ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 7, pp. 1424–1429. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © Ya.M. Grigor'ev, I.M. Gusev, M.Yu. Skripkin, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 7, pp. 1074–1079.

Structure of $NR_4BR–H_2O$ and $CoBr_2–NR_4BR–H_2O$ Solutions According to Electronic and IR Spectroscopy Data

Ya. M. Grigor'ev, I. M. Gusev, and M. Yu. Skripkin

St. Petersburg State University, Universitetskii pr. 25, St. Petersburg, 198504 Russia
e-mail: grigorjev@lumex.ru

Received February 11, 2011

Abstract—Absorption spectra of $NR_4Br–H_2O$ and $CoBr_2–NR_4Br–H_2O$ (R = Et, Bu) aqueous solutions were measured within the range of 1000–25000 cm^{-1}, and the influence of tetraalkylammonium cations on the equilibrium between cobalt octahedral and tetrahedral complexes was revealed. The specificity of hydration interactions in solutions under study in various concentration ranges and resulting from them difference in spectral characteristics were analyzed. Variously directed changes in positions of bands in the region of stretching vibrations, a composite frequency of 5200 cm^{-1}, and the first water overtone occurring due to the concentration variation were found.

DOI: 10.1134/S1070363211070048

The cobalt(2+) ion in various conditions can form both octahedral and tetrahedral complexes with halide ligands that is accompanied by a color change of the solution [1]. This essential change in optical properties defines the interest of researchers of this phenomenon to electronic spectra in visible region, where the absorption bands readily assignable from the viewpoint of the crystal field theory are located. Intermolecular interactions in solution play an important role in the formation of various complex species, however visible spectra are low informative for their analysis, as the solvents are optically transparent in this spectral region. Therefore, to study solvation processes including aquation, vibration spectroscopy is applied [2–4] and positions of vibration bands of solvent molecules are analyzed. In particular, the position of the stretching vibration band of water and its intensity make it possible to estimate the strength of hydrogen bonds in a solution: A linear dependence between bond energy and the shift of this band is often observed [5]. One of difficulties connected with such researche is a high value of absorption coefficient of aqueous solutions at 3600 cm^{-1} that makes necessary the application of labor-consuming procedures. Results of such experiments essentially depend on an applied method, and their interpreting is a subject of permanent discussions. In this connection the short-range IR region, where bands of combination vibrations of water molecules are present, is often used for measuring spectra of aqueous solutions.

The aim of the present work was to study binary $NR_4Br–H_2O$ solutions and triad $CoBr_2–NR_4Br–H_2O$ (R = Et, Bu) solutions not only in visible region of the electron spectrum, but also in the region of 1000–7800 cm^{-1} by the IR spectroscopy method. We intended to find how hydration processes were reflected in various absorption bands and how they varied with the solution restructuring. Tetraethyl- and tetrabutylammonium bromides were chosen as variable salt components. Ions NR_4^+, being hydrophobically hydrated species, interact with water molecules of the nearest environment to the minimal degree, but significantly affect the strength of hydrogen bonds in a solution as a whole [6–8]. As for bands of the proper vibrations of these complex species, they do not overlap with water vibration bands.

The complexity of the subjects under study does not allow us to rely on rigorous quantitative interpretation of IR spectra of aqueous solutions. Several complexes of various compositions are present in these systems simultaneously, and the absorption bands have a complex structure. The quantitative approach to the study of spectra of such systems requires equilibrium constants in the solution under study to be determined, which presents a complicated and occasionally ambiguously solved problem. For the interpretation of results of this study it was sufficient to accept the standard explanation of the shape of the stretching vibration band: the short-wave part corresponded to weakly-bound water molecules and the long-wave part, to stronger-bound molecules.

Electron absorption spectra. Spectra of $CoBr_2$–NR_4Br–H_2O aqueous solutions in visible region are presented in Fig. 1. The absorption in the range of 400–500 nm corresponds to octahedral complexes $[Co(H_2O)_{6-n}Br_n]^{2-n}$ (n = 0–2). The intensity of this band remains constant up to NBu_4Br concentrations of ~2.3 M, then it decreases owing to the decreasing fraction of octahedral complexes. The absorption at 700 nm corresponding to cobalt tetrahedral bromide complexes $[Co(H_2O)_xBr_{4-x}]^{x-2}$ (x = 0, 1, 2) becomes noticeable in the spectrum starting from the concentration of ~1.5 M. Such character of concentration variations is typical for cobalt(II) halide complexes: octahedral and tetrahedral species are present simultaneously in solution, and as the concentration changes, intensity is redistributed between the corresponding absorption bands [9–12].

It follows from the spectra shown in Fig. 1 that the range of concentrations of tetraalkylammonium bromides can be separated in two regions: up to 1.5 M only octahedral complexes are present in solution, and at greater concentrations tetrahedral species start to be formed. This phenomenon is usually explained by binding water in hydrate spheres of the second electrolyte ions (in this case, of tetraalkylammonium bromide). However a special character of the hydration of tetraalkylammonium ions, a weak interaction of bromide ions with water, and their disability to form hydrated shells do not allow us to use here this conception. Most likely, the reason of variation of geometry of cobalt complexes is the displacement of water molecules from a volume under consideration by tetraalkylammonium ions accompanied by an essential decrease in the volume concentration of water and also a decrease in the activity of water resulting from the formation of "local icebergs" [13]. Both these factors should result in the shift of equilibrium (1) to the right.

$$[CoBr_x(H_2O)_{6-x}]^{2-x} + Br^- \leftrightarrow CoBr_{x+1}(H_2O)_{3-x} + 3H_2O, \quad (1)$$
$$x = 1, 2.$$

Variation of absorption intensity of tetrahedral complexes deserves special attention: in a solution containing NEt_4Br the intensity has appeared considerably lower than for NBu_4Br at the same concentration. This essential difference was not noticed earlier. It is seen from Fig. 1 that at the same concentrations (0.1 M of $CoBr_2$ and 2.7 M of NR_4Br) the solution with NBu_4Br has the maximal optical density A of 1.2 in a layer of l 0.2 mm, and the solution with NEt_4Br, 0.95 in a layer of 3.1 mm. According to Bouguer's law, the ratio A/l is equal to the product of an extinction coefficient by a concentration; for the $CoBr_2$–NBu_4Br–H_2O solution it is equal to 6, and for the $CoBr_2$–NEt_4Br–H_2O solution, to 0.3, the difference exceeding one order of magnitude. The absorption spectra of both solutions are similar in shape, and it is most likely that the extinction coefficients of the complexes differ only slightly. Hence, the detected difference should be assigned to different concentrations of forming tetrahedral complexes. It can be explained by the above-mentioned shift of equilibrium to the side of the formations of tetrahedral complex species, which is caused by a decrease in the volume concentration of water: NBu_4^+ ions occupy essentially greater volume of space than NEt_4^+ ions. A solvent immobilization also occurs owing to strengthening hydrogen bonds in solution and a possibility of "dissolution" of water molecules in hydrocarbon radicals at the formation of cation–cation associates by tetrabutylammonium ions [14].

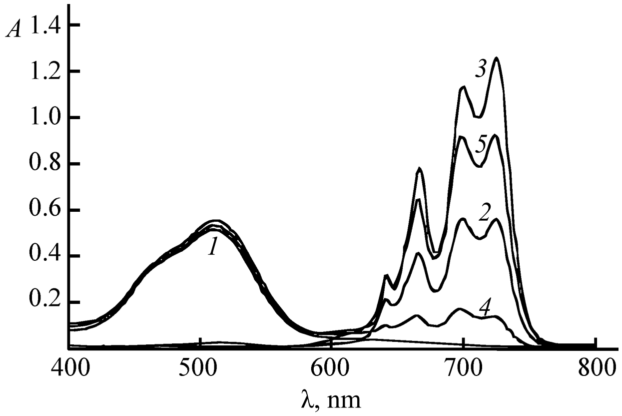

Fig. 1. Absorption spectra of 0.1 M $CoBr_2$–x M NR_4Br–H_2O solutions. R = Bu: (*1*) x = 1.0, layer 1 cm; (*2*) x = 2.0, 1 cm; (*3*) x = 2.7, 0.2 mm; R = Et: (*4*) x = 2.35, 1 cm; (*5*) x = 2.7, 3.1 mm.

IR spectra in the region of fundamental tones of water vibrations. Spectra of broken multiple total internal reflection of water and tetrabutylammonium bromide solutions in the region of bending vibrations of water are presented in Fig. 2a. At low NBu_4Br concentrations the bending vibration band does not differ from that of pure water. Starting from NBu_4Br

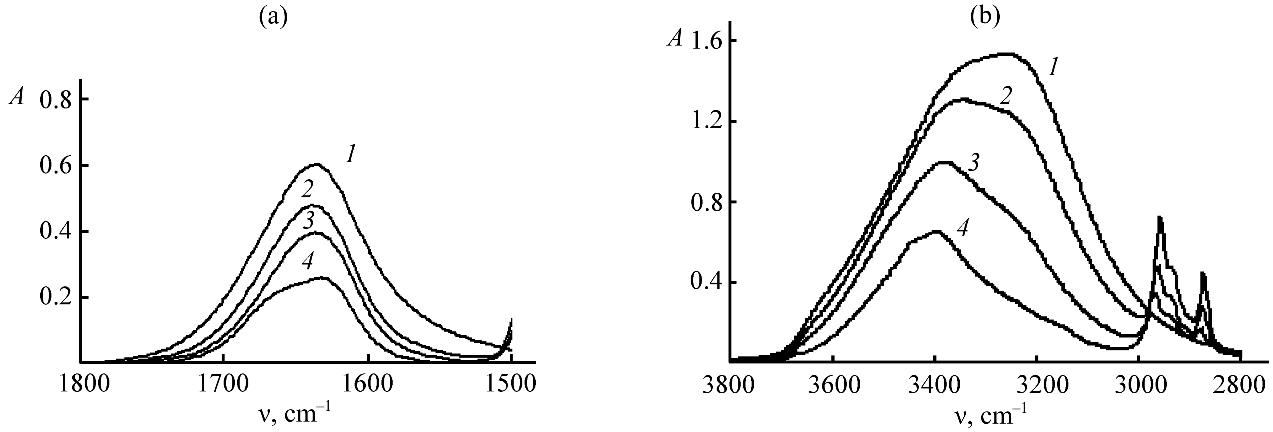

Fig. 2. Spectra of broken multiple total internal reflection of $NBu_4Br–H_2O$ solutions in the region of (a) bending and (b) stretching vibrations of water: (*1*) 0 M, (*2*) 2.0 M, (*3*) 2.35 M, and (*4*) 2.7 M NBu_4Br.

concentration of about 1.5 M, the symmetrical band at 1640 cm^{-1} becomes distorted and turns to a band with two latent maxima at 1620 and 1660 cm^{-1}. Apparently, at high NBu_4Br concentrations water molecules are divided into two unequal groups: a major part is characterized by a band at 1620 cm^{-1}, and a smaller, by a band at 1660 cm^{-1}. It is commonly supposed [5] that upon the formation of hydrogen bonds the band of bending vibrations is weakly displaced to the short-wave side opposite to the shift of stretching vibrations. It suggests that the bands at 1660 and 1620 cm^{-1} are responsible for the strengthening and weakening of water bonding with an environment, respectively. The first effect in the systems under study is caused by hydrophobic interactions involving tetraalkylammonium cations and the formation of "local icebergs" [13], whereas the second, by the action of bromide anions on water. The long-wave shift is most pronounced for the binary solution water: tetrabutylammonium bromide at high salt concentrations (Fig. 2a) in spite of the fact that hydrophobic effects should become stronger as the concentration of tetraalkylammonium ions increases. However for the tetrabutylammonium cation the formation of cation–cation associates is characteristic [15], which is accompanied by a decrease in hydrophobic effects as compared with an ensemble of nonassociated particles. On passing to the triad $CoBr_2–NBu_4Br–H_2O$ solution similar dependence of spectral characteristics on the NBu_4Br concentration with certain weakening of the long-wave shift is observed, which seems to be caused by binding bromide ions in complex species. The absence of cation–cation association in the case of tetraethylammonium ions is responsible for the practical constancy of the spectral contour shape for $NEt_4Br–H_2O$ and $CoBr_2–NEt_4Br–H_2O$ solutions.

Alongside with the above difference in spectral properties of solutions under study some common trends are observed also at low and high NR_4Br concentrations in IR spectra. It is seen from Fig. 2 that water absorption bands in all solutions become contracted as the NBu_4Br concentration increases. To explain this observation, we can refer to the consideration based on the fluctuational mechanism of hydrogen bonds formation [16]. According to it, the increase in average energy of hydrogen bonds in a solution results in a broadening of bands in IR and Raman spectra of molecules bound by hydrogen bonds. Then the increase in the concentration of bromide ions, which form weaker bonds with water than the water–water bonds, should reduce a range of values of hydrogen bond energy and result in a band contraction. The formation of clathrate-like structures of "local icebergs" also acts in the same direction, though hydrogen bonds in them are stronger, but fluctuations are much weaker.

The spectra of multiple broken total internal reflection of $NBu_4Br–H_2O$ binary solutions in the region of the water stretching vibration in the range of concentrations from 0 up to 2.7 M are given in Fig. 2b. Bands with frequencies less than 3000 cm^{-1} refer to C–H vibrations and do not hinder our consideration. It is commonly supposed that a proton pulls electron density on itself at the hydrogen bond formation, the frequency of a corresponding bond decreases, and a

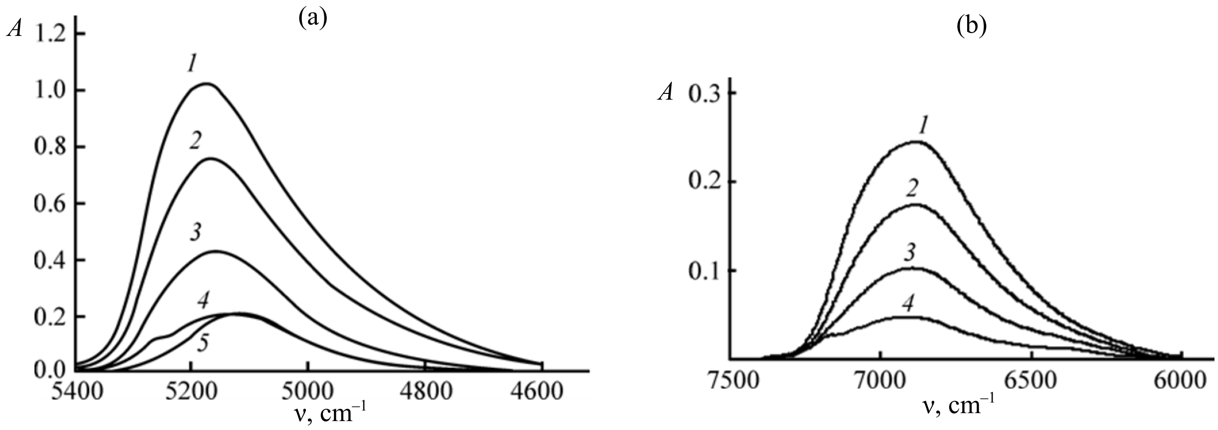

Fig. 3. Absorption spectra of NBu_4Br–H_2O solutions in the near IR region. [(*1*) 0 M, (*2*) 2.0 M, (*3*) 2.35 M, (*4*) 2.7 M and of NEt_4Br–H_2O (*5*) 2.7 M]. (a) region of combination vibrations, (b) region of the first overtone of stretching vibrations.

“red” shift takes place [5]. Such explanation is valid for rather simple systems, for example, for dilute solutions with individual hydrogen bonds.

Another effect is observed in the systems under consideration with a complicated net of hydrogen bonds and the presence of hydrophobic hydration. For all studied binary and triad systems the intensity of a long-wave shoulder at 3250 cm^{-1} decreases and the band of O–H vibrations is narrowed as the tetraalkylammonium bromide concentration increases. The same effect was earlier observed for the absorption band of water stretching vibrations in solutions of sodium halides [17]. Liu et al. assined the decrease in the long-wave absorption to the action of the electric field of sodium cations and halide ions on the dipole moment of water molecules. However, it remains unclear why this effect is limited to a long-wave part of the absorption band while the short-wave part remains unchanged. The absorption at 3250 cm^{-1}, which characterizes strong hydrogen bonds, is known to be characteristic for ice [3] and also for polymeric associates of alcohols [5]. We can assume by analogy with ice that strongly bound water molecules located in pure water aggregates (“icebergs”) absorb at 3250 cm^{-1} and that rather weakly bound molecules absorb at 3400 cm^{-1}. Hydrophobic effects in solutions of tetraalkylammonium salts promote the formation of “icebergs,” regions with strong cooperative hydrogen water–water bonds and a band at 3250 cm^{-1} probably correspond to them. As the concentration of the salt in a solution increases, large “icebergs” break up, and the intensity of the band decreases (Fig. 2b).

Finally, it is necessary to pay attention to a weak peak at 3670 cm^{-1} apparent only in spectra of solutions with high (more than 1.5 M) tetrabutylammonium bromide concentrations. This band was earlier assigned to vibrations of relatively free OH groups of water in asymmetric complexes [3]. In fact, as it was shown in [14] on the basis of NMR data, cation–cation associates formed at such salt concentrations can “dissolve” water in themselves, which will exist in the form of individual molecules in channels between hydrocarbon moieties. Such cation-cation associates are not formed in tetraethylammonium bromide solutions that is the reason which causes the absence of this peak in the spectrum of the corresponding system.

Spectra in the near IR region. The absorption spectra of solutions of tetraalkylammonium bromides in the concentration range from 0 up to 2.7 M in the region of 5200 cm^{-1} (region of combination vibrations) are shown in Fig. 3a. Here, and also in the spectra of other investigated solutions, a red shift up to 50–70 cm^{-1} takes place as the concentration increases. Earlier it was noted that the frequency δ varies only slightly as the NR_4Br concentration increases, and the frequency ν increases approximately by 200 cm^{-1}. Thus, there is no direct correspondence here between the shifts of bands of fundamental tones and a composite frequency. As is known, the absorption bands with composite frequencies appear in a spectrum if these vibrations are anharmonic. In this case the band position in a spectrum depends on particular mechanisms of disturbance of harmonic properties. In other words, in the studied solutions the anharmonicity of vibrations of molecules participating in hydrogen bonding is the cause of the red shift of a composite frequency band. It is of interest to compare this observation with the case of pure water spectra where bands at 3600, 5200, and 6900 cm^{-1} behave equally on heating: all of them move in the short-wave region [18]. We can suggest that in the case under consideration the effect is observed because of special features of NR_4^+ ions influencing the aqueous solution structure and properties of the net of hydrogen bonds.

At high concentrations of tetraalkylammonium bromide, starting from 1–1.5 M, two weak bands at 5270 and 5305 cm^{-1} appear on the short-wave edge. Earlier the presence of bands in this region was observed, for example, a band in the neighborhood of 5300 cm^{-1} was observed in a triethylamine aqueous solution near to the basic band at 5170 cm^{-1} [19]. In very dilute solutions of water in acetone and in other solvents the band assigned to monomeric water molecules was observed at 5250 cm^{-1} [20].

A series of works describes a doublet in the short-wave wing of the absorption band related to water stretching vibrations in dilute solutions in CCl_4. The absorption spectrum of water in a mixture of pyridine with CCl_4 containing a doublet in the band of stretching vibrations at 3700 cm^{-1} is given in [3]. It was concluded on the basis of several observations [2] that such splitting refers to symmetrical and asymmetrical water vibrations and depends on the degree of binding water molecules with a solvent, the splitting decreasing from 100 to 20–30 cm^{-1} as this bond becomes stronger.

When measuring the spectra of tetraethylammonium bromide solutions we failed to detect peaks in the range of 5200–5300 cm^{-1} (Fig. 3a), which suggests that special features of the interaction of tetrabutylammonium ions with water promoted their appearance. The reasons for the appearance of bands at 5270 and 5305 cm^{-1} can be different: (a) they correspond to the symmetrical and asymmetrical stretching vibrations of water molecules in cavities of cation-cation associates NBu_4^+; (b) two cavities of various configurations are formed inside of such associate or there is one large cavity where a water molecule can be in various positions; (c) possibly bands of composite tetrabutylammonium ions vibrations manifest themselves in this manner, for example, a band of $\nu + 2\delta$C–H vibrations; (d) as the band of bending vibrations is split, this fact can be responsible for the doublet of the composite frequency.

Absorption spectra of solutions in the region of the first overtone of water stretching vibrations are shown in Fig. 3b. The absorption in the vicinity of 7200 cm^{-1}, noticeable at greater concentrations of tetrabutylammonium bromide corresponds to a composite frequency of C–H vibrations, $2\nu + \delta$ [21]. In solutions containing tetraethylammonium bromide, where the amount of such bonds is smaller, this absorption is undistinguished. Unlike other spectral regions, the maximum of the absorption of the first overtone band is not displaced as the tetraalkylammonium bromide concentration varies. The appearance of this combination band is also caused by anharmonicity of vibrations of water molecules, which participate in the formation of hydrogen bonds. As is the case with the composite frequency band, here we can assume that the vibrations have such anharmonic properties which keep constant the band position in the spectrum. We can refer to a series of works (for example, [22]), in which the variation of anharmonic properties of the first overtone band of the OH stretching vibration with the hydrogen bond formation was studied, and an appreciable red shift was detected. The systems (alcohols–CCl_4) studied there are rather simple in comparison with the solutions under consideration in this work, where NR_4^+ ions play an essential role.

The long-wave wing of the overtone band at high NR_4^+ concentrations is slightly distorted and the intensity in the region of 6550–6600 cm^{-1} decreases. The distortion of the contour can be connected also with anharmonic properties of water, but most likely it is caused by redistribution of the intensity similar to that observed for stretching vibrations. As well as in that case, the observed decrease in absorption intensity in the long-wave wing can be explained by a decrease in the fraction of strongly-bound water molecules. For both bands (composite frequency and overtone), as the concentration of tetraalkylammonium bromide increases, the same decrease in the half-width as for the fundamental tones, is observed. Obviously, the explanation given above for the fundamental tone band is applicable here.

The spectra in the short-range IR region for binary and triad solutions almost do not differ from each other, and addition of cobalt changes spectral characteristics insignificantly. Therefore we can draw a conclusion that the principal reason influencing a solution structure is the variation of the concentration of tetraalkylammonium ions.

EXPERIMENTAL

To prepare solutions, we used analytical-grade tetraalkylammonium bromides and pure-grade cobalt bromide twice recrystallized from water. The concentration of bromide ions was determined by mercurimetric titration with a $Hg(NO_3)_2$ solution and diphenylcarbazone as an indicator. The concentration of cobalt ions in triad solutions was determined by chelatometry at pH 5 (acetate buffer) with xylenol orange as an indicator. Concentration of tetraalkylammonium bromide in triad solutions was calculated from the difference.

Spectra were recorded on Shimadzu UV1800 and Perkin Elmer BXII spectrophotometers in cells with layer thickness from 200 μm up to 2 cm. To measure spectra in the region of 3600 cm^{-1}, we used an attachment for recording in the mode of broken multiple total internal reflection with a ZnSe cell with five reflections under an angle of 45°.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 09-03-00755-a).

REFERENCES

1. Ballhausen, C.J., *Introduction to Ligand Field Theory*, New York: McGraw-Hill, 1962.
2. Zundel, G., *Hydration and Intermolecular Interaction. Infrared Investigations with Polyelectrolyte Membranes*, New York: Academic Press, 1969.
3. Karyakin, A.V. and Kriventsova, G.A., *Sostoyanie vody v organicheskikh i neorganicheskikh soedineniyakh* (State of Water in Organic and Inorganic Compounds), Moscow: Nauka, 1973.
4. Kabish, G. and Kalman, E., *The Chemical Physics of Solvation*, 1986, part B, p. 1.
5. Pimentel, G.C., *The Hydrogen Bond*, McClellan, A.L. and Pauling, L., Eds., San Francisco: Freeman, 1960.
6. Wen, W.-Y. and Saito, S., *J. Phys. Chem*., 1964, vol. 68, no. 9, p. 2639.
7. Kustov, A.V., *Zh. Neorg. Khim*., 2009, vol. 54, no. 2, p. 368.
8. Lindenbaum, S. and Boyd, G.E., *J. Phys. Chem*., 1964, vol. 68, no. 4, p. 911.
9. Hemmingsson, S. and Holmberg, B., *Inorg. Chem*., 1980, vol. 19, no. 8, p. 2242.
10. Kerridge, D.H., Nikolic, R., and Stojic, D., *J. Chem. Soc. Dalton*, 1986, no. 6, p. 1663.
11. Savovic, J., Nikolic, R., and Veselinovic, D., *J. Sol. Chem.,* 2004, vol. 33, no. 2, p. 287.
12. Vranes, M., Gadzuric, S.B., and Zsigrai, I.J., *J. Mol. Liquids*, 2007, vol. 135, no. 1, p. 135.
13. Kuhnel, V. and Kaatze, U., *J. Phys. Chem*., 1996, vol. 100, no. 51, p. 19747.
14. Masuda, Y., Tobita, J., and Muramoto, A., *Bull. Chem. Soc. Japan*, 1998, vol. 71, no. 7, p. 1555.
15. Padday, J.F., *J. Phys. Chem*., 1967, vol. 71, no. 11, p. 3488.
16. Lin Y.-S., Auer B.M., and Skinner J.L., *J. Chem. Phys*., 2009, vol. 131, no. 14, p. 144511.
17. Liu, D., Ma, G., Levering, L.M., and Allen, H.C., *J. Phys. Chem., B*, 2004, vol. 108, no. 7, p. 2252.
18. Czarnik-Matusewicz, B. and Pilorz, S., *Vibrational Spectroscopy*, 2006, vol. 40, no. 2, p. 235.
19. Braginskaya, T.G. and Sibilev, A.I., *Molekulyarnaya fizika i biofizika vodnykh sistem* (Molecular Physics and Biophysics of Aqueous Systems), 1976, issue 3, p. 62.
20. Dickens, B. and Dickens, S.H., *J. Res. Nat. Inst. Stand. Technol*., 1999, vol. 104, no. 2, p. 173.
21. Iwamoto, R., *Appl. Spectroscopy*, 2009, vol. 63, p. 354.
22. John, U. and Nair, K.P.R., *Spectrochim. Acta*, *A,* 2005, vol. 61, no. 12, p. 2555.