ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 3, pp. 415–422. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.G. David'yan, A.G. Kudrev, L.A. Myund, M.K. Khripun, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 3, pp. 359–367.

Structure of Aqueous Solutions of Group IIIA Metals Perchlorates by Near Infrared Spectroscopy

A. G. David'yan, A. G. Kudrev, L. A. Myund, and M. K. Khripun

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: GDavidian@yandex.ru

Received June 7, 2012

Abstract—The state of water in aqueous solutions of group IIIA metal perchlorates at 25°C was studied by the IR spectroscopy in the range of 5400–7500 cm^{-1}. The optical density values of the solution measured at different wavelengths were combined in a matrix of experimental data of the uniform dimension. The matrices were chemometrically analyzed. A number, spectra, and concentration profiles of the spectral forms existing in the solution were determined. By the principal component method, the IR spectra of the studied systems are grouped into the mathematical clusters according to the nature of the cation–water interaction in the solution. The combined use of the infrared spectroscopy and chemometric analysis showed that the structural changes in the solution predicted by the generalized phenomenological model are due to the existence and interconversion of the spectral forms.

DOI: 10.1134/S107036321303002X

Detecting regularities in the change of the different properties of the water-salt systems at the variation of their nature and concentration is necessary for the development of model of the structure of the electrolyte solutions. The comparison and generalization of the extensive experimental data obtained by different methods and objects are only possible if the model representations of the structure of water and aqueous electrolyte solutions exist. Such representations have been designed for diluted [1] and concentrated solutions [2]. A model of the structure of concentrated solutions, a so-called generalized phenomenological model of the electrolytes structure, can be extended to the whole concentration range of the existence of a homogeneous solution. According to the model, the characteristic feature of the solution is the appearance of the structures of new solvent when the electrolyte concentration increases. It is reflected in the solubility polytherm [2, 3]. The proper structure of the liquid water, which is dominant in the hypoeutectic region of the solution, where the Frank–Wen model [1] can be applied, is disrupted. In the solution of the hypereutectic concentrations the water becomes the dissolved substance and a part of the cybotactic groups, which are the structural units of a concentrated solution and comprise the dissolved salt and water hydrating this salt. A boundary between two areas is the eutectic concentration, a singular point on the salt solubility polytherm, in which water and certain crystal hydrates or anhydrous salts crystallize from a solution as the temperature decreases. The general view of the solubility polytherm suggests the structural changes in the electrolytes solutions [4]. The presence of structural changes in the solutions was experimentally confirmed. Using small and constant additives of the probing ions (Tb^{+3}, Nd^{+3}, Mn^{+2}) in the different concentration regions of the sample solution Khripun et al. [5–7] detected the changes in the state of the nearest environment of the probing ions by means of luminescence, electronic spectroscopy, and proton magnetic relaxation methods. As a result, a change of the dominant structures in binary solutions was found, when the concentration increases. This is in accordance with the change in the crystallization curves in the solubility polytherm.

The solubility polytherms of aluminum, gallium, and indium are characterized [8] by the eutectic position in the range of very low concentrations (~1 M), the presence of water-containing compounds $M(ClO_4)_3 \cdot nH_2O$ (n = 28–37), the glass transition areas, and the similarity of the general view of the polytherm in the hypereutectic area with those of the acids, including $HClO_4$. This is a fundamental difference between the mentioned polytherms and the polytherms of the metal perchlorates of the group I [4], II [9], and IIIB [10]. The perchlorates of the triply charged cations of main group III behave like Werner aquoacides.

It is known that the $M(ClO_4)_3–H_2O$ systems, where M = Al, Ga, In, are characterized by a pronounced hydrolysis [11]. According to [11], the values of the logarithms of the constants of the first hydrolysis step: $M^{+3}_{aq} + H_2O \leftrightarrow (MOH^{+2})_{aq} + H^{+}_{aq}$, are larger than those of the metal cations of group II. For the M^{+3}_{aq} ions the multilayer hydration shells may exist. Using IR spectroscopy it has been found [12], that the second hydration shell of Al^{+3} contains no less than 8.4 molecules of water. By the X-ray diffraction data on the aqueous solutions of gallium and scandium perchlorates [13, 14] a number of the water molecules in the second hydration shell was found to be 18 and 16, respectively.

A common method of studying the water state in the solution is the IR spectroscopy. In [15] the IR spectra of sodium, magnesium, zinc, and aluminum perchlorates were studied in the region of the first overtone of water (near infrared range, NIR spectra). The IR spectra of aluminum, chromium, and rhodium perchlorates in the region of the main tone $\nu_{OH,OD}$ of the isotopically substituted water are presented in [12]. In [16] the reflection spectra of sodium, lithium, and magnesium perchlorates in the region of the main tone $\nu_{OH}(H_2O)$ were examined. The published data on the IR spectra of aqueous solutions of electrolytes containing the triply charged cations in the NIR region concern mostly the dilute solutions. The absorption bands of the stretching vibrations of water in the spectra of aqueous salt solutions in the regions of the main and the first overtone are considerably broadened. This is due to a variety of states of the water molecules in a solution: water not connected with the ions; water coordinated to the cation/anion; "acidic" water, which appears at the formation of the strong hydrogen bonds between the molecules of the first and second hydration shells. Given that in the case of the highly overlapping bands the traditional approach [17] to the interpretation of the IR spectral data is little use because of errors in the formation of a complex contour with the model components, we have attempted to apply a chemometric analysis to the concentration dependence of the NIR spectra. The examples of studying the aqueous solutions using the NIR spectroscopy followed by the chemometric analysis of the spectra obtained were not found in the literature.

The aim of the present work is to develop a new method for studying the structure of aqueous electrolyte solutions based on the concept of the structural changes with changing the concentration of the solution. The objects of study are the group III metal perchlorates. The ClO_4^- ion is characterized by a weak complexing, electron-donor, and proton-acceptor properties [18], which helps to reveal the influence of the nature of the cation on the solution properties.

To improve the understanding of the solutions nature, we used the chemometric analysis of the spectral data, which does not require the prior decomposition of the total band into the components. The chemometric analysis was performed according to the scheme that has been tested on the complexing systems with the non-polymer ligands [19, 20] and applied for the description of protonation of some polyribonucleotides [21] and short DNA sequences [22, 23].

In contrast to the conventional approach, where some of the significant measurements are selected, in chemometrics the data compression methods are used to extract the useful information. The idea of these methods is to represent the original data using new variables [24]. In this case two conditions must be fulfilled. Firstly, the number of new variables should be significantly less than the number of the initial variables. Secondly, the loss from this data compression should be comparable to the noise in the data. The data compression can provide useful information in a compact form suitable for visualization and interpretation. The most convenient method of the data compression is a principal component method [24–27].

According to the Bouguer–Lambert–Beer law, the absorption matrix $\mathbf{A}_{exp}(N_p, N_w)$, ($N_p$ is the number of experimental points, N_w is the number of spectral channels) is the product of the coefficient matrix of the molar absorption $\mathbf{E}(R, N_w)$ and concentration matrix $\mathbf{C}_f$ (N_p, R) (R is the number of spectral forms):

$$\mathbf{A}_{exp} = \mathbf{C}_f\mathbf{E} + \delta, \qquad (1)$$

where δ is an experimental error.

First, the number of key factors should be determined equal to the number of forms of the compounds in the equilibrium mixture whose interconversion causes the dispersion of the absorption. In this work, to calculate the R value we used the principal component method [28–30], which gives the unique solution of Eq. (1) describing the dispersion maximum by means of a fixed number of variables:

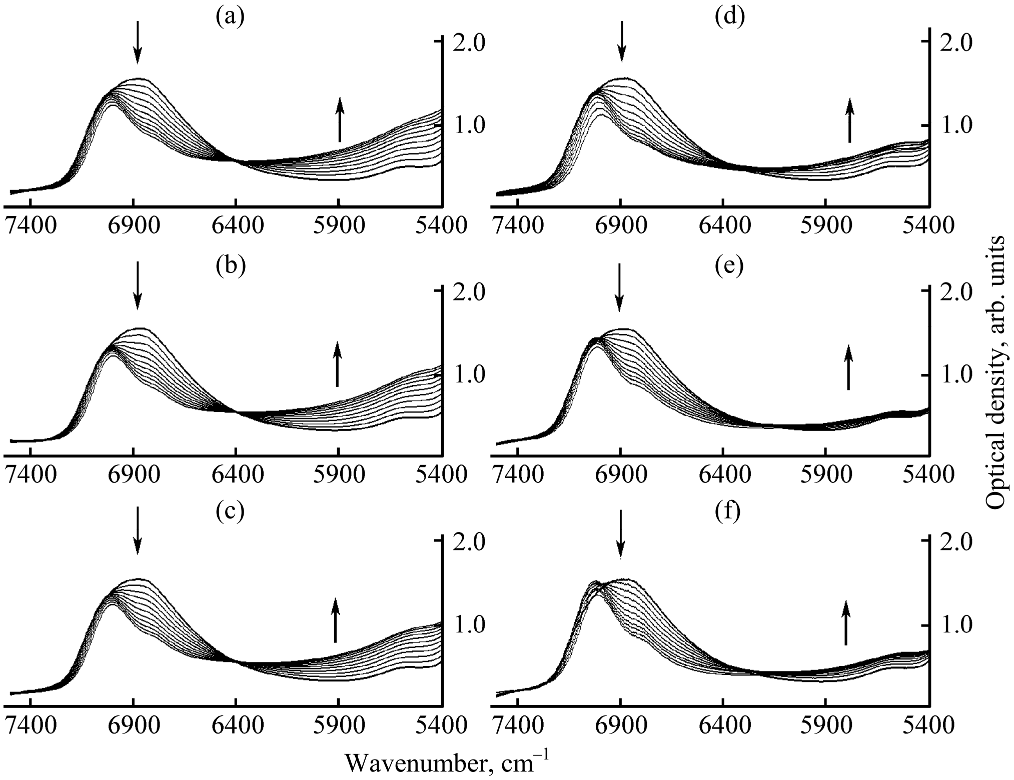

Fig. 1. IR spectra of water and $M(ClO_4)_3$ aqueous solutions at varying concentration. (a) $Al(ClO_4)_3$ without acid excess; (b) $Ga(ClO_4)_3$; (c) $In(ClO_4)_3$; (d) $Sc(ClO_4)_3$; (e) $Y(ClO_4)_3$; (f) $La(ClO_4)_3$. The arrow direction indicates the change in the optical density with increasing salt concentration in the solution.

$$\mathbf{A}_{\text{exp}} = \mathbf{Sc}\cdot\mathbf{Lo}^{\text{T}} + \tau = \mathbf{A}^* + \tau, \qquad (2)$$

where **Sc** и $\mathbf{Lo}^{\text{T}}$ are the orthogonal matrices, respectively, with the number of columns and rows equal to the rank of $\mathbf{A}_{\text{exp}}$ matrix (equal to the number of basic factors); $\mathbf{A}^*$ is $\mathbf{A}_{\text{exp}}$ matrix reproduced with R; τ is a reproduction error. A number of key factors is chosen so that the scaled reproduction error τ^* is less than the experimental error ($\tau^* < \delta$). The obtained R value is the key to further mathematical modeling of equilibrium in the system. Matrices calculated by the principal components method have no real physical meaning. The MCR-ALS procedure (Multivariate Curve Resolution-Alternating Least Squares) allows for decomposing the $\mathbf{A}_{\text{exp}}$ matrix by Eq. (2) into the spectra matrix of R spectral forms and the concentration matrix of these forms by introducing a number of limitations in the iterative fitting by least squares method. The profiles calculated by the MCR-ALS method were used to construct a chemical model of the system based on the observance of the law of mass action and mass balance equations.

Methods of the spectral measurements analysis are combined in a MCR-ALS computer procedure (“soft” modeling) [31, 32]. The use of “soft” modeling allows the calculation of the abstract concentration profiles using the matrix of experimental data without postulating the chemical processes occurring in the system. During the iterative fitting in a MCR-ALS procedure some limitations were used to provide a physical meanings to the obtained solution.

Due to certain advantages the concentration dependence of the spectral characteristics of the absorption bands of water in the IR spectra can be obtained with a sufficient accuracy in the near infrared range (NIR). The IR spectra of aqueous solutions of $M(ClO_4)_3$ (M = Al, Ga, In, Sc, Y, La) of different concentrations in the first overtone of water region (Fig. 1) were recorded. To get more information, the spectra of aqueous solutions of lithium and sodium perchlorates were registered. The concentrations of the studied solutions are given in Table 1.

The absorption maxima in the range of 7000–7050 cm^{-1} are assigned [15] to the water in the hydration shell of perchlorate ion [$\nu_{\text{OH}}^{02}(H_2O\cdots ClO_4^-)$]. In the concentrated solutions of the group III metal

Table 1. Compositions of the initial solutions and the solutions used in the spectral measurements

Salt	c_M (M^{+3}), M	c_M (ClO_4^-), M	Perchloric acid excess per 1 mol of salt, γ^a	Step of the initial solution diluting for spectral measurements
$Al(ClO_4)_3$-1	1.246	7.84	3.29	0.1246
$Al(ClO_4)_3$-2	1.88	8.20	1.36	0.188
$Al(ClO_4)_3$-3	1.30	3.90	0	0.130
$Ga(ClO_4)_3$	2.20	7.04	0.18	0.220
$In(ClO_4)_3$	2.23	7.00	0.14	0.223
$Sc(ClO_4)_3$	3.37	10.41	0.089	0.337
$Y(ClO_4)_3$	2.68	9.00	0.35	0.268
$La(ClO_4)_3$	2.76	8.28	0	0.276
$LiClO_4$	4.20	4.20	0	0.420
$NaClO_4$	8.16	8.16	0	0.410

[a] $\gamma = [c_M(ClO_4^-) - 3c_M(M^{+3})]/c_M(M^{+3})$.

Table 2. Results of the analysis of the spectral data matrix by the principal components method

System	Number of the principal component	Proper value of the data matrix	Dispersion described by the principal component, %	Dispersion described by the sum of principal components, %
3-$Al(ClO_4)_3$–H_2O	1	3.12×10^2	98.825	98.825
	2	3.7×10^0	1.174	99.999
	3	3.73×10^{-3}	0.001	100.000
	4	1.46×10^{-4}	0.000	100.000
$La(ClO_4)_3$–H_2O	1	2.8×10^2	99.051	99.051
	2	2.61×10^0	0.921	99.975
	3	6.62×10^{-2}	0.023	99.998
	4	4.37×10^{-3}	0.002	100.000
	5	6.41×10^{-4}	0.000	100.000

perchlorates (Table 2) the absorption band $\nu^{02}_{OH}(H_2O\cdots ClO_4^-)$ is located at 7030±5 cm^{-1} and at 7030±5 cm^{-1} in sodium and lithium perchlorates solutions. The absorption maximum of pure water is observed in the range of 6850–6880 cm^{-1}. When the concentration rises, the absorption in the frequency range of 7000–7050 and 6400–5400 cm^{-1} increases and in the absorption maximum of pure water decreases. The decrease in the absorption of water as a solvent with increasing salt concentration correlates with the idea of destroying the water structure by electrolytes. According to [12], an increase in the absorption in the frequency region of 6400–5400 cm^{-1} is connected with the formation of the first and the second hydration shells of the cations in solutions of aluminum, gallium, and indium perchlorates. For concentrated solutions of the group III metal perchlorates there is an absorption in the spectra in the region shifted by 65 cm^{-1} relative to the maximum absorption of water, to 6800±10 cm^{-1}. These absorption bands should be attributed to the water of third coordination shell of the triply charged cations, which is the most remote from the cation in the structure of the dominant hydrated form of the corresponding perchlorate in the solution. Similar to the spectra of sodium perchlorate solution [15], the maximum at 6825±5 cm^{-1} in the spectra of lithium perchlorate solutions should be attributed to the water of the first coordination shell of the lithium and sodium ions.

All IR spectra of the studied aqueous solutions (group III metal perchlorates, lithium and sodium perchlorates) were analyzed by the principal component method. The diagram in the coordinates of the first and second principal components is represented in Fig. 2. Each point on the diagram corresponds to the spectrum of one of the test solutions.

As can be seen from Fig. 2, the objects are grouped in the mathematical clusters depending on the nature of the cation of the dissolved salt. The first cluster consists in the metal perchlorates of the main group, the second, and third the group IIIB metal perchlorates, and the fourth, lithium and sodium perchlorates. Depending on the nature of the cation, an accordance is seen between the cluster location and the nature of cation–water interaction in the aqua-complex. Thus, the first cluster is formed by the cations characterized by the strong M^{+3}–H_2O interaction. The hydration enthalpy (ΔH^0_h) of the cations in the first cluster is in the range from –4200 to –4800 kJ mol^{-1}. The second and third cluster contain the cations of the group IIIB metals with the ΔH^0_h value equaled from –3400 to –3800 kJ mol^{-1}. The fourth cluster contains the cations with the ΔH^0_h value attaining from –450 to –550 kJ mol^{-1} (the group I metal cations) [33]. The use of multifactor chemometric analysis to broad unresolved bands in the NIR region of the spectra of aqueous solutions of the group III metal perchlorates led to the differentiation of the investigated objects depending on the cation nature. The principal components method enabled us to find the similarities and differences in the behavior of the salts of metals of the main and subgroups.

In the $M(ClO_4)_3$ solutions of the hypoeutectic concentrations the cation nature almost was not revealed. The absence of the cation influence is due to the domination of water structure in this area.

By an example of aluminum and lanthanum perchlorates, the results of the analysis of matrices data by the principal components method are represented in Table 2. Only two or three spectral forms are sufficient to describe the observed changes in the aluminum or lanthanum perchlorate solutions, respectively. Table 3 shows the number of the principal components equal to the number of the spectral forms in the solution: two spectral forms in the solutions of lithium, aluminum, gallium, and indium perchlorates, and three spectral forms in the solutions of sodium, scandium, yttrium and lanthanum perchlorates. Figure 3 shows the spectra of forms and the abstract distribution diagrams of the stoichiometric Al and La perchlorates.

The results show that curve *1* in Fig. 3 belongs to the spectral form, which correlates with the spectrum of pure water. Curve *2* corresponds to the spectral form, which correlates with the spectrum of the concentrated solution in the studied series. According to the phenomenological model of the structure of the concentrated solutions of electrolytes [2], in such solutions the cybotactic groups dominate. The accumulation of the latter leads to the separation from the solution of a solid nonahydrate. It can be assumed that the second spectral form corresponds to the specified cybotactic group. According to the X-ray scattering method, the cybotactic group in the concentrated aqueous solution of aluminum perchlorate contains two formula units of the salt nonahydrate [34]. The unit cell of crystalline $Al(ClO_4)_3 \cdot 9H_2O$ also contains two formula units [34]. For gallium and indium perchlorates there is an analogy with aluminum perchlorate, since they form a single cluster in the principal components coordinates. Curve *3* in Fig. 3 corresponds to the spectral form, which appears in a diluted solution and disappears in a concentrated solution.

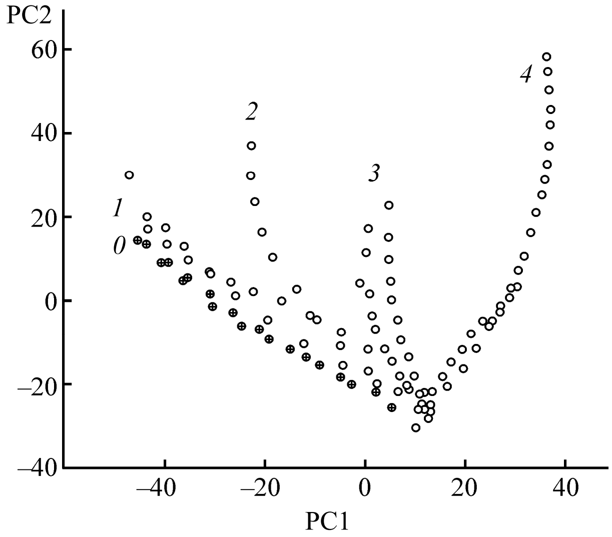

Fig. 2. Diagram of the principal components method for the combined matrix of experimental data for the aqueous solutions of $M(ClO_4)_3$ and $MClO_4$. (*1*, *2*, *3*, *4*) are clusters of IR spectra of aluminum, gallium, indium (*1*), scandium (*2*), yttrium, and lanthanum (*3*), lithium and sodium perchlorates solutions (*4*) in the coordinates of the first (PC1) and the second (PC2) principal components, (*0*) are all three $Al(ClO_4)_3$ solutions.

Compared with the three spectral forms in the acidified solution (Table 3), the presence of two spectral forms in the aluminum perchlorate solution without the acid is due to the strong hydrolysis. The latter causes the superposition of all possible forms of hydroxides, including hydrated cation. The acidification of the aluminum perchlorate solution with perchloric acid leads to the hydrolysis suppressing. This allows the formation of a cybotactic group in the system, and $Al(ClO_4)_3 \cdot 9H_2O$ crystallizes from the saturated solution [34].

It is known [35] that in the concentrated solution the hydrolysis becomes localized. The formed stable

Table 3. Number of the spectral forms in the studied salt–water systems

Salt	Concentration range, M	Number of the spectral forms	Crystal hydrate composition	Number of formula units in the unit cell of crystal hydrate
$Al(ClO_4)_3$-3	0–1.3	2	–	–
$Al(ClO_4)_3$-1	0–1.25	3	$Al(ClO_4)_3 \cdot 9H_2O$	2
$Al(ClO_4)_3$-2	0–1.88	3	$Al(ClO_4)_3 \cdot 9H_2O$	2
$Ga(ClO_4)_3$	0–2.2	2	$Ga(ClO_4)_3 \cdot 9H_2O$	2
$In(ClO_4)_3$	0–2.23	2	$In(ClO_4)_3 \cdot 9H_2O$	2
$Sc(ClO_4)_3$	0–3.37	3	$Sc(ClO_4)_3 \cdot 9H_2O$	2
$Y(ClO_4)_3$	0–2.68	3	$Y(ClO_4)_3 \cdot nH_2O$	–
$La(ClO_4)_3$	0–2.76	3	$La(ClO_4)_3 \cdot 6H_2O$	–
$LiClO_4$	0–4.2	2	$LiClO_4 \cdot 3H_2O$	2
$NaClO_4$	0–8.16	3	$NaClO_4 \cdot H_2O$	8

bridges (cation$\cdots$OH$^-\cdots$H$_3$O$^+$) bind the water of the second and, possibly, the third hydration shells. Therefore the corresponding multi-aqueous crystal hydrates must exist. This is evidenced by the view of the solubility polytherm. In the spectra of the solutions of aluminum, gallium, and indium perchlorates in the concentration range of 1.5–1.8 m at the temperatures below 0°C there are maxima of the freezing points of

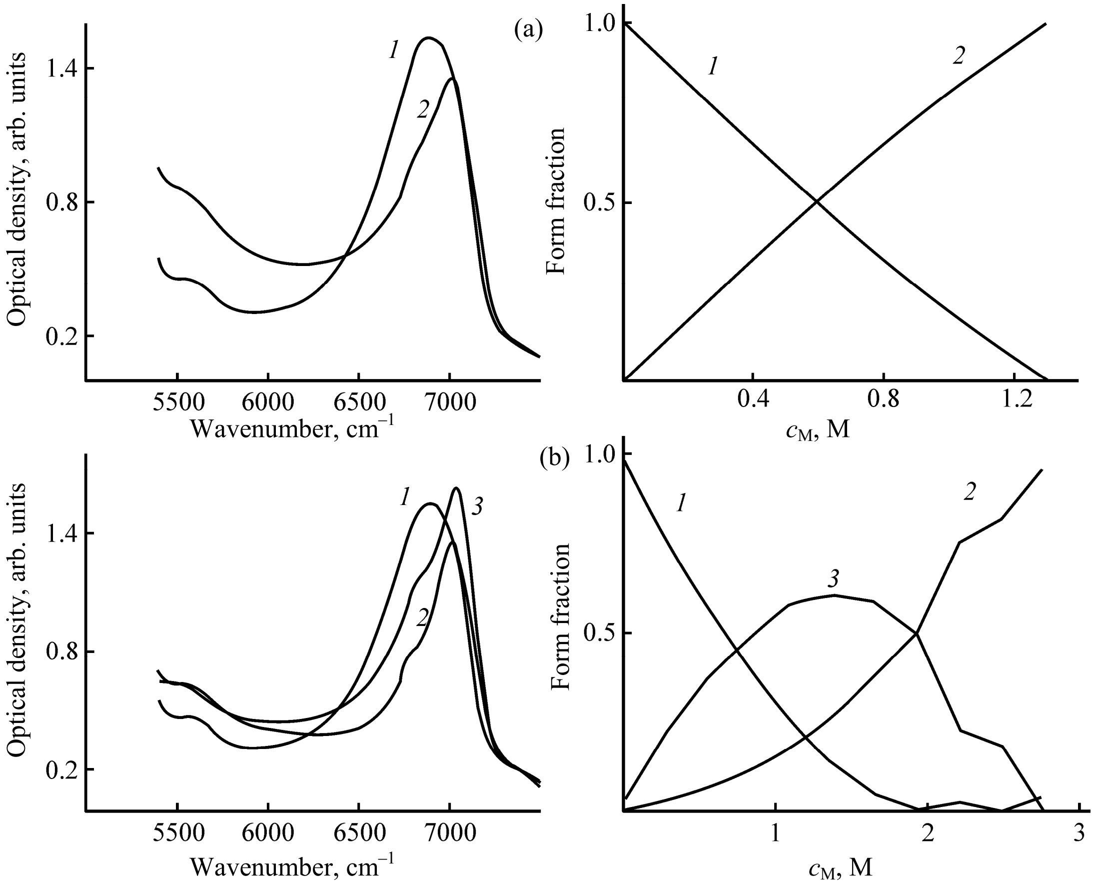

Fig. 3. Spectra of the forms (a) calculated by MCR-ALS method and distribution diagrams of the spectral forms (b) in aluminum (a) and lanthanum perchlorate solutions (b). See notation in the text.

solutions that correspond to the composition of salt·nH$_2$O, where $n = 28–37$ [8].

The role of the perchlorate ion in the formation of the structure of aqueous solutions in the presence of cations of the group III metals is different. The state of the ClO_4^- ion depends on the nature and concentration of the solution. In the solutions of aluminum, gallium, and indium perchlorates, as the concentration of water decreases with respect to the salt concentration, the number of water molecules in the cybotactic group reduces. The ClO_4^- ion enters into the second coordination shell of the cation. It is proved by the change in the tetrahedral symmetry of the ClO_4^- ion in aluminum perchlorate solution starting from the concentration of 1.5 m. As a result, the $\nu_1(ClO_4^-)$ band, forbidden in the free tetrahedral perchlorate ion, appears in the IR spectrum [36]. The appearance of the ClO_4^- ion in the second hydration shell of the cations is caused by the structure of the solution of hypereutectic concentrations. This process is called structurally forced [2]. In the concentrated solutions of the group IIIA metal perchlorates where the water loses its solvent function, the ClO_4^- ion exhibits a proton-acceptor ability. An ability to form the hydrogen bonds, which is not characteristic of the ClO_4^- ion, is confirmed by the X-ray diffraction data of crystalline aluminum, gallium, indium, and scandium perchlorates. In aluminum, gallium, scandium [34], and indium perchlorate nonahydrates [37] the ClO_4^- ion is linked by four hydrogen bonds with the water molecules, two of which are the bonds with the water molecules in the second coordination shell of the cation, and two others are the bonds with the water molecules from the first coordination shell of the cation [34]. Another situation is observed for the lanthanum perchlorate, where the hydrolysis is practically absent. The X-ray data show that in the structure of crystallized $La(ClO_4)_3·6H_2O$ the ClO_4^- ion has no hydrogen bonds with water molecules. It is located in the cavities created by the aquacations [38]. The absence of hydrogen bonding in $La(ClO_4)_3·6H_2O$ allows to conclude that it will not exist in the concentrated solution.

Thus, the combined application of the infrared spectroscopy and chemometric analysis showed that the structural changes in the solution, as predicted by the generalized phenomenological model, are caused by the existence and interconversion of the spectral forms.

EXPERIMENTAL

Aluminum perchlorate was prepared by dissolving the freshly precipitated alumina hydrate [39] in 57% perchloric acid, followed by recrystallization from distilled water. An acid-free solution of $Al(ClO_4)_3$ was obtained by mixing equivalent amounts of barium perchlorate of analytical grade and chemically pure aluminum sulfate solutions. The resulting $BaSO_4$ precipitate was removed by centrifugation followed by passing the solution through a glass frit filter. Gallium perchlorate was obtained by the reaction of 70% perchloric acid (chemically pure) with the corresponding oxide (analytical grade) and then twice recrystallized from distilled water. Indium perchlorate was prepared by dissolving indium of spectral grade in distilled perchloric acid. The reaction was carried out by heating in the presence of mercury in order to avoid the indium oxide formation. Scandium, yttrium, and lanthanum perchlorates were obtained by the action of 57% chemically pure perchloric acid on the corresponding oxides of analytical grade, followed by double recrystallization from distilled water.

Concentrated solutions of these salts were analyzed for their content of metal cations [40] and the ClO_4^- anion [41]. The analysis error was 0.5%. The diluted salts solutions were prepared by diluting the concentrated solutions by weight or by volumetric method. The compositions of the initial solutions are presented in Table 1.

The IR spectra were recorded on a Spectrum BX spectrometer in the first overtone of water at 5400–7500 cm^{-1} with a step 2 cm^{-1} with a concentration step shown in Table 1 at 25°C. The solutions were prepared just before the spectra recording. The test solution was placed into a glass cell (l = 0.1 cm, the number of scans was 50).

For each $M(ClO_4)_3–H_2O$ system studied the $\mathbf{A}$ (N_w, N_s) matrix, where N_w is the wavelengths number and N_s is the number of measured spectra, was composed based on the experimental data. For processing by the principal component method the general matrix $\mathbf{A}_{gen}$ was composed by combining all matrices.

REFERENCES

1. Frank, H.S. and Wen, W.-Y., *Disc. Faradey Soc.*, 1957, vol. 24, p. 133.
2. *Rastvory kak khimicheskie sistemy. Donorno-aktseptornye reaktsii v rastvorakh Solutions such as chemical systems. Donor-acceptor reactions in solutions* (Solutions as Chemical Systems. Donor-Acceptor Reactions in Solutions), St. Petersburg: Izd. SPbGU, 2010.
3. Khripun, M.K., *Doctoral (Chem.) Dissertation*, St. Petersburg, 1993.

4. Kirgintsev, A.N., Trushnikova, L.N., and Lavrent'eva, V.G., *Rastvorimost' neorganicheskikh veshchestv v vode* (Solubility of Inorganic Substances in Water), Leningrad: Khimiya, 1972.
5. Khripun, M.K.,, Efimov, A.Yu., and Chervonenko, K.Yu., *Zh. Strukt. Khim*., 1993, vol. 34, no. 2, p. 105.
6. Khripun, M.K.,, Efimov, A.Yu., and Shmatko, A.G., *Zh. Strukt. Khim*., 1985, vol. 26, no. 3, p. 88.
7. Khripun, M.K., *Koord. Khim*., 1992, vol. 18, no. 7, p. 768.
8. Pestova, O.N., David'yan, A.G., Myund, L.A., and Khripun, M.K., *Zh. Obshch. Khim*., 2011, vol. 81, no. 8, p. 1237.
9. Pestova, O.N., *Candidate Sci. (Chem.) Dissertation*, St. Petersburg, 2006.
10. David'yan, A.G., Book of Abstracts, *V Vseross. konf. studentov i aspirantov "Khimiya v sovremennom mire"* (V All-Russian Conf. of Undergraduate and Graduate Students "Chemistry in the Modern World"), St. Petersburg, 2011, p. 174.
11. Latysheva, V.A., *Vodno-solevye rastvory: sistemnyi podkhod* (Water–Salt Solutions: A Systems Approach), St. Petersburg: Izd. SPbGU, 1998.
12. Bergstrom, P.A., Lindgren, J., Read, M., and Sandstrom, M., *J. Phys. Chem*., 1991, vol. 95, no. 20, p. 7650.
13. Smirnov, P.R. and Yamaguchi, T., *Zh. Fiz. Khim*., 2006, vol. 80, no. 1, p. 94.
14. Smirnov, P., Wakita, H., and Yamaguchi, T., *J. Phis. Chem. (B)*, 1998, vol. 102, no. 24, p. 4802.
15. Subramanian, S. and Fisher, H.F., *J. Chem. Phys*., 1972, vol. 76, no. 1, p. 84.
16. Chen, Y., Zhang, Y.H., and Zhao, L.J., *Phys. Chem. Chem. Phys*., 2004, vol. 6, p. 537.
17. Schmidt, W., *Optical Spectroscopy in Chemistry and Life Sciences. An Introduction*, Weinheim: Wiley, 2005.
18. Shchyukarev, S.A., *Neorganicheskaya khimiya* (Inorganic Chemistry), Moscow: Vysshaya Shkola, 1970, vol. 1.
19. Kudrev, A.G., *Koord. Khim*., 1999, vol. 25, no. 2, p. 152.
20. Kudrev, A.G., *Zh. Neorg. Khim*., 2001, vol. 46, no. 5, p. 854.
21. Kudrev, A.G., *Polym. Sci. (A)*, 2000, vol. 42, p. 527.
22. Gargallo, R., Eritya, R., and Kudrev, A.G. *Zh. Obshch. Khim*., 2010, vol. 80, no. 3, p. 462.
23. Bucek, P., Gargallo, R., and Kudrev, A.G., *Anal. Chim. Acta*, 2010, vol. 683, p. 69.
24. *http: // www.chemometrics.ru.*
25. Esbensen, K., *Analiz mnogomernykh dannykh* (Analysis of Multivariate Data), Chernogolovka: IPKhF RAN, 2005.
26. Smith, G.L., *Analyt. proc*., 1991, vol. 28, p. 150.
27. *http://www.spectroscopyeurope.com.*
28. Malinowsky, E.R. and Howery, D.G., *Factor Analysis in Chemistry*, New York: Wiley, 1980.
29. Linas, J.R. and Ruis, J.M., EVM pomogaet khimii (Computer Helps Chemistry), Leningrad: Khimiya, 1990, p. 182.
30. Esbensen, K., *Multivariate Analysis in Practice*, Trondheim: Camo AS, 1994.
31. Tauler, R. and de Juan, A., *In Practical Guide to Chemometrics*, London: Taylor & Francis Group, 2006.
32. *http://www.ub.edu/mcr/ntheory.htm.*
33. Latysheva, V.A., *Vestn. SPbGU*, *Ser. 4*, 1998, vol. 4, no. 25, p. 99.
34. David'yan, A.G., Pestova, O.N., Starova, G.L., Gurzhii, V.V., Myund, L.A., and Khripun, M.K., *Zh. Obshch. Khim.*, 2012, vol. 82, no. 4, p. 533.
35. Latysheva, V.A., Myund, L.A., and Glebovskii, D.N., *Zh. Fiz. Khim*., 1972, vol. 46, no. 5, p. 1330.
36. Khripun, M.K.,, Myund, L.A., Baranova, G.I., Smirnova, O.A., and Maslennikova, T.N., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 4, p. 550.
37. Ilyukhin, A.B. and Malyarik, M.A., *Zh. Neorg. Khim.*, 1999, vol. 44, no. 4, p. 532.
38. Glaser, J. and Johansson, G., *Acta Chem. Scand. (A)*, 1981, vol. 35, p. 639.
39. Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie veshchestva* (Pure Chemicals), Moscow: Goskomizdat, 1955.
40. Sharlo, G., *Metody analiticheskoi khimii. Kolichestvennyi analiz neorganicheskikh soedinenii* (Methods of Analytical Chemistry. Quantitative Analysis of Inorganic Compounds), Moscow; Leningrad: Khimiya, 1965.
41. Samyuel'son, O., *Primenenie ionnogo obmena v analiticheskoi khimii* (Application of Ion Exchange in Analytical Chemistry), Moscow: Inostr. Literatura, 1955.