrogen Bond. Collection of Papers* (Nauka, Moscow, 1981).
15. A. V. Koryakin and G. A. Kriventsova, *State of Water in Organic and Inorganic Compounds* (Nauka, Moscow, 1973).

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