

## Original Article

# THE USE OF ELECTRICAL INDUCED SELECTIVE DRIFT OF SOLVATED IONS IN SOLUTIONS PHENOMENA IN TECHNOLOGIES

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### Abstract

The possibility of the use the phenomena of the electrical-induced selective drift of cationic aquacomplexes in the water solution of the salts for creating of the new, non-electrode, power-saving technology of the solution enrichment by desired element is shown. The development of the naturally-scientific basis of this technology has showed that inertial properties of formed in the solution over-molecular structural units - clusters depends from that's dimensions. Dimensions of these clusters are in limits from scores of angstrom to fractions of micron, at the same time liquid mediums are the base of functioning both biological and technological systems. This work shows new approach for theoretical describing of salts solution in dielectric liquids and contains some data on the realized experiments.

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### 1. INTRODUCTION

In experiments [1] the phenomenon of the induced selective drift of cationic aquacomplexes in water solutions of salts under action of asymmetric electric fields which frequency does not exceed tens of kilohertz was revealed itself. At that the grid electrodes placed in a solution and forming the field, have been isolated from the solution, the current through border between a solution and an electrode was absent. Action of the variable magnetic field on the water solution of salt also excited intensive mass-transport. Experimental data and theoretical estimations [2] have shown, that excitation of rotary-onward motions of solvated cations (clusters) with various inertial properties can become a basis for technology of separation of rare earth elements in water solutions of their salts. The further theoretical and experimental researches have demanded to use new not contradicting and complementary approximations, and specify existence of new applications of solvation process of ions in solutions of salts in liquid, polar dielectrics. As it was clarified the conditions providing use of solvation process for the decision of various applied problems, first of all are determined by the sizes of solvated ions (clusters). In the present work is showed the generalization of results of researches which have been directed on studying of relations between these conditions and properties of clusters.

### 2. THE INDUCED DRIFT OF SOLVATED IONS

The general physical model of process of selective drift of cationic aquacomplexes in water solutions of salts under

action of asymmetric electric and variable magnetic fields is based on following positions.

Each cation (anion) causes the polarization of surrounded solvent (water): the "atmosphere" is forming around each cation (anion) with abundance of polarized molecules of the water. This "atmosphere" is shielding cation's (anion's) field. The generalized electronic shell of each polarized molecules of water is deformed concerning unperturbed configuration, when full spin of the molecule is a zero. The perturbation is excited by the action of the cation's (anion's) electric field. The deformation of the shell result in the part of nucleus' charge or electrons in the water's molecule will be uncompensated. This uncompensated part of a charge represents a polarizing charge of a molecule of water in a non-uniform electric field of the charged particle - cation (anion). Thus the polarizing charge of molecules of water is determined by a charge of a particle which they shield. The sum of polarizing charges of all molecules, associated around of one particle, is equal to a charge of the particle (on absolute value). The polarized charge is positive if molecules of water are shielding anion, and negative if they are shielding cation. This "atmosphere" ("fur") with abundance polarized molecules of water is solvate shell.

Not excited aquacomplex, which solvated shell is not deformed, is neutral. The shell carries out function of the screen which interferes with action of a constant component of the high-frequency electric field. Deformation of solvated shell and, hence, formation at

aquacomplex a polarizing charge, creates conditions for action of a constant component of a field and, hence, for excitation of the oriented drift of aquacomplex.

For today the mechanism the ion-molecular of interaction remains not clear. There are experimental data which testify that the size of solvated shells in water electrolytes makes some tens sizes of molecules of water. There are also experimental data which testify that introduction of a volumetric electric charge in the weakly-conducting liquid is accompanied by formation over-molecular structural units - "clusters" which linear sizes make about 1 micron. For definition of amplitude-frequency parameters of the electric fields providing excitation of induced selective drift of solvated ions, correct definition of the sizes solvated shells was required. Thus the traditional approach to consideration of properties solvated ions, based on the approximation of Debye-Hukkel, did not give quantitative result on the sizes of environments. In this connection the problem of the description of the solvation process in terms of electrostatics of continuous environments has been stated and solved.

### 3. SINGLE ION IN LIQUID POLAR DIELECTRIC

Quantitative measure of polarization of dielectrics is the vector of polarization  $\vec{P}$ . For homogeneous dielectric, being a homogeneous electric field:

$$\vec{P} = \bar{n} < \vec{p}_0 >, \quad (1)$$

where  $< \vec{p}_0 >$  - the value of the central component of the constant dipole moment of a molecule of dielectric along intensity of a field,  $\bar{n}$  - average quantity of molecules in unit of volume of dielectric.

The density of a polarizing charge is defined by the ratio:

$$\rho_{pol} = -\nabla \vec{P}, \quad (2)$$

in which the vector of polarization  $\vec{P}$  is linearly connected with a vector of intensity of the electric field  $\vec{E}$  created by an ion:

$$\vec{P} = \chi \cdot \varepsilon_0 \cdot \vec{E}, \quad (3)$$

where  $\chi$  - a dialectical susceptibility of a dielectric,  $\varepsilon_0$  - an electric constant of vacuum.

The ion, having a charge  $q$ , creates in the dielectric ambience the field which distribution is described by the ratio:

$$\vec{E} = \frac{q \cdot \vec{r}}{4 \cdot \pi \cdot \varepsilon_0 \cdot \aleph \cdot r^3}, \quad (4)$$

where  $\aleph = 1 + \chi$  - relative dielectric permeability,  $\vec{r}$  - the radius-vector, which begin complies with the geometric center of the ion.

It was shown, that because dipole-dipole interaction between molecules of water the forming of "molecular bridges" in water under high-intensity electric field action. For that process the critical electric field  $E_{cr}$  exist.

Under  $E > E_{cr}$  polarized molecules will be connected by dipole-dipole interaction and focused in a direction of the field of the central ion. Under  $E < E_{cr}$  thermal movement

of molecules should destroy the bridges. The ratio is corresponding a condition  $|E| = |E_{cr}|$  is received, and allowing defining radius of the cluster:

$$\frac{1}{r_{cl}^2} \cdot \ln \frac{C_1}{r_{cl}^a} \approx \frac{1}{\alpha} \left[ (p_0^2 + 2 \cdot \alpha \cdot k \cdot T)^{1/2} - p_0 \right]. \quad (5)$$

The given condition means, that at  $r = r_{cl}$  the field of the central ion "is balanced" by opposite directed field of "bridges" of the formed by dipoles. That is, "fur coat" from the built dipoles shields the central ion. The decision of the equation (5) gives value  $r_{cl}$ . Constant  $C_1$  is defined by corresponding boundary conditions.

### 4. THE SELF-COORDINATED FIELD IN THE WATER SOLUTION OF SALT

According to representation about the self-coordinated field there is such distribution of an electric field in system of the cooperating charged particles which creates the distribution of particles exciting a field. Salt solution is possible to consider as system of cooperating cations, anions, positive and negatively polarized molecules of water. Certainly, in the solution there are no polarized molecules of water, but their distribution (at first approximation) does not influence distribution of the charged particles.

For a finding of the self-coordinated field we shall use Poisson equation:

$$\Delta \varphi = -4\pi q \quad (6)$$

and Boltzman distribution:

$$n_k = \tilde{n}_k \exp\left(-\frac{Z_k e \varphi}{kT}\right), \quad (7)$$

where  $n_k$  - concentration of particles with charging number  $Z_k$  in a point with potential  $\varphi$ . For electrons, for example,  $Z = -1$ . But in a solution are not present free electrons. For cations  $Z = m$ , and for anions  $Z = -m$ , where  $m$  - valency of metal which salt is dissolved.  $\tilde{n}_k$  in distribution (7) is a concentration of particles with charging number  $Z_k$  in a point with the zero potential, equal to average concentration of these particles on all volume of a solution.

Further an index «i» we shall designate cations, an index «a» - anions, «p+» - polarized and being around of anions molecules of water, «p-» - molecules of water around cations.

Average concentration  $\tilde{n}_k$  satisfies to a condition of quasi-neutrality:

$$\sum_i \tilde{n}_i Z_i + \sum_a \tilde{n}_a Z_a + \sum_{p^+} \tilde{n}_{p^+} Z_{p^+} + \sum_{p^-} \tilde{n}_{p^-} Z_{p^-} = 0, \quad (8)$$

which reflects that fact, that the solution as a whole (from outside) is neutral.

It is necessary to consider that charging numbers of cation and anion are equal on absolute value, but opposite, and charging numbers of the polarized molecules of water are determined by around of what they associated: around anions  $Z_{p^+} > 0$ , and around cations  $Z_{p^-} < 0$ .

Thus,

$$\sum_k \tilde{n}_k Z_k = 0, \quad k=i, a, p^+, p^-. \quad (9)$$

Also following connections take place:

$$Z_a = -Z_i = Z; \quad Z_{p^-} = \frac{1}{N_a} Z_a;$$

$$Z_{p^+} = \frac{1}{N_i} Z_i; \quad \tilde{n}_{p^-} = N_a \tilde{n}_a;$$

$$\tilde{n}_{p^+} = N_i \tilde{n}_i; \quad \tilde{n}_a = \tilde{n}_i = n_m;$$
(10)

where  $N_a$  - number of molecules of water, associated around of one anion;  $N_i$  - number of molecules of water, associated around of one cation;  $Z$  - valency of metal, which salt is dissolved;  $n_m$  - concentration of molecules of salt in a solution, if to consider they are not dissociated.

Volume charge thus,

$$q = e \sum_k Z_k n_k, \quad (11)$$

where  $e$  - the module of a charge of electron (in system of SI  $1,6 \cdot 10^{-19}$  C).

The decision of equation of Poisson in which distribution of a volumetric charge is defined by expression (11), for spherical symmetric distribution of potential (cation or anion) looks like:

$$\varphi = \frac{C}{r} \exp(-\chi r), \quad (12)$$

where constant of insulation is:

$$\chi = \left( \frac{8\pi e^2}{kT} Z^2 n_m \right)^{0.5}. \quad (13)$$

The inverse value  $l = \frac{1}{\chi}$  refers to as length of insulation

and it is possible to consider, that its value defines radius of solvation sphere within the limits of which the polarized molecules of water are built. They also insulate a field of cation (anion). Thus, value of cluster radius (solvated cation or anion) can be estimated, using:

$$r_{cl} \approx \left( \frac{8\pi e^2}{kT} Z^2 n_m \right)^{-0.5}. \quad (14)$$

## 5. EXPECTED VALUES OF FREQUENCES OF EXCITATION OF EFFECT

The values of frequencies received in approximation of the single ion in liquid polar dielectric, do not exceed units of kilohertz for various components of rotary-onward motions solvated ions-clusters. The sizes certain thus clusters and characteristic values of frequencies of an electric field have allowed to estimate values of parameters at which it is necessary to expect display of effect of the electroinduced drift aquacomplexes in water solutions of salts. Really, the oriented drift was observed experimentally at the frequencies making units of kilohertz. The further experimental researches of conditions of the maximal effect event have shown that in the certain cases the full separation factor achieves great values at essentially smaller frequencies. It has caused of carrying out of estimations of the sizes of clusters with use of other assumptions and approximations.

Values of the frequencies corresponding to various components of rotary-onward motions of cation aquacomplexes, and values of the frequencies corresponding to transition of oscillatory movements in rotary, received in approximation of existence the self-coordinated field in a solution, make units of hertz at concentration of salt in water of the order of one gram on litre.

In these approximations, effect of the electroinduced selective drift of the cationic aquacomplexes should be expected at the frequencies of an electric field which are not exceeding units of Hz.

Thus as, as follows from the ratio (14), the size of the cluster inversely to a square root from value of concentration of salt in water. Values of the frequencies, in turn, are inversely to value of the moment of inertia of the cluster.

The moment of inertia is proportional to the equivalent mass of the cluster, which is the quantity of molecules of water in the solvated shell  $g = (r_{cl}/r)^3$ , and the square of radius of cluster  $r_{cl}^2$ . It turns out, that the moment of inertia  $I \sim r_{cl}^5$  and values of the frequencies of excitation of various components of motions  $\nu \sim r_{cl}^{-5}$ . Thus, values of frequencies  $\nu \sim n_m^{2.5}$ .

It is necessary to expect, that at increase in concentration of salt in 3-5 time of value of frequencies of excitation of various components the movements, appointed in approximation of existence of the self-coordinated field in a solution will increase in 15-60 time.

## 6. THE POSSIBLE APPLICATIONS OF THE PROCESS OF THE INDUCED TRANSPORT OF SOLVATED IONS

If it is possible to consider the cost price of nuclear fuel in the size is defined only by a technological level of its manufacturing, then its cost is defined by a number not dependent on perfection of technology of factors. For example, uranium-containing the ore extracted in gold-bearing mines, can be offered in the world market under the lowest price. This fact will be caused not by perfection of technology of extraction of ore, and that it is extracted in passing with gold-bearing ore on the same manufactures. In this connection from thorium-containing of minerals is distinguished monazite. Power and quantity of deposits of monazite sand allows considering it, as one of potential sources of raw material for large-scale thorium nuclear power. In monazite (Ce, La, Y, Th) PO<sub>4</sub> contains about 12 % of thorium dioxide ThO<sub>2</sub>. At action on monazite the concentrated solutions of acids, for example nitric or hydrochloric, the mix of salts of cerium, lanthanum, yttrium and thorium are formed. Modern technological receptions allow allocating from this mix a thorium concentrate in the form of this or that chemical compound. The remained pulp represents very valuable raw material for reception or in the form of connections, or in the pure state rare-earth metals. Thus, realization of a technological variant in which the thorium concentrate is a passing material at reception of concentrates of cerium, lanthanum and yttrium is possible.

The demand and the price for these elements are very high. Thus, enough caused there is a necessity of search and development of new technological receptions of enrichment of water solutions of a mix of salts rare-earth metals on one of them. This process can be named the element enrichment of a water solution of a mix of the salts.

The experiments specifying an opportunity of use of the phenomenon of induced selective drift of cationic aquacomplexes in water solutions of salts under action of asymmetric electric fields for element enrichment of the water solution of a mix of salts of yttrium and cerium have been lead.

Experiments were spent in a technological cell which scheme is shown on Figure 1.

The internal volume of a technological cell was filled with a water solution of a mix of salts  $\text{Ce}(\text{NO}_3)_3$  and  $\text{Y}(\text{NO}_3)_3$  with concentration 3,5 and 3 g/l, accordingly. Circulations of a solution were not. Sampling was made from branch pipes 1, 2 and 3. On potential grids the asymmetric voltage is connect up in conformity with the scheme described in work [2].

For specified above parameters of the field primary drift of the cations of  $\text{Ce}^{3+}$  aside potential electrodes and increase of their concentration in the central section is observed. Enrichment of a water solution of a mix of salts  $\text{Ce}(\text{NO}_3)_3$  and  $\text{Y}(\text{NO}_3)_3$  by aquacomplexes of cerium in the central section in a various degree occurs in an interval of frequencies 1,6-7 kHz at the same intensity of a field and factor of asymmetry. The increase in frequency above 7 kHz complicates a picture of the directed drift of aquacomplexes of cerium.

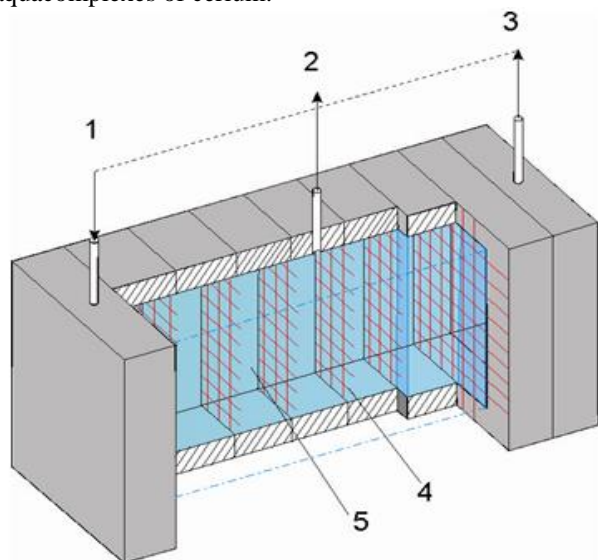


Figure 1. Technological cell: 1 - the branch pipe for submission of a solution; 2 - the branch pipe for selection of a solution; 3 - the branch pipe for selection and the organizations of compulsory circulation of a solution; 4 - the potential grid isolated from a solution; 5 - the solution

At submission on an input of a dividing element on the basis of a technological cell of an initial mix two component (a water solution of a mix of salts  $\text{Ce}(\text{NO}_3)_3$  and  $\text{Y}(\text{NO}_3)_3$  with concentration 3,5 and 3 g/l, accordingly) factors of division in an element without circulation of a

solution after 4 hours of influence of a field with intensity  $E^+ = 14,3 \text{ V/cm}$ , factor of asymmetry  $A^+/A^- = 0,66$ , with frequency 1,6 kHz have made: in selection 1,00499; in the bank 1,00179; full 1,00679. In a solution there was an enrichment on cations of  $\text{Ce}^{3+}$ .

Thus, the established conditions of display of effect in a water solution of salts of cerium and yttrium show an opportunity of its use in technology of element enrichment of water solutions of salts at complex processing nuclear raw materials. Enrichment of a water solution of a mix of salts  $\text{Ce}(\text{NO}_3)_3$  and  $\text{Y}(\text{NO}_3)_3$  by aquacomplexes of cerium at potential electrodes in a various degree occurs in an interval of frequencies 1,6 - 7 kHz. Realization of a technological variant in which the thorium concentrate is a passing material at reception of concentrates of cerium, lanthanum and yttrium is possible.

The modified scheme of extraction clearing of the solution of nitrate of thorium allows taking from refined water target rare-earth elements. In technological scheme, well checked up in practice, the new part is added, allowing taking industrially significant quantities target rare-earth elements (for example, yttrium or cerium).

In case of complex hydrochloric acid technologies rare-earth metal raw material the basic scheme of extraction the rare-earth elements from refined water, containing a hydrochloric acid and chlorides of the rare-earth elements, will not change. Certainly, optimum combinations of parameters of the electric field acting on a water solution of a mix of chlorides will be others. Thus orders of sizes of intensity of an electric field and its frequency will not change. The design of a dividing cell, the scheme and power of system of formation of an asymmetric electric field of high frequency will remain constant. Thus, the developed technology is universal in relation to the scheme of the extraction clearing of thorium and to technology rare-earth metal raw material.

## 7. CONCLUSIONS

The salvation process of ions in solutions of salts in liquid, polar dielectrics provides an opportunity of development of essentially new technologies and techniques. The conditions providing use of process mass transfer for the decision of various applied problems, first of all are defined by the sizes of solvated ions (clusters).

In particular, action of periodic electric fields with various combinations of frequency, intensity and the attitude of amplitudes of intensity in half-cycles on solutions of salts in polar dielectrics causes excitation of rotary-forward motion solvated ions (clusters) and, hence, mass transfer. The frequency of this fields does not exceed tens of kilohertz the amplitude of intensity in solutions - tens volt on centimeter. Thus electrodes by means of which in volume of solution various in solutions configurations of an electric field are created, insulating 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, it can be necessary in a basis of technology of element enrichment of solutions of salts of metals. It is possible to expect, that will find appendices and other effects arising at influence of electromagnetic waves on solutions of salts which represent



set of solvated ions - clusters and not associate polar molecules of solvent-dielectric.

Values of the sizes of the solvated ions - clusters in solutions of the salts, certain in approximation of the oriented association of the polarized molecules of solvent ions and in approximation of existence of the self-coordinated field volume of a solution of salt, differ more than on the order. The frequencies of an asymmetric electric field corresponding excitation of rotary-onward of the solvated ions - clusters and certain in these approximations differ almost on three orders.

It is probable, that at concentration of salt in the solutions providing performance of the condition  $n_i \ll n_p$  where  $n_p$  – the number of solvent molecules in unit of volume,  $n_i$  - the same for quantity of ions, that is at concentration up to 0,1 g/l, it is possible to assume quantity of molecules of solvent, that: the potential becomes smaller on distances, smaller distances between most close located solvated ions. Then the density of a charge is that other, as density of the

polarizing charge formed by polarization of molecules of solvent. At significant concentration salvation process is more precisely described in approximation of existence of the self-coordinated field volume of the solution, and values of frequencies of the maximal display of effect of the electric field induced selective drift strongly depend on values of concentration.

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