

Electrophysical methods of separation of metal cations in the moving salts solution

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Abstract. The results of experiments on the excitation of the phenomenon of selective drift of solvated ions under the influence of an external "asymmetric" electric field to the circulating solution of calcium chloride and magnesium salts in a polar liquid dielectric – water are shown. The purpose of the experiments was to determine the influence of the field frequency and amplitude of the field strength on the excitation phenomenon, and the study of the operating characteristics of the testing apparatus - a dividing cell. The dependences of the separation efficiency of solvated cations from the frequency of the external field and the excitation threshold of the phenomenon from the field strength in the separation cell are defined.

1. State of the research

Earlier discovered phenomenon of selective drift of solvated ions under the influence of an external "asymmetric" electric field [1] for today found only one practical application in technology of the separation of cerium and yttrium cations formed during the investigation of the properties of spent nuclear fuel [2]. At the same time, the directions, in which the use of the phenomenon may bring a significant effect, sufficient clearly marked in a number of papers [3, 4, 5]. The main reason for the small number of practical uses of the observed phenomenon were two factors: a shallow study of the question of hardware implementation of technical systems that operate on the basis of the phenomenon, and the lack of experimental data on the influence of the electric field frequency on the effectiveness of separation processes solvated ions in moving (circulating) solutions.

This paper presents the results that once again confirm the importance of the observed phenomenon, its stability and reproducibility, as well as enabling to create a relatively simple experimental installation for searching of application to phenomenon of selective drift of solvated ions under the influence of an external "asymmetric" electric field. The term "asymmetric" electric field was introduced in experiments on excitation of selective drift of ions [1] and has an important meaning as the "normal" sinusoidal potential does not cause the observed phenomenon.

2. Experimental section

Block diagram of the experimental installation is shown in Figure 1. The main power source of variable frequency signal was audio-frequency generator GZ-109 1, the signal from which is fed to the input of pre-amplifier RUB2250 2 with its own power supply NES-100-12 3.



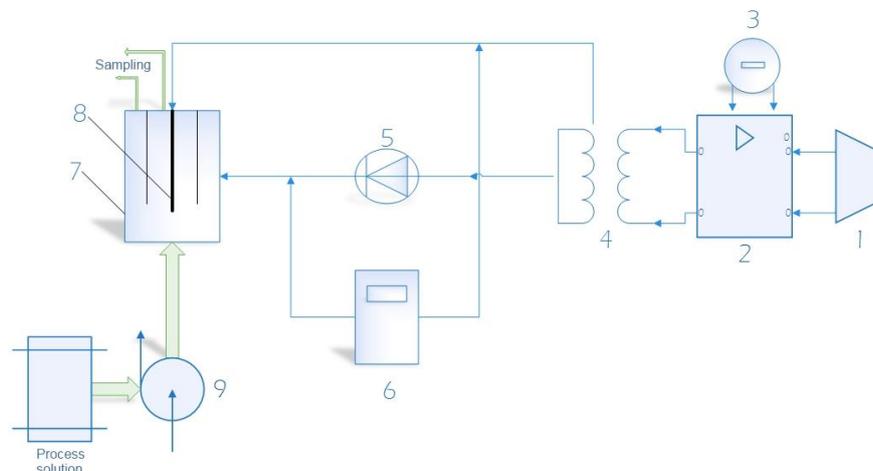


Figure 1. Block diagram of the experimental installation.

The potential, amplified by transformer 4, goes through the asymmetric waveform forming device 5 and applied to the central electrode 8 of the testing apparatus 7. Here, the second electrode is grounded. The signal was recorded with an oscilloscope 6. During the experiments the process solution from the tank was fed by a peristaltic pump 9 into a lower section of the testing apparatus. In experiments were used a dilute mixture of solutions of calcium and magnesium chlorides mark "chemically pure". A general view of the testing apparatus, which is a cylinder with arranged coaxially basic structural elements inside shown in Figure 2.

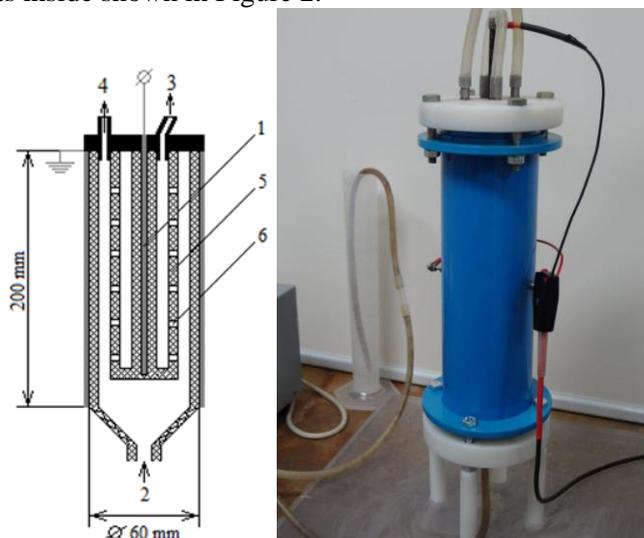


Figure 2. General view and a schematic representation of the experimental installation in the front section.

In the center is a potential electrode 1 of the steel rod, hermetically isolated from the process solution with polyvinylchloride pipe. Grounded steel electrode of cylindrical shape hermetically isolated from the process solution by the polyethylene film. The entire volume of the process solution supplied to the lower section of the installation, divided by polyethylene perforated cylinder 5 on the inner and outer zones. This cylinder performs the function of a separator between the zones of enrichment and depletion by target ions of the solution.

Perforation of cylinder 6 is formed as a vertical oblong openings arranged azimuthally symmetric along the generatrices of the cylinder along its entire surface. The openings allow moving ionic components of the process solution from one zone to another. Process solution fed through the nozzle

2 to the lower section of the installation and moving up along both zones with the same linear speed. Sampling at the top of the installation of each zone was carried out autonomously by the fittings 3 and 4 and the drain hose, equipped with special screw clamps. With these clamps carried regulating the output volume of the solution at inner and outer zones. Wherein, solution velocity in the inner zone is 4-7% higher than the velocity of the solution in the outer zone. In all experiments, the character of solution motion is corresponded to laminar liquid flow regime, and the linear velocity of the solution is not more than 4 cm / min.

During experiments solutions was sampled from both inner and outer zones at defined time intervals. Analysis of samples for magnesium and calcium ions was performed on atomic emission spectrometer with inductively coupled plasma iCAP 6300 Duo.

The result of the statistical analysis of experimental data showed that the measurement error in all of the experiments did not exceed in relative proportions 0.014 from average. It should be noted that using a device 5 (Fig. 1) was formed positive halfwave of the initial sinusoidal signal and volumes of fluid in inner and outer zones were exposed only to positive potential field of sinusoidal shape. This provided an abrupt movement of positively charged solvated cations to the electrode with zero charge 7 from the potential of a positively charged electrode 6 (Fig. 2).

The main objective was to detect a change of concentrations of calcium and magnesium cations in solutions at the inner and outer zones at certain range of frequencies. This fact would indicate that the selective transfer of one type of cation from the outer to the inner zone take place. In order to provide forced passage of cations from the outer zone into the inner, the linear velocity of the solution should be somewhat higher. Such a mode of fluid movement was mounted with clamps (Fig. 2) in each experiment. It has previously been shown [1] that the effects of changes in concentrations of ions in dilute solutions when applied to these asymmetric electric fields were observed at frequencies of hundreds of hertz. Considering this circumstance, in this paper, the research was carried out in the frequency range from 10 to 1500 Hz.

3. Discussion of experimental results

Fig. 3 shows the variation in the concentration of calcium ions in inner (curve 1) and outer (curve 2) zones in the frequency range from 20 to 180 Hz.

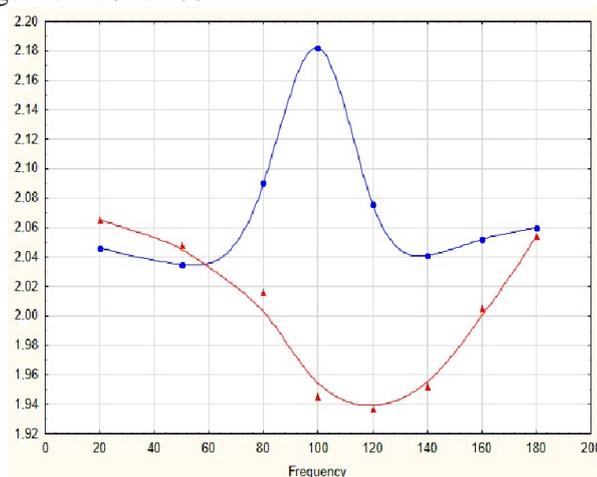


Figure 3. Influence of frequency on content of calcium ions in the separation zone at a voltage of 285 V (field strength in the cell 86.4 V/cm) and the initial concentration of 2.065 g/l. The circles marked concentration in the inner zone, triangles-concentration in the outer zone.

Earlier, in theory, it was shown [1] that the excitation of the phenomenon should be expected at frequencies of tens of Hertz, when a self-consistent field is formed in solution, and the size of the solvated ion-cluster, formed by the ion and molecules of solvent, forming solvation shell, is inversely

proportional to the square root of the salt concentration values in a solvent. The values of frequencies, by-turn, is inversely proportional to the value of the moment of inertia of the cluster.

As seen, in range of 80-120 Hz is observed a distinct increase in the content of calcium ions in the inner zone of the process solution with a clearly defined maximum. Importantly, that the corresponding concentration decrease takes place in outer zone, i.e. there is a redistribution of the concentration of one ion component between zones of process solution, which is essentially the separation process. Probably, that in this frequency range there is a deformation changes in the structures of the solvation shells of calcium ions, and, possibly, partial destruction of the external solvation layers, where the binding energy of the molecules of the solvation water with the central ion has a minimum value in comparison with the water molecules that composing the primary solvation shell. This circumstance give rise to conditions for directed transfer of desolvated ions in a potential field that, in accordance with the terminology adopted earlier, determines the effect of electrically induced selective drift [1]. Since each electrolytic solution has a property of electrical neutrality, then any change in its local electric charge in local volume - positive or negative - should lead to the instantaneous compensation of this charge by moving of the corresponding sort of ions in this volume. Thus, in this case, if calcium ions being transferred from the outer to the inner separating zone, producing in the latter the excess content of positively charged ions, then in an equivalent amount of magnesium ions should be transferred from the inner zone into the outer. This phenomenon can be interpreted as a process of electromigration transport, as well, as the exchange process between ions of different sorts. Thus, the decrease in the content of magnesium ions in the inner zone, and, on the contrary, increase in concentrations of these ions in the outer zone should take place. Indeed, if we look at fig. 4, it is obvious that a change in the concentration of magnesium ions in relation to the content of calcium ions in the inner and outer zones of separation in the specified frequency range has inverse relationship.

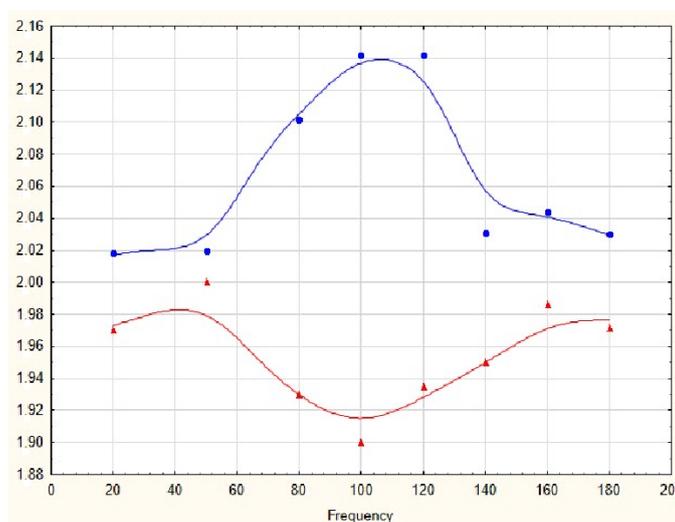


Figure 4. Variation in the concentration of magnesium ions in the separation zones at a voltage of 285 V (field strength in the cell 86.4 V/cm) and the initial content of 1.986 g/l. The circles marked concentration in the inner zone, triangles-concentration in the outer zone.

By its form, the frequency dependence of calcium ions content has a resonant character, i.e., the concentration extremes of these ions is defined in a fairly narrow range of frequencies. The same can be said about the frequency dependence of the content of magnesium ions (Fig. 5). However, the extreme values of the concentration of magnesium ions are observed in the separation zones at higher frequencies, i.e., when the external field energy is excess the threshold values for the resonance phenomena of the same calcium ions. This is due, apparently, to the difference in bond length of solvation shell with the central ion. The radius of the outer electron shell in magnesium ion is smaller than that of calcium ion, so the Coulomb interaction of the magnesium ion and the water molecules

that are part of solvation shells, forming a shorter bond that corresponds to higher eigenfrequency. Cations have only a coordinating effect on the solvent molecules in the first and second solvation spheres [6], and the number of solvent molecules in the solvation shell is determined by the shielding radius of cationic charge by cumulative charge of polarized solvent molecules [1, 7].

It has been shown in theory [1] that the directional drift of solvated ions also excited at the frequencies, corresponding to the various components of the rotational-translational motion of the system "ion - solvation shell", and at the frequencies, corresponding to the transition of the oscillatory motion into rotary.

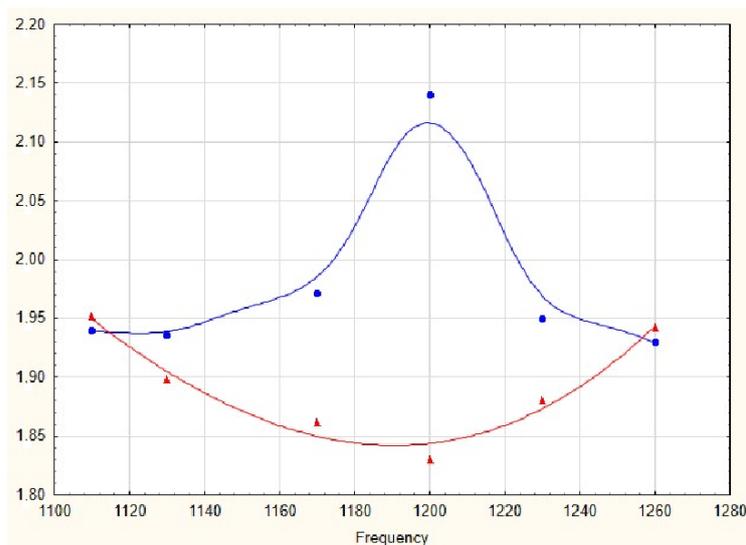


Figure 5. Frequency dependence of magnesium ions in the separation zone at a voltage of 285 V (field strength in the cell 86.4 V/cm) and the initial concentration of 1.931 g/l. The circles marked concentration in the inner zone, triangles-concentration in the outer zone.

The frequency values amounts to units of kHz. Resonance can be expected:

- at the frequency of the cooperative rotational motion of the molecules of H₂O, combined in the solvation shell relatively to an axis, passing at a distance, equal to the outer radius of the solvation shell from the center of gravity;
- at the frequency of the cooperative rotational motion of the molecules of H₂O, combined in the solvation shell relatively to the center of gravity of the solvated ion-cluster;
- at a frequency of rotational movement of the cluster as a whole;
- and the frequency of transition of oscillatory motion into rotational.

Formula for the calculation of the defined frequency values are obtained and given in the monograph [1].

Consequently, for the resonant deformation of solvation shells of magnesium ions will require higher energy value of an external electric field, which will increase with increasing frequency. Theoretical understanding of the electrically induced drift of solvated ions indicate that one of the factors causing this phenomenon is the value of the amplitude of the electric potential, which determines the intensity of the electric field. Experiments conducted at voltage value of 40 V (field strength in the cell 12.1 V/cm), have shown that within the errors of measurement the concentration of calcium and magnesium ions did not change and remained at their original values. Since the potential energy is the main characteristic of the electric field, apparently, there is a threshold value of electric field strength, which determines the minimum energy, which in a certain frequency range causes an effect of deformation of solvation shells of ions and consequently, their selective electrically induced drift. In this case, a threshold value of electric field strength is in the range from 12 to 100 V/cm. Depending to examine method of separation, measurements data define general separation factors of competing calcium and magnesium cations. In order to talk about single separation factor, complete

information on all possible mechanisms of selective mass transfer is required. Hypothetically, electrically induced drift at the interface between the outer and inner zones is the prevailing process, leading to the exchange of ions of different sorts between these zones. Additional moving force for moving ions from the outer zone into the inner, along with the electromigration transfer, can be an excess of hydrodynamic pressure, which occurs due to the difference in the velocities of the solutions in the inner and outer zones. In this connection, the influence of the ratio of velocities of the solutions in the separation zones on separation effect is the question, requiring separate consideration. Simultaneous mass transfer of a certain quantity of competing ions for a certain period of time through the border of outer and inner zones on the entire area of their contact can apparently be interpreted as a single separation factor.

4. Conclusion

1. The conducted experiments proved the ability to use previously discovered phenomenon of electrically induced selective drift of solvated ions in salt solutions under the influence of asymmetric electric field for the organization of the technological process of solutions enrichment by the target metal.

2. It was found that the excitation of effect of the selective electrically induced drift of solvated ions may be observed in at least in two frequency ranges. Within each of the intervals are the frequencies corresponding to the Eigen frequency of the system "ion - solvation shell" as a spherical rotator (rotation of solvation shell around the central ion) or as a system of rigidly connected central ion and a hollow shell.

3. Frequency dependence of the content of calcium and magnesium ions in the mixture of their chloride solutions was studied and was showed, that for each of the competing ions there is a certain frequency range in which the speed of the directional drift of one of them increases significantly.

4. It is shown that effect of ions separation depends essentially on the value of supplied potential - the main characteristics of the external electric field.

5. The technological scheme of the process of separation of ionic mixtures by the method of electrically induced selective drift with an applied alternating electric field was developed and an experimental installation that implements this process was constructed.

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