



Clusters Formation in Salts Solution in Polar Dielectric Liquids and Electrically-induced Separation of Solvated Ions

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Authors' contributions

This work was carried out in collaboration between both authors. Author IVS designed the study and wrote the first draft of the manuscript. Author MAK managed the analyses of the study. Both authors read and approved the final manuscript.

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ABSTRACT

The aim of study is to demonstrate that separation of solvated ions in solution of mix of salts under the action of external periodic electric field happens because of around ions there are formed clusters consisting of molecules of solvent and the sizes of such clusters have dimensions $\sim 0.1 \mu\text{m}$.

In investigations the sizes of clusters theoretically were defined and experimentally value of frequency of external electric field which action excites the effect of separation of the solvated ions was defined.

Experiments were done in the Technical Physics Chair of the National Research Tomsk Polytechnic University.

At theoretical determination of the dimensions of clusters Poisson's equation was solved and was considered that polar molecules of solvent are oriented under the action of electric field of an ion. The chemical composition of samples of solutions was determined by means of the X-ray excited fluorescent radiation analysis method.

Theoretical estimates and results of experiments confirmed the assumption that clusters which are formed around ions in solutions have the dimensions $\sim 0.1 \mu\text{m}$.

Results of investigation testify that placing of volume distributed electric charge of ion in

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dielectric liquid is accompanied by formation of the supramolecular particles, which we called "clusters", linear sizes of which is significantly more than first and second radiuses of solvation (~ 1 Angstrom) and reach size $\sim 0.1 \mu\text{m}$. At such sizes inertial properties of clusters and their natural frequencies give the chance to operate their movement by means of action of external electric field on solution.

Keywords: Solution; cation; solvation; electric field; directed motion; separation.

1. INTRODUCTION

In experiments when external periodic electric field acts to solution of mix of salts in water the effect of separation of the hydrated cations was found. Thus electrodes which form electric field were electrically isolated from solution. Potential of one of electrodes changed in time as a sine and with different amplitudes in half-cycles. We called such electric field asymmetric and the ratio of values of amplitudes – asymmetry coefficient. Results of research of this effect are presented in the monograph [1]. When the frequency of change of potential (frequency of an external field) was ~ 100 Hz up to 2 kHz separation of the solvated cations in solution was observed. At increase in frequency the effect disappeared.

It was natural to assume that the frequency of external electric field has to correlate with natural frequency of particles moving of which is directed in volume of solution under the action of this field. These particles are formed by cations and solvent molecules which are associated around cations. Such particles are called as solvated cations. According to existing point of view the sizes the solvated cations don't exceed 10 Angstrom and no more than 2 layers which are formed by solvent molecules around a cation are taking in account. Estimates showed that value of natural frequency of solvated cations oscillations is ~ 10 MHz and more. But we found effect with significantly smaller frequencies. It is meant that the size and mass of a particle which consists of a cation and solvent molecules around it must be significantly more than 10 Angstrom. It is possible to assume that under certain conditions in solution when solvent is polar dielectric (for example water) around ions in the connected state there is large number ($\sim 10^5$) of molecules of solvent.

The purpose of our investigation is to determine the sizes of particles which are formed in salt solution in polar dielectric liquid and check the opportunity to use the founded effect for separation of cations of different metals.

2. FORMATION OF CLUSTERS IN SOLUTIONS OF SALTS IN POLAR DIELECTRIC LIQUIDS

Condition and properties of molecules of solvent of both types – cations and anions – which are under action of electric fields in solution are described by identical laws. As changes of cations concentration in solution was measured in experiments, subjects of the description in the paper are cations.

2.1 Cation's Electric Field Distribution in Solution

Solvent is dielectric liquid. Molecules of solvent are the polar molecules (for example, water). Distribution of density of polarizing charge induced by an ion in volume of solvent is defined by the relation:

$$\rho_{polar} = -\nabla \vec{P} \quad (1)$$

in which the vector of polarization \vec{P} is linearly related with the electric field strength \vec{E} which is created by the ion:

$$\vec{P} = \chi \epsilon_0 \vec{E} \quad (2)$$

where χ is the dielectric susceptibility of the solvent and ϵ_0 is the electric constant.

Ion having the charge of q creates the field distribution of which in the dielectric solvent is described by the relation:

$$\vec{E} = \frac{q\vec{r}}{4\pi\epsilon_0\aleph r^3} \quad (3)$$

where $\aleph = 1 + \chi$ is the dielectric permeability of solvent, \vec{r} is the radius-vector with origin at the ion geometrical center.

The relation (1) is mathematical model of physical process of formation of a resultant charge in the dielectric caused by non-uniform polarization.

Taking into account that the radial component of the electric field strength vector

$E_r = \frac{q}{4\pi\epsilon_0\aleph r^2}$, and the field of the central ion is spherically symmetric, it is easy to

obtain the relation:

$$\rho_{polar} = \chi \frac{q}{2\pi\aleph} \frac{1}{r^3} \quad (4)$$

Thus, density of the induced (polarizing) charge is inversely proportional to the third degree of the distance counted from the center of an ion.

When electric field is absent, molecules are randomly oriented in various directions. Therefore the total dipolar moment in unit of volume is equal to zero.

In the electric field of a central ion (cation or anion) at once there are two processes: first, the additional dipolar moment because of forces acting on electrons (electric polarizability) is induced; secondly, electric field seeks to focus (to direct) each of molecules, creating resultant, non-zero moment in unit of volume. Collision of molecules at their chaotic Brownian motion doesn't allow them to keep strictly fixed orientation, but formation of the ordered structure around an ion nevertheless is possible. We called this structure as "cluster".

In the first approximation the molecule of dielectric solvent can be considered as the dipole having the dipolar electric moment:

$$\vec{p}_0 = Q\vec{l} , \quad (5)$$

where Q is the absolute value of the total positive and total negative charges located, respectively, in the centers of these charges; \vec{l} is the distance between centers of positive and negative charges.

Such dielectric is called as polar dielectric, molecules (atoms) of which have the electrons located asymmetrically relatively to the nuclei of constituting atoms (for example H_2O , HCl , NH_3 , CH_3Cl , etc.). In such molecules the centers of positive and negative charges don't coincide, being, practically, at constant distance from each other. Molecules of polar dielectrics on their electric properties are similar to rigid dipoles which have a constant dipolar moment $\vec{p}_0 = const$.

The rigid dipole placed in a uniform external electrostatic field, is under action of couple of forces with the moment equal to:

$$\vec{M} = [\vec{p}_0 \vec{E}] . \quad (6)$$

The moment of couple of forces \vec{M} is directed perpendicularly to the plane passing through vectors \vec{p}_0 and \vec{E} , and from the end of vector \vec{M} rotation from \vec{p}_0 to \vec{E} must happens on the shortest way, passing counterclockwise.

In real molecules of polar dielectrics besides the turn of axes of dipoles along a field, it takes place the deformation of molecules, and in them some induced dipolar moment is created.

If polar dielectric isn't placed in external electric field, as a result of chaotic thermal motion of molecules vectors of their dipolar moments are directed chaotically. Therefore the sum of the dipolar moments of all molecules is equal to zero in any physically infinitesimal volume ΔV . (Thus $\Delta V \gg v_0$, where v_0 is the volume of one molecule, and volume ΔV contains very large number of molecules).

When entering dielectric into external electric field there is the dielectric polarization, consisting that in any elementary volume ΔV there is a total dipolar moment of molecules, other than zero. Dielectric which is in such state is called the polarized dielectric. In polar dielectrics there is the orientation polarization. Thus external electric field seeks to direct the dipolar moments of rigid dipoles along the direction of electric field. It is interfered by the chaotic thermal motion of the molecules seeking "to scatter" dipoles randomly. As a result of joint action of a field and thermal movement there is the preferred orientation of the dipolar electric moments along the field, increasing with increase in the strength of electric field and reduction in temperature.

Quantitative measure of polarization of dielectric is the polarization vector \vec{P} . As vector of polarization is called the ratio of the electric dipolar moment of small volume ΔV of dielectric to this volume:

$$\vec{P} = \frac{1}{\Delta V} \sum_{i=1}^N \vec{p}_i, \quad (7)$$

where \vec{p}_i is the electric dipolar moment of i -th molecule; N is the total number of molecules in volume.

This volume has to be so small that in it electric field could be considered uniform. At the same time the number of molecules N in volume ΔV has to be rather great in order that it was possible to apply statistical methods of description.

For the uniform polar dielectric which is placed in uniform electric field:

$$\vec{P} = \bar{n} \langle \vec{p}_0 \rangle, \quad (8)$$

where $\langle \vec{p}_0 \rangle$ is the average value of a component of the constant dipolar moment of a molecule along direction of the field.

If polar dielectric is placed in the external electric field of small strength, the dielectric susceptibility may be calculated with use of Langevin-Debye formula:

$$\chi = \frac{\bar{n} p_0^2}{3 \epsilon_0 k T}. \quad (9)$$

Taking into account that $\chi = \epsilon - 1$, it is easy to obtain the equation:

$$\rho_{polar} = \frac{\bar{n} p_0^2}{3 \epsilon_0 k T} \frac{q}{2 \pi \epsilon_0} \frac{1}{r^3}, \quad (10)$$

and Poisson's equation may be written in the form:

$$\nabla^2 \psi = -\frac{2}{3} \frac{\bar{n} p_0^2 q}{(\epsilon_0 \epsilon)^2 k T} \frac{1}{r^3}. \quad (11)$$

The equation (11) in spherical geometry may be written in the form:

$$\frac{d^2\psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr} = \frac{a}{r^3}, \quad (12)$$

where

$$a = -\frac{2}{3} \frac{\bar{n} p_0^2 q}{(\epsilon_0 \mathcal{N})^2 kT}.$$

Boundary conditions for Poisson's equation in relation to a considered case will be written in the form:

$$\psi(r = r_0) = \psi_0; \psi(r \rightarrow \infty) = 0, \quad (13)$$

where r_0 is the ionic radius, ψ_0 is the ion's potential. Equality to zero of potential on infinite from a point charge follows from basic principles of electrostatics and electrodynamics of continuous matter. Potential of an ion decides as the potential of uniformly charged sphere (q is the value of charge) with radius r_0 [2]:

$$\psi_0 = \frac{1}{4\pi \epsilon_0} \frac{q}{r_0}. \quad (14)$$

For Y^{3+} cation $q = 4.8 \cdot 10^{-19}$ C, $r_0 = 1.06 \cdot 10^{-10}$ m, $\epsilon_0 = 8.854 \cdot 10^{-12}$ C / V·m. Thus for Y^{3+} cation $\psi_0 = 40.699$ V.

The equation (12) is the linear non-uniform equation of the 2nd order with variable coefficients. Its solution may be written in the form:

$$\psi(r) = -\frac{1}{r} \left(\ln \frac{C_1}{r^a} - a \right) + C_2, \quad (15)$$

Where C_1 and C_2 are the constants determined by boundary conditions (13). It is clear that according to the second boundary condition $C_2 = 0$, and use of the first boundary condition gives the possibility to define:

$$C_1 = r_0^a \exp(r_0 \psi(r_0) + a). \quad (16)$$

For example, C_1 is 1 for cations Y^{3+} and Ce^{3+} . Value of constant a is $-1.951 \cdot 10^{-10}$ for $T = 298$ K and $q = 3|\bar{e}|$, where \bar{e} is the electron charge.

Strength of electric field as function of argument r , in spherical system of coordinates, in case of the central symmetry is defined by the relation:

$$E_r(r) = -\frac{d\psi}{dr} = -\frac{1}{r^2} \ln \frac{C_1}{r^a}. \quad (17)$$

2.2 Solvent Molecules Held by Cation's Electric Field

Theoretical and experimental studies of processes of functional nanostructures formed in liquids [3] showed that due to a dipole–dipole interaction of molecules of dielectric liquids (in particular, water) formation of molecular “bridges” in the liquid which is placed in electric field between electrodes is possible. Thus there is a critical electric field E_{cr} for formation of molecular “bridges”:

$$E_{cr} = \frac{1}{\alpha} \left[(p_0^2 + 2\alpha kT)^{1/2} - p_0 \right], \quad (18)$$

where α is the polarizability of a molecule of liquid.

On the Fig. 1 the function $E_r(r)$ in limits $0.1\mu\text{m} \leq r \leq 0.75\mu\text{m}$ for cations Li^+ , Cd^{2+} , Y^{3+} placed in water is presented.

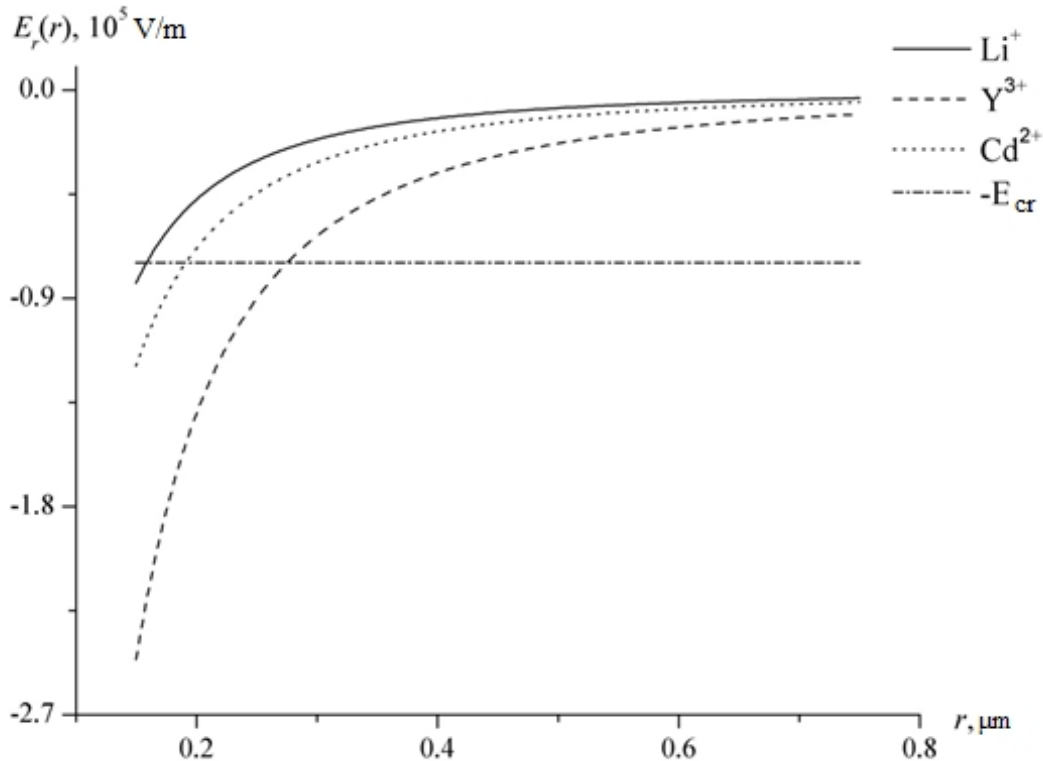


Fig. 1. Radial dependence of the electric field strength for Li^+ , Cd^{2+} , Y^{3+} cations at temperature of 298 K

At $|E| > |E_{kp}|$ polarized molecules of solvent will be connected by dipole–dipole interaction and directed along the field of the central ion. At $|E| < |E_{kp}|$ thermal motion of molecules of solvent has to destroy “molecular bridges”.

It is possible to assume that around the central ion the large number of molecular "bridges" is built, and each of "bridges" is a chain of the molecules of solvent built along electric field if ion. These “bridges” form the coating of the ion shielding its field. The cluster consists of the central ion and the polarized molecules of solvent surrounding ion are formed.

Radius of such cluster r_{cl} can be estimated from a condition $|E| = |E_{cr}|$ that is from the relation:

$$\frac{1}{r_{cl}^2} \ln \frac{C_1}{r_{cl}^a} \approx \frac{1}{\alpha} \left[(p_0^2 + 2\alpha kT)^{1/2} - p_0 \right]. \quad (19)$$

This condition means that at $r = r_{cl}$ the central ion field is compensated by the field of "bridges" of the built dipoles. That is, coating consisting of the built dipoles shields the central ion. The solution of the equation (19) gives values of r_{cl} which are presented in Table 1.

Table 1. Sizes of clusters for ions of Li^+ , Mg^{2+} , Ca^{2+} , Cd^{2+} , Y^{3+} , being in water, at temperature of 298 K

Cation	Cluster radius, μm
Li^+	0.115
Mg^{2+}	0.119
Ca^{2+}	0,128
Cd^{2+}	0.162
Y^{3+}	0.275

At such sizes of clusters value of own frequency of their oscillations ~ 1 kHz. It is possible to assume that exactly due to formation of such clusters action of external electric field on solution excites directed motion of cations. As cations of different atoms have different inertial properties that parameters of directed motion of different cations in solution will differ.

3. EXPERIMENTS ON SOLVATED CATIONS SEPARATION

Selective drift (directed motion) of cationic aqua complexes in solutions under external asymmetric electric field action was studied in experimental separation cell construction of which is shown on Fig. 2.

The cell was loaded with solution of mix of salts CaCl_2 and MgCl_2 in water. Concentration of salts was 2 g/l. The structure of samples of solution was defined by means of the X-ray excited fluorescent radiation analysis. Thus the characteristic spectrum was excited by the

brake radiation of the chromic anode and was registered by planar semiconductor Si:Li detector. Generation of brake radiation was in a mode of the X-ray tube: 20 kV, 100 μ A.

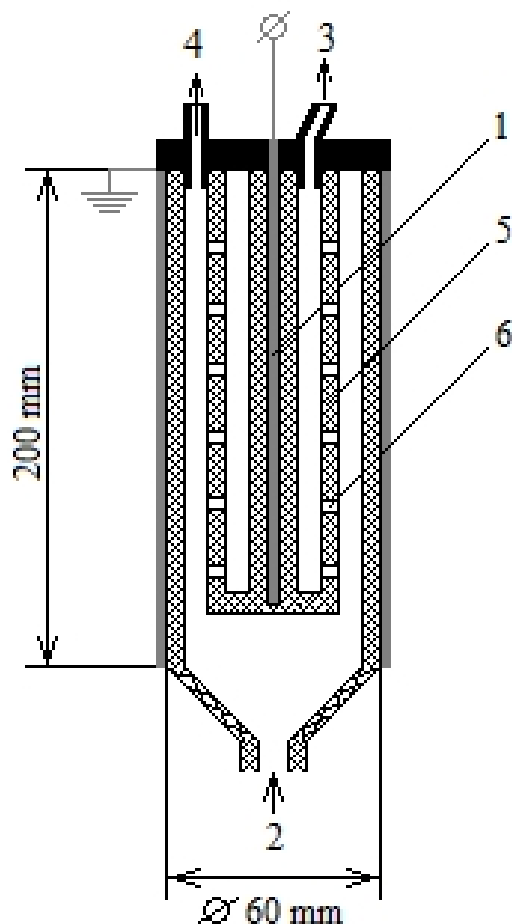


Fig. 2. Separation cell: 1 – potential electrode, 2 – input of solution, 3 – output of enriched solution, 4 – output of depleted solution, 5 – internal cylinder for separation of solution flow, 6 – openings (all the elements are made from insulating materials)

Potential of one of electrodes of separation cell changed in time as sine, but with different amplitudes in half-cycles $U(t) \approx A(1 + 2 \sin \omega t - \sin 2\omega t)$. Speed of pumping of solution through a cell was 7 l/h.

On Fig. 3 the spectrum of fluorescent radiation of the sample of solution is shown as an example.

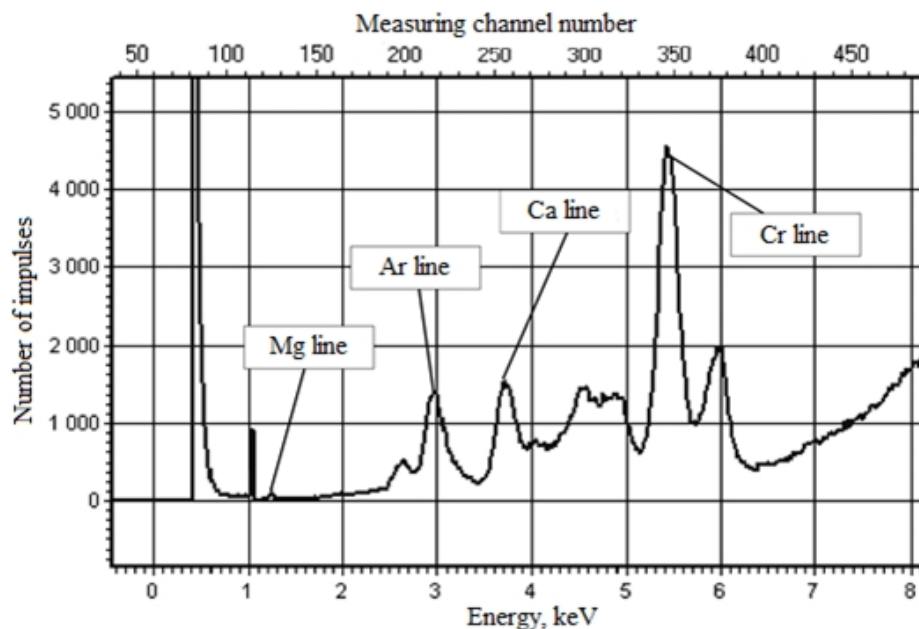


Fig. 3. Example of reading of spectrum by means of Software SPECTR7

Intensity of the line of chemical element is proportional to its concentration. Intensity of the Ca and Mg lines were always normalized on intensity of the Ar line. It is thus supposed that the content of argon in air during all measurements is constant (0, 93%).

On Fig. 4 the spectrum of radiation of sample of solution at input of the separation cell (position 2 in Fig. 2) is shown.

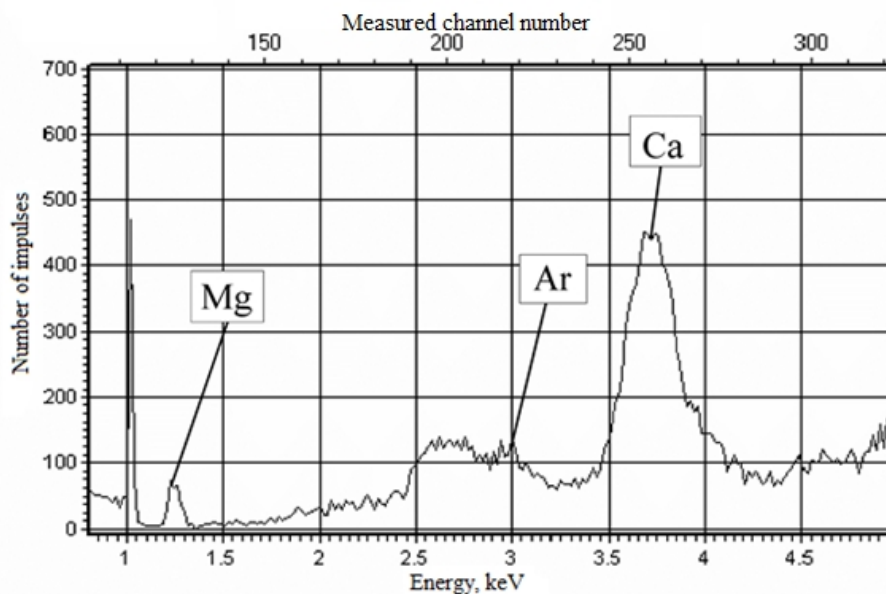


Fig. 4. The spectrum of sample of feeding solution

On Fig. 5 the spectrum of radiation of sample of solution which is enriched with Ca ions at output of the separation cell (position 3 in Fig. 2) is shown.

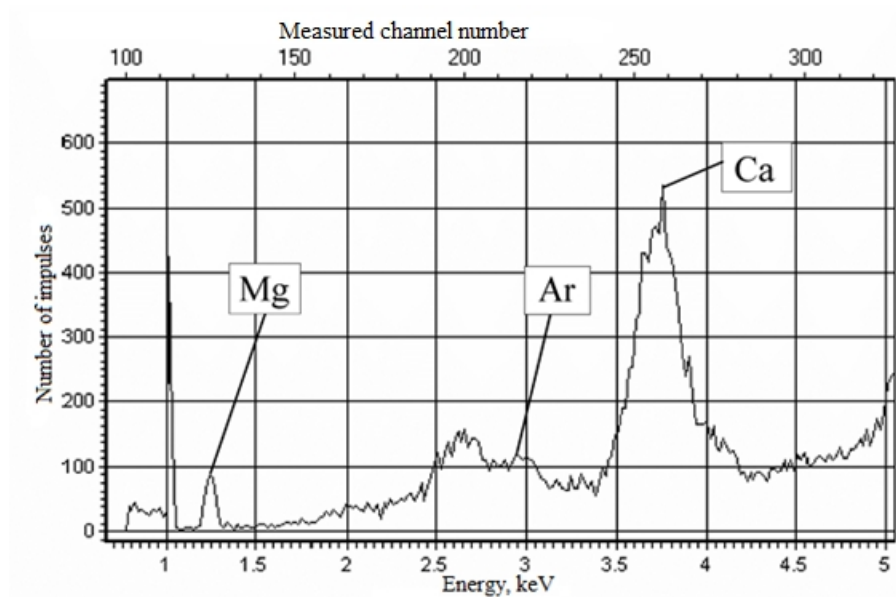


Fig. 5. The spectrum of radiation of sample of solution which is enriched with Ca ions

On Fig. 6 the spectrum of radiation of sample of solution which is depleted in Ca ions at output of the separation cell (position 4 in Fig. 2) is shown.

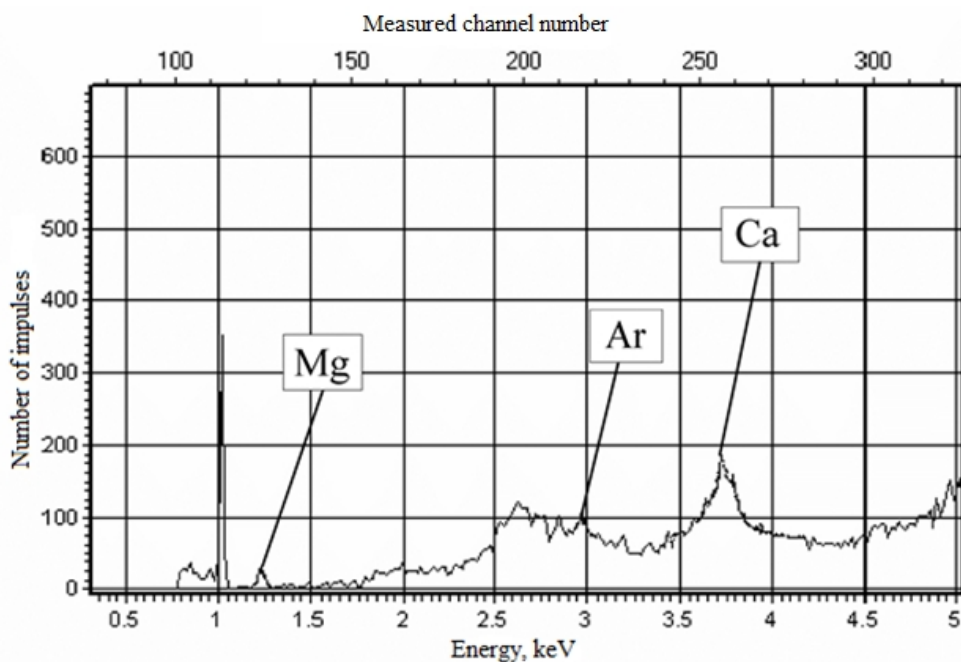


Fig. 6. The spectrum of radiation of sample of solution which is depleted in Ca ions

4. DISCUSSION

Changes of concentration of ions in solution which are shown on Figs. 5 and 6 happened when the frequency of potential U was 1.5 kHz and amplitude of potential A was 170 V.

Thus the effect of separation of the solvated ions is exciting when the frequency of external electric field is ~ 1 kHz. As this frequency has to correlate with natural frequency of the solvated cations, the sizes of the solvated ions (clusters) has to be $\sim 0.1 \mu\text{m}$. At such sizes the moment of inertia of a cluster corresponds to frequency ~ 1 kHz.

The process of ions salvation in solutions of salts in liquid polar dielectrics provides an opportunity of development of essentially new technologies and techniques. The conditions providing use of mass transfer process for the resolution of various problems of application, first of all are defined by the sizes of solvated ions (clusters). In particular, action of periodic electric fields with various combinations of frequency, strength and the dependence of amplitudes of strength in half-cycles on solutions of salts in polar dielectrics causes excitation of rotary-forward motion solvated ions (clusters) and, hence, mass transfer [4]. The frequency of these fields does not exceed tens of kilohertz and the amplitude of field strength in solutions not exceeds tens of volts on centimeter. Thus electrodes, by means of which in volume of solution various configurations of an electric field are created, are isolated from solutions. Experimental data and theoretical estimations show, that distinction of inertial properties of the solvated ions, caused in the different sizes of the solvated shell, can be necessary in a basis of technology of element enrichment of solutions of salts of metals. It is possible to expect, that it will find utilizations also in other effects exiting by the influence of electric and magnetic fields on solutions of salts.

5. CONCLUSION

At present time the mechanism of ion-molecular interaction in solutions is not clear. There are experimental data which testify that the size of solvated ions covers in water electrolytes is equal to several tens of sizes of water molecules. There are also experimental data which testify that placing of volume distributed electric charge in dielectric liquid is accompanied by formation of the supramolecular particles linear sizes of which reach value about $1 \mu\text{m}$.

At determination of amplitude-frequency parameters of electric fields by means of which it is possible to excite an ion-selective mass transfer in solution, we needed correct determination of the sizes of covers which are formed from solvent molecules around ions. Thus the traditional description of solvated ions properties based on Debye-Huckel approach, led us to that the ion-selective mass transfer in solution has to take place with frequencies of external electric field ~ 10 MHz. Nevertheless, really ion-selective mass transfer in solution was excited with frequencies ~ 100 Hz.

Therefore the problem of the description of process of orientation and holding of dielectric solvent molecules in the field of ion was posed and solved. Results of the solution of this problem testify that placing of volume distributed electric charge of ion in dielectric liquid is accompanied by formation of the supramolecular particles, which we called "clusters", linear sizes of which is significantly more than first and second radiuses of solvation (~ 1 Angstrom) and reach size ~ 0.1 microns. At such sizes inertial properties of clusters and their natural frequencies give the chance to operate their movement by means of action of external electric field on solution.

CONSENT

The way of ions separation in solution by means of asymmetric electric field action is patented by authors (the patent of the Russian Federation No.2428759, priority date 09.06.2009). Both authors declare that written informed consent was obtained from the patient (or other approved parties) for publication of this case report and accompanying images.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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