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Chapter

Features of the Ionic State of Indium in Perchlorate Solutions and the Physicochemical Properties of Indium Perchlorate

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Abstract

The possibility of the formation of India perchlorate and mixed ligand complexes has been studied. It is assumed that during the extraction of indium in aqueous solutions of hydrochloric acid at various concentrations and constant ionic strength maintained by the addition of perchloric acid, indium is present in the organic phase in the form of ionic aggregates $HClO_4 \cdot HInCl_4$. To study the hydration of Ions, the method of electrical conductivity was carried out in the "$In(ClO_4)_3$ - $HClO_4$ - H_2O" system. The structure of aqueous solutions of India perchlorates was determined by IR spectroscopy. The structures of trivalent perchlorate India have been established.

Keywords: perchlorate ion, indium, gallium, complexation, ionic state, NMR, IR, extraction, coordination number

1. Ionic state of indium in perchlorate solutions

It is known that perchlorate ion does not form complex compounds even with extremely strong complexing metal ions [1]. The difficulty in preparing perchlorate metal complexes is the lack of suitable solvents. Water molecules and most non-aqueous donor media displace such a weak ligand as the ClO_4^- ion from the inner sphere of the compound. The formation of a coordination bond between the perchlorate ion and the complexing cation is possible only in acceptor or very weakly donating solvents. The successful synthesis of perchloro-complexes in work [2] is associated with the use of anhydrous perchloric acid as a reaction medium.

These fairly well known provisions are fully confirmed for indium perchlorate, which is proved by various research methods [3–19]. The absence of coordination interaction of acid ions in the "In^{3+} - ClO_4^- – H_2O" system is indicated by the spectra of Raman scattering [5–11]. IR spectra [12] including near infrared [13–15] and spectroscopy of disturbed total internal reflection [13, 16], NMR signals [17, 18]. However, partial formation of ion pairs between them is allowed [8, 18].

In the Raman spectra of the perchlorate solution, only the lines of the ClO_4^- anion and the aquocomplexes of the In^{3+} ion ·aq were found [6]. Raman and IR spectroscopic studies of indium hydration in perchlorate solutions revealed octahedral hexaaquocation $[In(H_2O)_6]^{3+}$. According to the data of the Raman spectra, the

aquocomplex is stable in acidic perchlorate solutions, and in the studied concentration range, neither inner sphere nor hydroxostructures are formed [9].

There is no evidence of the complexing effect of the highly concentrated electrolyte $NaClO_4$ 1.1÷9.1 M and by electrophoresis [19]. Spectrophotometrically in the ultraviolet region of the spectrum, there were no significant signs of direct interaction in aqueous solutions of $In(ClO_4)_3$ salts [20]. Also, no intrinsic complexation influencing the activity of In^{3+} was reliably detected up to a sodium perchlorate concentration of 16 mol/kg [19, 21] and with an $In(ClO_4)_3$ content of more than 4 M [6, 9].

Similar results, denying the likelihood of coordination interaction of In^{3+} with ClO_4^-, were obtained when studying the solvation of cations by NMR on H^1 and P^{31} nuclei in aqueous-organic mixtures [22].

The proton-magnetic resonance measurement of the coordination number of perchlorate water-organic systems testifies to the six fold coordination of water molecules around the indium cation and to the absence of strong evidence of contact ion pairing [23, 24]. It was not possible to detect the binding of indium to perchlorate ions ClO_4^- by special experiments carried out in mixed water-non-aqueous mixtures and organic media [25].

The absence of complex compounds of indium with perchlorate ion is also indicated by the data of liquid extraction, in particular, three n-octylamine does not extract indium from a solution with an $HClO_4$ concentration less than 2 M [4]. At the same time, from concentrated solutions of perchloric acid for cationic reagents - alkylphosphoric acids (for example, di-2-ethylhexylphosphoric acid; **Figure 1**) - a possible extractable form of indium compounds is the complex cation $[InClO4]^{2+}$ [26]. It is also assumed that during the extraction of indium in aqueous solutions of hydrochloric acid at its various concentrations and constant ionic strength maintained by the addition of perchloric acid, indium is present in the organic phase in the form of ionic aggregates $HClO_4 \cdot HInCl_4$ [27]. The latter formation is possibly caused by the coextractability of perchloric acid due to its higher extraction affinity as compared to hydrochloric acid. In the aqueous phase, there are only chloride complexes, which are subjected to extraction with various oxygen-containing solvents.

The likelihood of the formation of perchlorate and mixed-ligand complexes also applies to extraction systems based on 4-methyl-2-pentanone and 4-methyl-2-pentanol, the extractable forms of which are compounds of the composition $[In(ClO_4)_3]$, $[InHal(ClO_4)_2]$, $[InHal_2(ClO_4)]$, where bromine, iodide, or thiocyanate ion is present
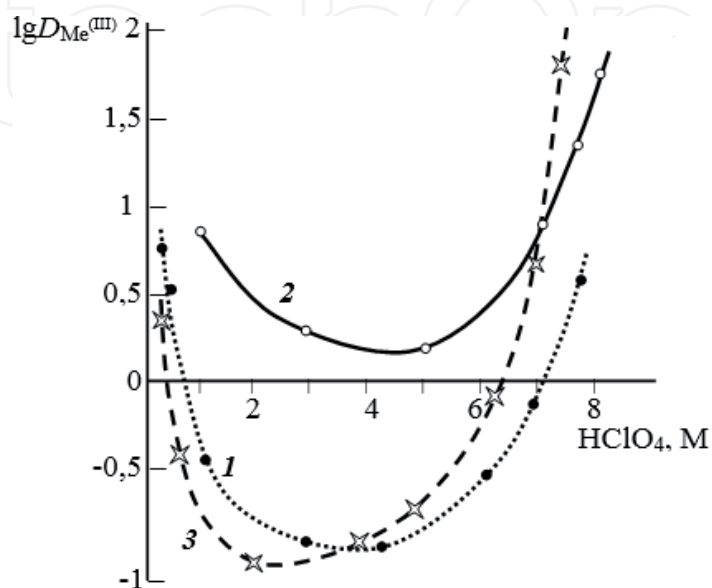

Figure 1.
Extraction of III subgroup metal ions with di (2-ethylhexyl) phosphoric acid depending on the concentration of perchloric acid: 1 - Ga (III), 2 - In (III), 3 - Tl (III) [26].

as the halide and pseudohalide of the ligand. The aqueous phase is characterized by a constant ionic strength of 4.0 due to the salt background of sodium perchlorate and salts of NaBr, NaJ or NaSCN of variable concentrations. The role of $NaClO_4$ in liquid distribution is reduced not only to a change in the activity and composition of the solution, but also to the extraction of ion pairs of charged indium complexes, which greatly increases in the presence of perchlorate ions [28].

An example of the special effect of perchlorate ion on the extraction behavior of indium (III) is its interaction in a mixture of extractants 1-phenyl-3-methyl-4-acylpyrazol-5 (PhMAPr) with tri-n-phosphine oxide (TOPhO) in toluene [29] and PhMAPr with a base salt — Aliquat-336 [29]. If the reaction of interfluid distribution in a perchlorate medium proceeds according to the equation (1):

$$In^{3+} + 3HPhMAPr_{(o)} \leftrightarrow In(PhMAPr)_{3(o)} + 3H^+ \text{ with high } logK_{ex} = 1.50, \quad (1)$$
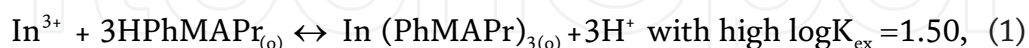
and from aqueous solutions of $H(Na)Cl$, ClO_4 during extraction with a mixture PhMAPr and TOPhO have a synergistic effect and the process is described by the equation (2):

$$[InCl_n]^{3-n} + (3-n)HPhMAPr_o + 2TOPhO_o \leftrightarrow InCl_n(PhMAPr)_{3-n} \quad (2)$$
$$\cdot 2TOPhO_o + (3-n)H^+$$

where n = 0–3, then in the case of perchlorate salt Aliquat-336, this phenomenon is not observed due to its finding in the form of $R_4N^+ClO_4^-$, although when using in the same system high-molecular-weight ammonium in chloride and nitrate forms, the effect of synergism is not only preserved, but also increased.

When studying the coordination properties of polyvalent metal ions, including indium, by titrimetric and ion-exchange methods, only weak signs of complexation in perchloric acid were noted [30].

The cation-exchange behavior of indium (III) ions in the presence of perchloric acid and an organic solvent in the form of methyl alcohol and acetone also indicates the absence of fundamental changes in the ionic state of indium in such a sorption system. Both in the presence and in the absence of these solvents, the indium ion interfacial distribution indices in the perchloric acid medium are higher than in the hydrochloric acid medium (picture 2) [31]. Thus, if the coordination properties of such acid ligands as halides, sulfate, thiocyanate [32], and to some extent nitrite [33] in aqueous-organic mixtures can be activated, which leads to the formation of more acid-saturated complexes, then the perchlorate ion under these conditions in relation to indium, as a complexing agent, remains very passive (**Figure 2**).

From other alternative points of view, attention is drawn to the study of the effect of the salting-out electrolyte on the distribution coefficient of indium during the extraction of its tenoyl-three-fluoroacetonate complex with benzene from aqueous perchlorate solutions, where the presence of complexation of indium with the perchlorate ion was confirmed.

The revealed relationship between the salting-out parameter and the stability of indium complexes with various anions formed in the aqueous phase indicates that the strength of the acidic complexes by the nature of the ligand changes in the series of salts: $NaCl >> NaNO_3 > NaClO_4$ [34].

A characteristic feature of indium perchlorate solutions, like other indium salts, is the extremely high viscosity of aqueous solutions of $In(ClO_4)_3$, due to the increased degree of hydration of the three-charged indium ion [6]. A simple substance with the composition $In(ClO_4)_3 \sim 8H_2O$ crystallizes from concentrated aqueous solutions of indium perchlorate [11], and in dilute perchloric acid, indium is in the form of the cation $[In(H_2O)_6]^{3+}$.
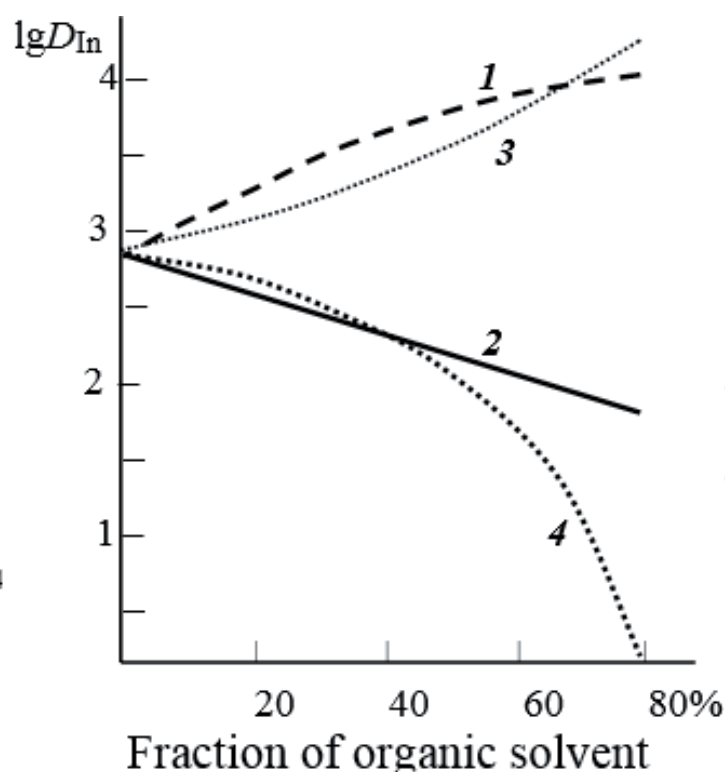
Figure 2.
Dependence of the distribution coefficients of indium in 0.1 M HClO$_4$ (1.3) and 0.1 M HCl (2, 4) on the content of the organic solvent: 1 and 2 - methanol; 3 and 4 - acetone [31].

2. Study of ion hydration by the method of electrical conductivity in the system

"In(ClO$_4$)$_3$ - HClO$_4$– H$_2$O" shows that the total number of water molecules oriented by the cation is n_{In3+} = ~ 9, which includes water molecules that make up the near and far environment of the cation. The decrease in n_{In3+} relative to the maximum value equal to 12 reflects the approach of the hydration and anionic environment of indium to what is characteristic of crystalline hydrates, and indium perchlorate crystallizes from an aqueous solution with eight water molecules. In the series of cations III of the Al^{3+}-In^{3+} subgroup, there is a tendency to a decrease in n_{Mes+} with an increase in the crystal chemical radius. The reason for this is the decrease in the polarizing ability of the cations. Consequently, this leads to a weakening of the bonds of near and outer-sphere water molecules with a probable increase in the residence time of anions near the [Me(H$_2$O)$_6$]$^{3+}$ cation [35].

The solubility of indium perchlorate salt at 0° and 25°C is 3.23 and 3.53 mol/kg H$_2$O, respectively. More accurately speaking about the macroscopic properties, about the possible composition of crystalline hydrates precipitating into the bottom phase, about the processes preceding crystal formation, allow the polytherms of solubility [36]. Their analysis shows that there is a qualitative similarity in the solubility polytherms of the aluminum subgroup perchlorates. The value of the molar fraction of water unbound to salt in the eutectic for perchlorates is constant (N_w = 0.94 ± 0.1). The freezing temperatures of eutectic compositions are close to −28 ÷ −31°C and all curves have an inflection - a maximum that corresponds to the existence of a chemical compound. In the case of indium perchlorate, this is a 28-aqueous crystal-line hydrate. In addition, after reaching the concentration of 2.8 mol/kg H$_2$O, the phenomenon of glass transition of this solution is observed. However, the position of the eutectic concentration on the solubility polytherm depends not so much on the nature of the cation as on the number of water molecules that are part of the

crystalline hydrate. The reason for the existence of compounds enriched with water in the eutectic should be sought in the fact that the stable bridges formed as a result of local hydrolysis (cation $\cdots$ OH$^-$ $\cdots$ H$_3$O$^+$) are able to retain a large amount of water. Thus, providing the possibility of the formation of high-water crystalline hydrates at temperatures below 0°C. However, as the solution concentrates, structurally forced processes begin. Rearrangement of one dominant structure into another containing a smaller number of water molecules in the cybotactic group. These processes are accompanied by glass transition (**Figure 3**).

The structure of aqueous solutions of indium perchlorates and the state of water were studied by IR spectroscopy in the region of the first overtone of water (NIR spectra) using chemometric analysis to the concentration dependences of the spectra. It is noted that hydrolysis occurs in indium (III) perchlorate solutions, and due to the high enthalpy of hydration of In3 +, exclusively solvate-separated ion pairs are formed. In other words, the formation of complexes of the composition In^{3+} (H$_2$O) n (ClO$_4$)$^-$ occurs, where n = 1–2 with a decrease in the symmetry of the ClO$_4^-$ ion: Td → C$_{3v}$ → C$_{2v}$ with an increase in the concentration of indium in solutions acidified with perchloric acid [14, 15].

Perchlorate ion has the shape of a regular tetrahedron. Its hydration shell consists of eight water molecules. The distribution of these shells around the ClO$_4^-$ ion is uniform. Presumably, it is low hydrating capacity [37].

Indium perchlorate salt is a hygroscopic substance readily soluble in water and it can be obtained by dissolving indium metal in perchloric acid at a moderate temperature. Its anhydrous modification crystallizes because of the interaction of silver perchlorate and indium chloride in a methanol solution. There are also several forms of indium hydroxopochlorates, which are precipitated in their solutions in the presence of sodium perchlorate [38]. At pH 4.82, a salt of the composition In$_4$OH(ClO$_4$)$_{11}$ was isolated, at pH 3.77 - In$_2$OH(ClO$_4$)$_5$, and in the pH range 2.56–3.14 - In$_4$(OH)$_3$(ClO$_4$)$_9$.

Determination of the apparent ionic volumes of particles by measuring the density of indium (III) perchloric acid solutions showed [39] that, depending on the degree of dilution, the formation of a compound of the composition [In(H$_2$O)$_5$ClO$_4$]$^{2+}$. However, there are no convincing reasons to consider the possible entry of the perchlorate ion into the inner sphere of the indium aquion.

According to X-ray diffraction data, the structure of a hydrated indium ion (III) in a 3 M aqueous solution of perchlorate is an aquo-complex, in which the first hydration shell contains six water molecules with a bond length of 2.15 ± 0.03 Å between In^{3+} and nearby H$_2$O [40].
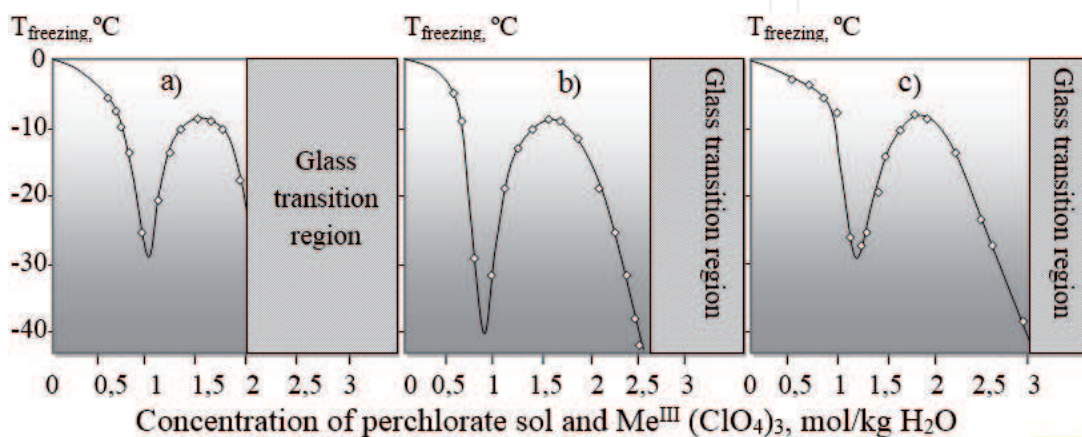

Figure 3.
Perchlorate solubility polytomes: (a) Al (ClO$_4$)$_3$, (b) Ga (ClO$_4$)$_3$, (c) In (ClO$_4$)$_3$ [36].

To establish the structure of trivalent indium perchlorate, the crystalline salt was obtained by dissolving indium (III) oxide in an equimolar amount of perchloric acid on heating– $[In(H_2O)_6](ClO_4)_3$. By isothermal evaporation at room temperature from an aqueous solution of In $In(ClO_4)_3$, crystals $[In(H_2O)_5](ClO_4)_3$ unstable in air were isolated. X-ray structural analysis of two forms of indium perchlorate - $[In(H_2O)_6](ClO_4)_3$ and single crystal $[In(H_2O)_6](ClO_4)_3 \cdot 3H_2O$ indicates that both these structures are formed by hexaaquocation $[In(H_2O)_6]^{3+}$ and perchlorate ions. In this case, $[In(H_2O)_6](ClO_4)_3 \cdot 3H_2O$ contains crystallization water molecules. But the structure of $[In(H_2O)_6](ClO_4)_3$ is cubic, and $[In(H_2O)_6](ClO_4)_3 \cdot 3H_2O$ is rhombic, each of them with the corresponding definite geometric parameters, in which the aquated indium complexes are close to the ideal octahedron. Special attention should be paid to the hydration state of indium perchlorates. In all likelihood, the hydration composition of its salt is not eight, but nine-water, consisting of six-coordinated water molecules and three crystallization ones. At the same time, the existence of a six-water modification unstable in air that does not contain molecules of crystallized water is possible. However, since the compound is highly hygroscopic, it is possible that partial dehydration occurs in the processes of pre-preparation of samples for chemical analysis $[In(H_2O)_6](ClO_4)_3 \cdot 3H_2O$ [41].

The available X-ray diffraction measurements carried out for perchlorate solutions of indium (III) at temperatures from 25 to 250° C under water vapor pressure indicate that the distance In^{3+} − oxygen (water) in the octahedral configuration of the aqua complex remains constant and equal to 2.14 ± 0.01 Å. In 1.0 M $HClO_4$ solutions, the formation of the ion pair In^{3+} − perchlorate $[InClO_4(H_2O)_5]^{2+}$ is observed, in which the distance In^{3+} − chlorine (perchlorate) changes from 3.14 to 3.12 Å with an increase in temperature to 250° C. At the same time, no noticeable destruction of the octahedral hydration shell of the aqua-ion of indium at temperatures up to 300° C was recorded [42].

In addition to the crystalline hydrate of the composition $In(ClO_4)_3 \cdot 8H_2O$, isolated from an aqueous solution, the corresponding dimethylforamide solvate $In(ClO_4)_3 \cdot 6(CH_3)_2NCHO$ was isolated by the preparative method of double recrystallization due to the solvation effect caused by the peculiarities of the chemical interaction of indium ions with molecules of an organic solvent [43].

The anhydrous salt of indium (III) perchlorate is obtained in the course of the exchange reaction between $InCl_3$ or InJ_3 with $AgClO_4$ in methanol solution [44].

Sequential thermal dehydration of indium perchlorate heptahydrate leads to the decomposition of the salt, the final product of which is indium trioxide [45].

When studying the effect of the composition and concentration of the water-salt system on the EMF of the cell $Hg_{(liquid)}//Hg_2Cl_{2(solid.)}/NaCl_{(saturated.)}/Na\textit{Ani}//Me(ClO_4)_n$, $In(ClO_4)_3/In_{(solid.)}$, где Me$n^+$ = Li, Na, Mg; Na$\textit{Ani}$ = 5416 M NaCl, 4,0 M $NaNO_3$, 3,72 M and 6,72 M $NaClO_4$ it was shown that the nature of the salts that form the salt bridge and their amount have a definite effect on the EMF of the cell. The greatest difference in the EMF values was noted when comparing the units of 4.0 M $NaNO_3$ and 6.72 M $NaClO_4$, and in the case of 3.72 M $NaClO_4$, the values are very close. The chemical composition and concentration of the salt background have the greatest effect on the emf and the activity coefficient of the In3 + cation ($\gamma \pm$): the $\gamma \pm$ values rapidly increase (by 5–6 orders of magnitude) with a change in the magnesium salt content from 0.5 to 4 M and up to 13 M sodium salts. Depending on the nature of the salt background, $\gamma \pm$ is ranked in the order $Mg(ClO_4)_2 > LiClO_4 > NaClO_4$ [21].

IR spectroscopy of the synthesized series of compounds of the cationic type $[In(\textit{Lig})_n](ClO_4)_3$, when n = 6, 4, 3, and 2, and the ligands are urea, dimethyl sulfoxide, Ph_3P, Ph_3PO_4, 2,2′-$\textit{Dipy}$, $\textit{En}$, 2,2,2′-three-pyridyl and others, indicates that the perchlorate ion is a part of the anionic part of the complex structure [46]. By means

of an exchange reaction in acetone solutions, hexa aqua salt $[In(H_2O)_6](ClO_4)_3$ under the action of dimethyl sulfoxide or dimethylformamide is easily converted into solvates $[In(DMSO)_6](ClO_4)_3$ and $[In(DMFA)_6](ClO_4)_3$ [47]. Subsequently, X-ray structural studies established the structure of the crystal complex of indium hexa (dimethylsulfoxide) perchlorate (III) $[In(ДМСО)_6](ClO_4)_3$ [48].

Thus, there are clearly no compelling reasons to consider the existence of complexes of indium with perchlorate ion, especially its anionic forms, as possible, and as a consequence, the indium ion in such a medium is a simple hydrated cation. Apparently, under certain conditions, it is possible to admit the formation of ion pairs, where the perchlorate ligand is localized in the outer sphere with respect to the central atom, i.e. attached to all aquo-ion.

Therefore, in the practice of studying the complexing properties of indium, as well as most other metal ions, salt perchlorate and perchloric acid are traditionally used to create a given ionic strength of a solution and as a source of acid anions that do not form complexes. And also in those cases when it is necessary to assess the interaction of cations, for example, with water, not complicated by the formation of their acidic complexes.

The macro-properties of aqueous solutions of electrolytes of the gallium subgroup are significantly influenced by the peculiarities of the interaction of metal cations with water. The regularities of changes in such characteristics as the bulk properties of perchlorate solutions, isobaric expandability, adiabatic compressibility and heat capacity (isobaric and isochoristic) [49, 50] were analyzed from the point of view of the specificity of reactions of metal cations with dipoles of water molecules, depending on their electronic structure p- and d-metals of the third group [51].

It is quite natural that the studied macroproperties change nonmonotonically in the gallium subgroup. In this case, the type of non-monotony corresponds to the unequal sensitivity of each property to one or another result of interaction with water. It can be seen from **Figure 4** that when passing from the dependences ΔF_κ to the dependences ΔV, ΔF_E and ΔC_p, the direction of the break in the Ga – In – Tl line gradually changes to the opposite. It follows from this that the ratio of the factors of water binding and its polarization is different for different properties. The factor of water binding predominates in the influence of the ΔF_κ compressibility, which leads to the appearance of a rather sharp maximum on the "ΔF_κ - $N_{Ga\text{-}In\text{-}Tl}$" contour at the point of the least vigorously hydrated indium ion. In the case of the characteristics of the specific volume ΔV, the effect of compression of the bound water is partly compensated by the formation of openwork outer-sphere associates, as a result of which the maximum on the ΔV curve disappears.

The course of the dependence "ΔF_E - $N_{Ga\text{-}In\text{-}Tl}$" is antibate to the curve "ΔF_κ - $N_{Ga\text{-}In\text{-}Tl}$", which may, firstly, be a consequence of the unequal degree of compaction of water molecules during hydration, and the greater the degree of compaction, the more ΔF_E, and, secondly, is due to different degrees of water polarization and localized hydrolysis of cations. Finally, the dependence "ΔC_p - $N_{Ga\text{-}In\text{-}Tl}$" demonstrates the absolute predominance of the effects of water polarization and localized hydrolysis over the influence of differences in the degree of water binding by cations, since the last of these factors should have caused the reverse course of the curve. Such a significant positive effect of water polarization and localized hydrolysis on heat capacity is apparently caused by corresponding changes in the set of frequencies of intra- and intermolecular vibrations of the aqua complex as a result of polarization, as well as redistribution of "O – H" bonds and hydrogen bonds due to local hydrolysis.

The comparisons made refer to the region of relatively dilute solutions. With an increase in concentration, the pattern of changes in properties from subgroup
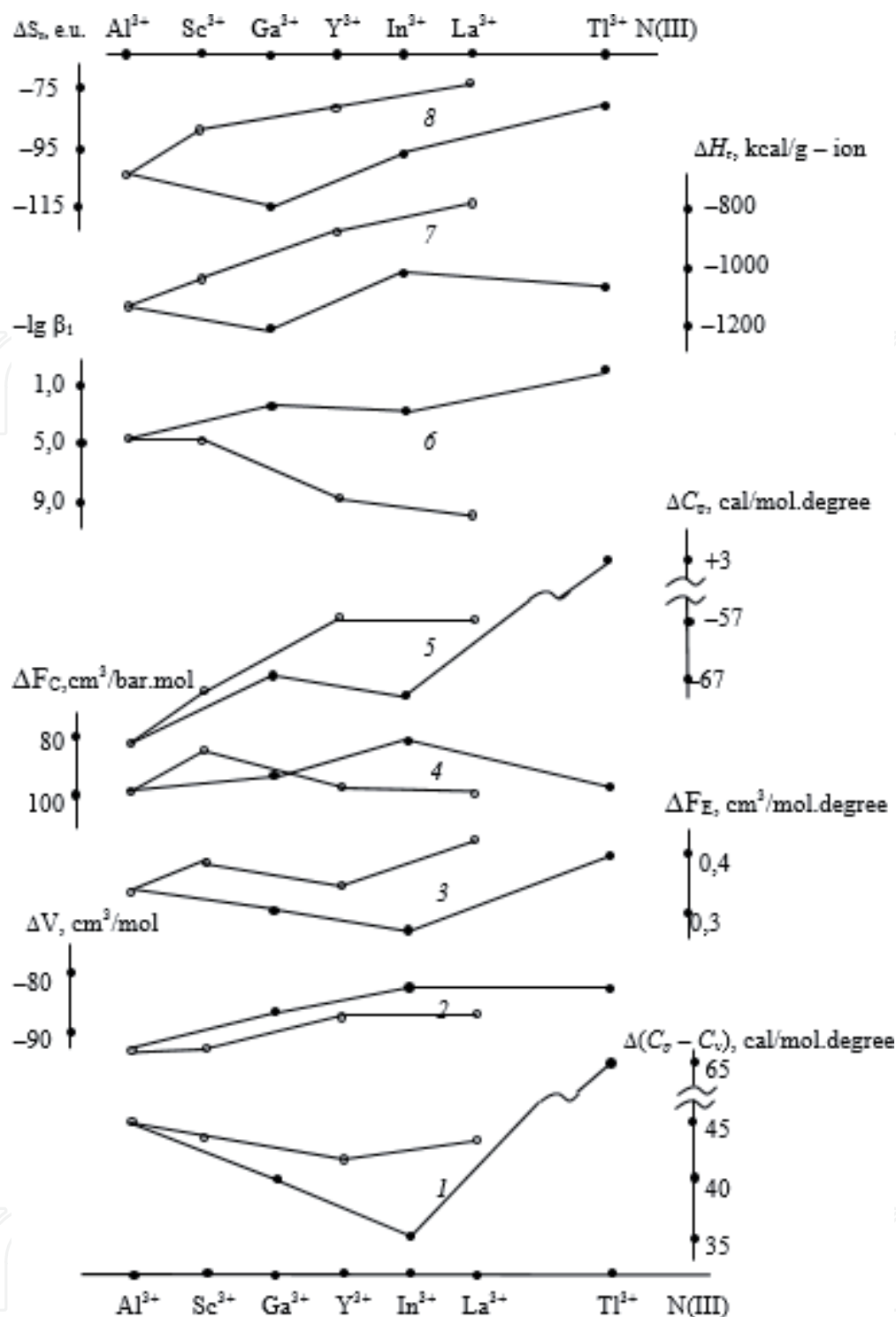
Figure 4.
Dependence of changes in macro properties during the formation of perchlorate solutions on the hydration characteristics of group III cations: 1 - Δ(Cp - Cv) (1.0 M solutions) (Cp and Cv isobaric and isochoric heat capacities); 2 - ΔV (specific volume); 3 - ΔFE (expandability); 4 - ΔFC (compressibility); 5 - ΔCr (0.5 M); 6 - log β1 (β1 is the constant of the 1st stage of cation hydrolysis); 7 - ΔHr (enthalpy of hydration of the cation); 8 - ΔSr (entropy of cation hydration) [51].

to subgroup, as well as within the subgroup, changes. For example, in **Figure 5** dependences "ΔV - N_{III}" for the subgroup of gallium and scandium change places with increasing salt concentration. This is probably because at low concentrations the ΔV values reflect largely the change in the volume of the outer-sphere water, and at high concentrations, the water in the inner coordination sphere of cations.

Comparison of the tendencies of changes in the bulk properties of solutions from concentration **Figure 5**, apparently, show that the relative compression of the
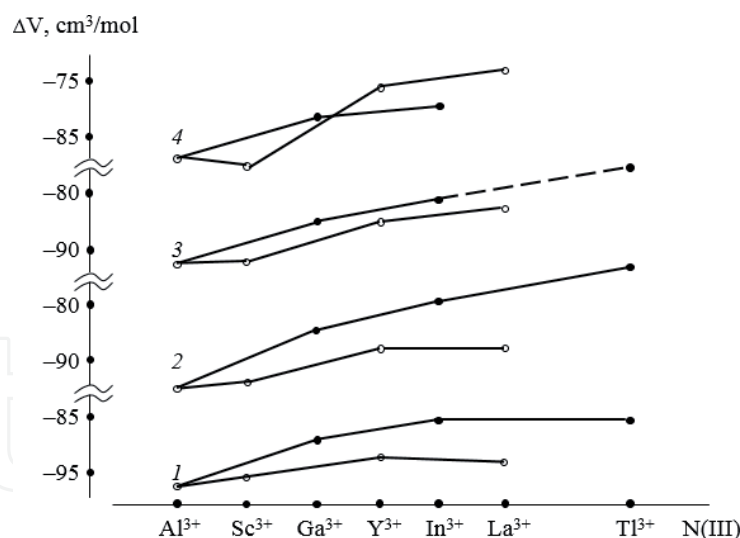
$\Delta V, cm^3/mol$

Figure 5.
Dependence of changes in specific volume during the formation of solutions perchlorates with concentration, mol/dm³: 1–0.1; 2–0.5; 3–1.0; 4–3.0 by nature trivalent cations [51].

outer-sphere water is greater for d-metal ions and the compression of water in the inner sphere is, on average, greater for p-metal ions.

In concentrated solutions, the regularities of changes in properties in both groups depend mainly on the state of water in the inner sphere: in the subgroup of d-elements - on the degree of its compression, and in the subgroup of p-elements - on the degree of attraction and polarization. In dilute solutions, an important role is played by the state of the outer-sphere water, namely the degree of its destruction or, conversely, structuring. However, if, in the p-subgroup, the structuring of the outer-sphere water is more typical, and for the d-subgroup, destructuring is most likely [51].

The viscosity and density of perchlorate solutions are significantly influenced by the ability of cations to hydrate. The increased relative kinematic viscosity and the relative activation energy of the aqueous flow of solutions of aluminum, gallium and indium perchlorates is obviously a consequence of the formation of a hydration shell with a branched network of very strong hydrogen bonds by the cation. Within the gallium subgroup, the positive hydration of the ion is expressed the weaker, the larger its radius [52].

In this case, although the anion is not an indifferent component, its nature does not play a particularly important role in the nature of changes in the macro-properties of solutions, since the perchlorate ion has an approximately equal effect on the destruction of the primary structure of water in all systems. The only exceptions are $Tl(ClO_4)_3$ solutions, where the formation of outer-sphere ionic associates with hydrated thallium (III) cations is evident [51].

From the analysis of the compensation spectra of the multiply disturbed total internal reflection, it follows that according to their destructive effect, the anions are arranged in a row $ClO_4^- > NO_3^- > > Cl^-$, and for sulfocation it is not found at all. The formation of a covalent bond "water cation" leads to the strengthening of H-bonds in water, and in the case of solutions of triple-charged cations, additional stabilization of the water structure takes place, which complicates the process of destruction of hydrogen bonds even with such a strongly destructive anion as perchlorate [16].

The interrelation between the formation of outer-sphere water associates and the phenomenon of hydrolysis is especially evident from the comparison of the heat capacities of perchlorates in the series of triply charged cations of metals of

the gallium subgroup with the values: 6 - lg β_1 (β_1 is the constant of the 1st stage of hydrolysis of the cation); 7 - ΔHr (enthalpy of hydration of the cation); 8 - ΔS_r (entropy of cation hydration) [51, 53, 54] where the polarizing effect of cations on water makes the greatest contribution to the heat capacity even in dilute solutions. All this, moreover, agrees with the results of studying the vibrational spectra of solutions of gallium and indium perchlorates, showing that the water molecules surrounding these ions are polarized not only in the first, but also in the second coordination layer, thus the fraction of polarized water molecules in these solutions is unusual. But high, their contribution to the heat capacity of the solution is also significant [55]. Thallium (III) perchlorate solutions have the highest heat capacity, but here it should be noted that the reason for this in this case may be not only water polarization and local hydrolysis, but also the tendency of Tl^{3+} ions to form perchlorate complexes [56].

The form of the dependences of the apparent molar heat capacity of the $P_{S\,P2}$ of group III metal perchlorates on the salt concentration deviates from the rectilinear, especially for $La(ClO_4)_3$ and $Tl(ClO_4)_3$ **Figure 6a**. The regularities of changes in $P_{S\,P2}$ are also explained in the light of ideas about the energy of interaction of ions with water, the state of water in hydration shells, and the effect of ions on the structure of water. In the gallium subgroup, the role of another factor, the hydrolysis of aquocations, increases significantly. Probably, the point for $Ga(ClO_4)_3$ owes its higher position to hydrolysis as compared with indium in **Figure 6b** [49].

Of the entire sum of contributions to the total change in the heat capacity of dissolution of perchlorates, the greatest effect of the specific nature of cations on the heat capacity of solutions occurs through the outer-sphere interactions (ΔC_V). As you can see (**Figure 6b**). for the considered types of electrolytes in a significant range of concentrations ΔC are negative, which may be due not only to the outer-sphere hydration of ions, but also to their destructive effect on a certain part of the outer-sphere water. It is not yet possible to separate these two effects. However, at high concentrations, the sign of ΔC_V hanges to the opposite, indicating, apparently, an increase in the role of the effect of outer-sphere aqueous, as well as ion-ion associates ([50], p. 266).

The recorded changes in the bulk properties of perchlorates of the aluminum subgroup from their concentration are also associated with the individual nature
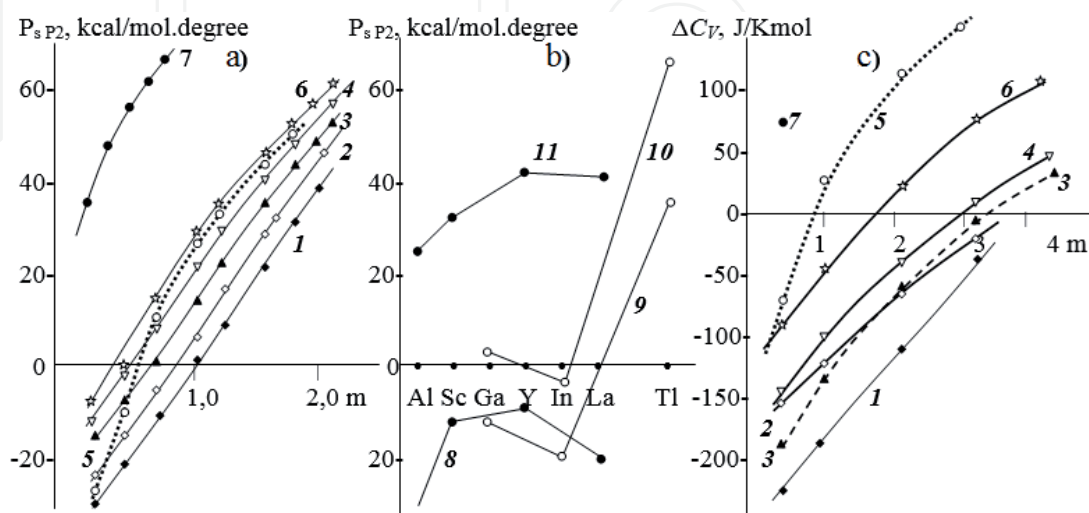

Figure 6.
Dependence of the apparent molar heat capacity of metal perchlorates (P_s) (a, b) [49] and the heat capacity due to outer-sphere interactions of ions (ΔC) (c) ([53], p. 266), on the concentration: 1 - $Al(ClO_4)_3$, 2 - $In(ClO_4)_3$, 3 - $Sc(ClO_4)_3$, 4 - $Ga(ClO_4)_3$, 5 - $La(ClO_4)_3$, 6 - $Y(ClO_4)_3$, 7 - $Tl(ClO_4)_3$, 8 and 9 $Me^{III}(ClO_4)_3$–0.1 m, 10–0.5 m, 11–3.0 m.

of the interaction of ions with water and among themselves. The densities of $Al(ClO_4)_3$, $Ga(ClO_4)_3$ $In(ClO_4)_3$ solutions at temperatures of 24, 25, and 27° C, the speed of sound, specific adiabatic compressibility and isobaric expandability in the concentration range from 0.1 m to saturation, and the shape dependences of apparent molar volumes (F_V), compressibility (F_K) and expandability (F_E).

As follows from **Figure 7** the values of F_V and compressibility F_K monotonically increase with an increase in the electrolyte concentration, but the F_V for $Al(ClO_4)_3$ - decrease, and in the case of $Ga(ClO_4)_3$ and $In(ClO_4)_3$, in all likelihood, pass through a maximum. The dependences of F_V on $m^{1/2}$ are straightforward, and F_K are curvilinear and for different cations they differ from each other both in their position and in the angle of inclination. The profile of the expansibility curves of PU differs greatly from the characteristics of volumes (F_V) and compressibility (F_K), including the sequence of arrangement of metal ions [49, 50].

The influence of the coordination number on the compressibility of cations is, of course, due to the fact that the coordination water in the first layer practically loses its compressibility. The fact of compressibility manifests itself rather through external-sphere water than through coordination water. This is probably why the hydration numbers of cations, calculated from the compressibility data, turn out to be higher than their c.n. The data are reflected in the **Table 1**, which also shows the change in the isochoric heat capacity of similar electrolytes [53].

The correlation between the polarizing forces of the cation (P) and the eutectic concentration of aqueous solutions of perchlorates (**Figure 8**) indicates that the higher the value of the polarizing force, the stronger the cation interacts with water molecules. Therefore, due to the greater polarizing force of the cations of the gallium subgroup, which characterizes the state of the "cation - water" bond, there is a significant destruction of the intrinsic structure of water and an increase in the number of water molecules drawn from the solution into the sphere of influence of the cation [13].

In addition to indium perchlorate salts, for elements of the aluminum subgroup, their iodates $Me^{III}(JO_3)_3 \cdot n H_2O$, are also known, including indium iodate with the composition $In(JO_3)_3 \cdot 2H_2O$ [57, 58]. In contrast to perchlorate, indium iodate is characterized by a low degree of solubility, which in water at a temperature of 25° C is ~0,05% by weight (logSP = 2.5), and slightly more passes into solution under the action of nitric acid, showing the maximum value of solubility equal to 16.9 g/dm^3 at a concentration of 300 g/dm^3 HNO_3.

Indium (III) is quantitatively precipitated from the solution in the pH range 1.9–7 with sodium (potassium) periodate with the formation of a precipitate
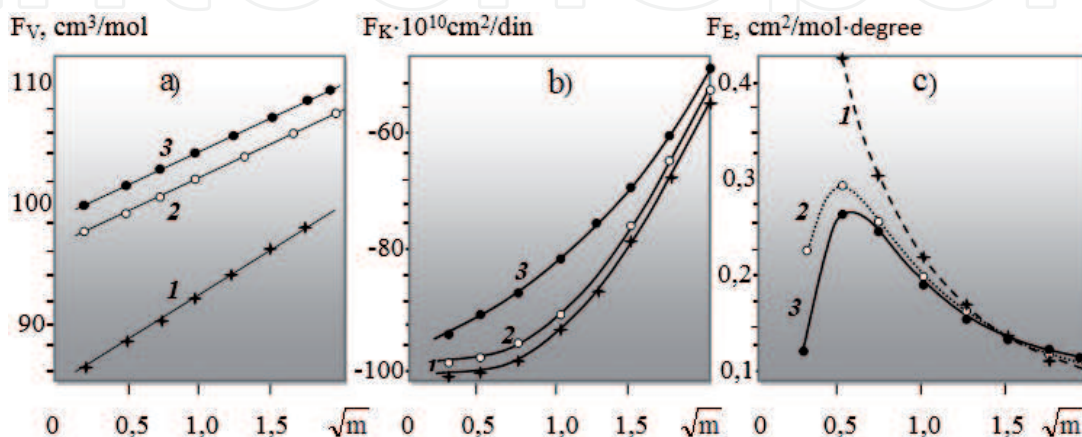

Figure 7.
Dependence of: a – apparent molar volumes (FV), b – compressibility (FK) and c – expandability (FE). From $\sqrt{m}$ perchlorates: 1 - $Al(ClO_4)_3$, 2 - $Ga(ClO_4)_3$ 3– $In(ClO_4)_3$ [49].

Electrolyte	Coordination number of cations	"Acoustic" hydration number	Change in isochoric heat capacity $-\Delta C_{V2}$ (J/K·mol) upon dissolution of subgroup III metal perchlorates on concentration (m)				
			0,5 m	1 m	2 m	3 m	4 m
$Al(ClO_4)_3$	6	12,4	411	373	296	223	
$Sc(ClO_4)_3$,	6	11,3	383	327	248	195	151
$Ga(ClO_4)_3$	7–8	12,5	343	290	233	186	144 (3,83 m)
$Y(ClO_4)_3$	6	13,2	320	276	211	163	114
$In(ClO_4)_3$	6	11,0	345	322	257	205 (3,19 m)	
$Tl(ClO_4)_3$	6	13,4	116				

Table 1.
Change in isochoric heat capacity.

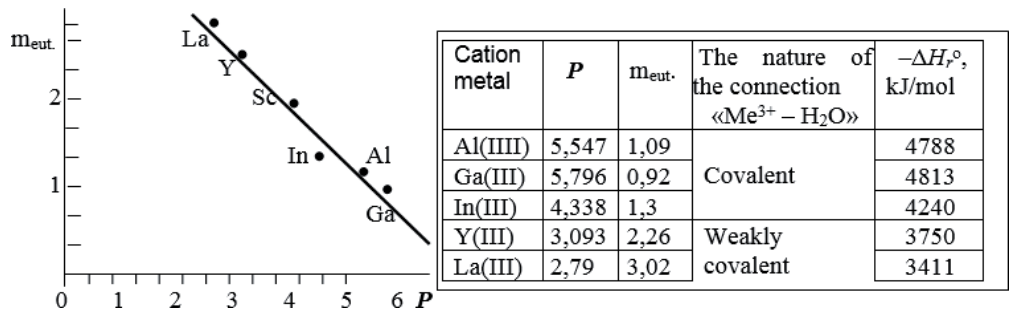| Cation metal	P	$m_{eut.}$	The nature of the connection «$Me^{3+} - H_2O$»	$-\Delta H_r°$, kJ/mol
Al(IIII)	5,547	1,09		4788
Ga(III)	5,796	0,92	Covalent	4813
In(III)	4,338	1,3		4240
Y(III)	3,093	2,26	Weakly	3750
La(III)	2,79	3,02	covalent	3411

Figure 8.
Correlation of the polarizing forces of cations (P) and the eutectic concentration (m_{eut}) of aqueous solutions of group III perchlorates $Me^{III}(ClO_4)_3$ ([50], pp. 124–126).

corresponding to formula $In_5(JO_6)_3$, the composition of which is constant at a temperature of 120–270° C. The crystalline compound of indium paraperiodate is slightly soluble in water, and respectively, in 1%, 0.3% and 0.5–1% carbonate, nitrate and ammonium acetate, but it is readily soluble in dilute mineral acids. The solubility of indium paraperiodate in water at 20° C is $6,4·10^{-4}$ g-mol/dm³ or $7,9·10^{-3}$ g/dm³. The gravimetric and titrimetric methods for the determination of indium using the periodate ion are based on these analytical characteristics [59].

Answering the question whether the ClO_4^- ion is included in the inner coordination sphere of indium, it can be considered proven that indium acidic complexes are not formed in aqueous solutions, and in this case we are only talking about the possibility of the outer-sphere interaction of ClO_4^- ions with aquocation. However, in a number of organic systems, apparently, their participation in complex formation is possible, but such states, being weaker than contact interactions, are rather difficult to fix. Perchlorate ion and perchloric acid in indium compounds perform primarily the function of a dehydrating agent; therefore, their presence leads to a change in the characteristics of the interaction of ions with water, which is reflected in the physicochemical properties of indium perchlorates.

Apparently, in relatively dilute solutions, the role of ClO_4^- is reduced to destructuring water, which contributes to the stabilization of hydration shells around hydrophilic indium cations. In concentrated solutions, ClO_4^- anions enter into some competition with cations for water, as a result of which, in particular, an increase in the asymmetry of coordination water molecules and its additional polarization is possible. Indium (III) cations attach a larger number of layers of water and, to varying degrees, affect its state, and through it, the action spreads further to the

property and the boundary medium. Thus, this causes either the destructuring effect or a change in the state of chemical bonds of ClO_4^- ions in concentrated solutions.

Thus, the ClO_4^- ion, being structure-forming and exhibiting a protoacceptor ability, in solutions of group III perchlorates forms exclusively solvate-separated ion pairs due to the high enthalpy of hydration of the corresponding metal cations.

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