

Investigation of the influence of temporary energy depositions on the structure of aqueous solutions

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Abstract

The researches results of properties of inorganic aqueous solutions of different chemical composition depending on physical impact parameters are presented in the article. It is shown that inorganic aqueous solutions are of the molecular nature and cannot be considered as electrolytes. It opens up new possibilities for development of innovative technical solutions in chemical technology.

Key words: AQUEOUS SOLUTIONS, MICROSTRUCTURE, NON-STATIONARY ENERGETIC IMPACT

Introduction

Realistic view on microstructure of inorganic aqueous solutions can have dominant influence on decisive impact on competitiveness of the created chemical and hydrometallurgical technologies, and also can be conducive to improvement of processes of leaching of mineral raw materials, electrolytic obtaining of various products, avoid the difficulties with recovering of etchant solutions in mechanical engineering, etc. For development of technological processes in chemical and metallurgical industry, the significant growth of chemical systems researches with an aim of their practical application takes place. The arising deterioration of mineral resources of the industry stipulates increase in researches of multicomponent inorganic aqueous solutions. Development of innovative solutions in chemical technologies, where inorganic aqueous solutions are used, requires realistic vision of microstructure and properties of solutions within a wide range of state parameters. The modern level of development of the solutions theory does not meet the requirements of practice and considerably lags behind the level of industrial technologies. Realistic vision of liquid microstructure is especially important for development of nanotechnologies, where stable formation of structures is required. Therefore, a relevant task is not only determination of aqueous solutions microstructure, but also control of a microstructure changes with use of change consistent patterns of solutions various properties in case of change of their chemical composition, concentration and parameters of external effects. However, although there is a large number of conflicting experimental data, the principle of spontaneous electrolytic dissociation at transition of solid substances into aqueous solution is considered as the basis of microstructure formation of aqueous solutions (electrolytes). Meanwhile, set of new data affects significantly the concept “electrolytic dissociation”, thus, also there are various theories and assumptions. The problem of ions solvation in solution is discussed especially attentively, as the assumption of ions solvation in principle is intended to reconcile the D. I. Mendeleev theory of solutions

with the theory of spontaneous (i.e. occurring at transition of solid body to the liquid state) electrolytic dissociation of Arrhenius S. In particular, it is possible to find:

- possibility of metal oxides association in solution-melts [1] with metal ions solvation by molecular formations;

- “the transition from a standard gaseous state to a standard liquid state should be considered as solvation” [2, p. 248]; i.e. practical data force to present a solvation in the form of simple phase first order transition (according to standpoint of advocates of ideas that liquid is condensed gas);

- liquid conduction is provided with a solvated electron – the “hydrated” electron, i.e. the electron, taken by the environment as a result of polarization of the molecules surrounding it, is a powerful reducer, “applied for synthesis of metal ions in uncommon oxidation levels” [4].

Therefore, we undertook a complex of researches on establishment of the principle of electrolytes microstructure formation, in particular, of research of vanadium mesogels formation on probes made of various materials. In paper [5], the result of researches of vanadic gel formation on a metal probe consisting of aqueous solution of vanadium pentoxide, where molecule structure on a probe is established ($12V_2O_5 \cdot x480H_2O$), was published for the first time by Suleymenov I. E. However, the analysis of the current scientific and technical literature shows that although more and more works, which authors consider the microstructure of liquid systems from the standpoint of the molecular theory, are published [e.g., 5, 7], the great majority of researches on development of innovative technological processes are based on the outdated ideas of a microstructure of inorganic aqueous solutions. In their researches, the ideas of the molecular nature of inorganic aqueous solutions are used [e.g., 7]. At the same time, the ideas of microstructure formation of oxide melts and inorganic aqueous solutions on the basis of the principle of spontaneous electrolytic dissociation continue to affect negatively the development of chemical science

and technologies [6]. In order to ground the realistic views on electrolytes microstructure, the researches on determination of electrolytes conductivity type, on determination of the principle of electrolytes microstructure formation, on influence of non-stationary power impacts on phase transitions in chemical systems with the involvement of electrolytes, etc. were being conducted for many years. The works of D.I. Mendeleev, M. Faraday, H. Davy et al. were taken as theoretical suppositions for complex of systematic researches. However, the works [6, 7] and numerous other authors' works, which published data on microstructure of liquids of various types and chemical composition, were used. In particular, it should be noted that M. Faraday's works were decisive in development of scientific ideas of chemical bond nature, development of atomic and molecular theory, practical application of electrochemical processes, magneto-optics, etc. These works were used at the management of researches on influence of non-stationary power impacts on chemical systems of various types. From the works of M. Faraday, we used the following: identity of energy performance in case of interaction of material objects and quantum nature of electric current [8]. These statements (along with D. I. Mendeleev's works on a structure of inorganic aqueous solutions) give the opportunity to explain experimentally the nature of these solutions in spite of difficulties in such researches performance.

Some experimental data, which explain the principles of microstructure formation of inorganic aqueous solutions, are stated below and give the grounds for development of innovative chemical technologies.

Experimental

At the first stage of researches, the analysis of diagrams of state of type water– chemical compound was carried out. It was shown that on state diagrams, the liquidus curve is described correctly by Le Chatelier in the case if molecular weight of chemical compound is determined correctly. The example of such analysis is given below (the analysis of state diagram is conducted by PhD Yu.I. Ogorodnikov). The calculated type of liquidus curves according to Le Chatelier equation and boundaries liquid-vapor according to Van't Hoff equation is presented in Fig. 1 by solid lines. The experimental data from reference books are shown by points.

It should be noted that liquidus curves on this state diagram are described by Le Chatelier equation only if the formula of fluorohydrogen acid is of the form H_2F_2 , but not HF. Therefore, a new formula of fluorohydrogen acid was suggested.

At the second stage of work, the impact of parameters of electric current on conductivity of inorganic aqueous solutions was investigated. Some experimental results, which from our standpoint show reality of ideas of inorganic aqueous solutions molecular nature most brightly and which can form the basis for improvement of technological processes, are presented.

Researches of influence of electric current parameters on the aluminate solutions state including industrial solutions of aluminous production were conducted inasmuch as behavior of these solutions differs from behavior of inorganic aqueous solutions of other chemical composition.

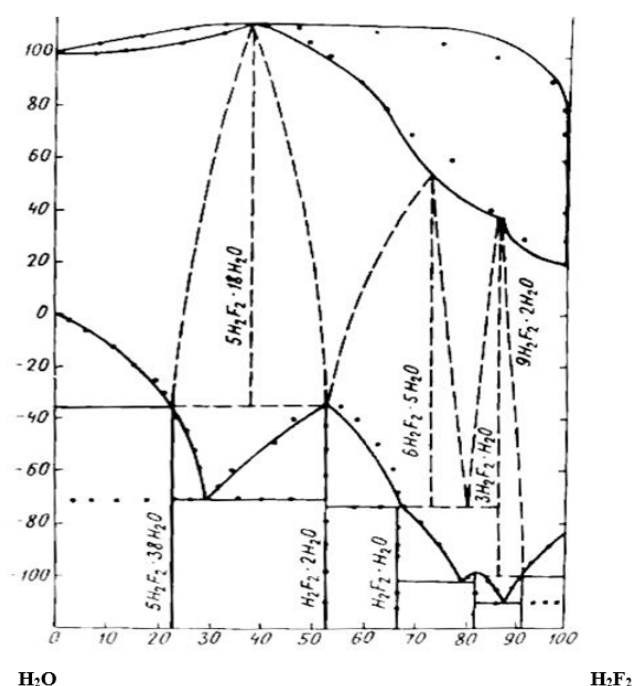


Figure 1. The analysis of state diagram $H_2O - HF$. The data on conductivity of aluminate solutions are presented in Table 1.

Table 1. Conductivity of aluminate solutions (platinum electrodes, concentration of $Na_2O-269.3$ g/l, the caustic module 1.7)

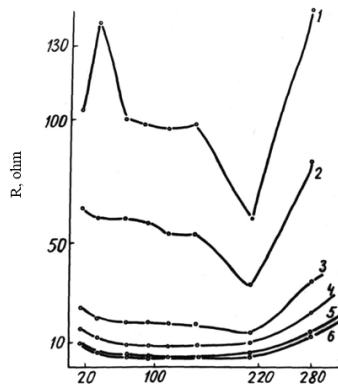
| Current frequency, Hz | Temperature, °C | | |
|--|-----------------|------|-----|
| | 25 | 50 | 70 |
| Conductivity, $ohm^{-1} \cdot cm^{-1} \cdot 10^{-2}$ | | | |
| 20 | 4,5 | 7,6 | 4,8 |
| 30 | 5,7 | 10,0 | 6,5 |
| 40 | 5,6 | 12,1 | 7,1 |
| 50 | 5,9 | 13,5 | 7,5 |
| 60 | 6,2 | 13,5 | 7,3 |
| 70 | 6,6 | 13,5 | 8,0 |
| 80 | 6,7 | 14,4 | 8,2 |
| 90 | 7,1 | 14,7 | 8,4 |
| 100 | 7,4 | 15,1 | 8,7 |

| | | | |
|-----|------|------|------|
| 120 | 7,9 | 16,7 | 9,2 |
| 140 | 8,6 | 17,2 | 8,9 |
| 160 | 9,3 | 17,6 | 9,3 |
| 180 | 9,6 | 18,1 | 9,9 |
| 200 | 9,7 | 18,1 | 10,0 |
| 250 | 10,0 | 20,0 | 11,3 |
| 300 | 10,2 | 21,8 | 12,5 |
| 400 | 10,3 | 24,3 | 14,0 |

As can be seen from the Table, the conductivity value is maximum at 50°C that can characterize the structural transformations in solution with temperature increase. In case of conductivity measurements of various types of liquid systems, it was found out that recalculation of liquid resistance into conductivity can conceal the deviations from the standard regularities. Therefore, data on resistance of the aluminate solutions depending on current frequency are given in Figure 2. As it is seen from the Figure, it is difficult to explain aluminate solutions behavior at low current frequency by features of cations and anions transport in solution. The factor of increase in concentration of sodium oxide in solution does not determine the consistent pattern of change of solution resistance.

As a part of study, the precipitation possibility of decomposition of the aluminate solutions by means of non-stationary electric currents was established. At that, in certain cases, not only decomposition precipitations by 3-4 times, but also the maximum depth of precipitation of aluminum oxide were reached under laboratory conditions. According to literary data this depth is reached during a long lapse of time (about one year and more).

The obtained data can form the basis for development of improvement methods of alumina technology. Thus, there is a probability of obtaining of production wastes, which can be recovered by the simplified technologies and without environmental load.



Designations of curves: 1 – 20 Hz, 2 – 30 Hz, 3 – 50 Hz, 4 – 100 Hz, 5 - 150 Hz, 6 – 200 Hz.

Figure 2. Dependence of aluminate solutions resistance on concentration of sodium oxide and frequency of electric current

Data on change of aluminate solutions resistance (Na_2O 250 g/l and $a_k=1.7$) depending on current intensity when using a double-electrode cell are presented in Table 2.

Table 2. Data on change of aluminate solutions resistance

| mA | 1 | 2 | 6 | 10 | 20 | 40 | 70 | 100 | 150 |
|-----|----|------|------|----|----|----|------|-----|------|
| Ohm | 36 | 36.7 | 37.5 | 33 | 30 | 21 | 14.6 | 13 | 11.3 |

At further increase in current intensity up to 500 mA, the solution resistance reduced to 9.5 Ohms. It is obvious that maximum transient of resistance when current change is against continual theories of solution structure. It was revealed that solution “remembers” changes in resistance indications. In case of passage of current for a long time (60 – 120 min), resistance indications were decreased, stabilized and kept for some time after de-energization of electrodes. After holding without electric current impact, the solution resistance becomes equal to initial indications. During research of elementary particles discrete flow impact (electric current was according to M. Faraday) on aluminate solutions, it was shown:

- dissolution of aluminum in inorganic aqueous solution can significantly depend on electric current parameters and application methods of electric signal to system;
- atoms of alkaline metals can be implanted into lattice of metal aluminum under the influence of electric current;
- in case of sodium ion evolution, chemical process with intensive heat evolution must take place on an aluminum electrode, i.e. the reaction of metal sodium with water is thermally active; but it is not observed;
- aluminum transition into solution is interpreted as nuclear interaction with sodium aluminate formation that can lead to temperature changes in solution volume; but this process is not observed.

Experimental data cannot be explained from the standpoint of charged atoms (or ions) in sodium aluminate solution.

Then, the influence of non-stationary electric currents on system metal–aqueous solution was researched. The sequence of unusual data was obtained. In particular, transition into aqueous solution of metals alkalis, which are considered as indissoluble. Dissolving was carried out in a normal double-electrode temperature-controlled cell at temperatures from 25 to 75°C. Metal molybdenum was dissolved in aqueous solution of potassium hydroxide. In Figu-

re 3, the dependence of dissolving rate of metal molybdenum on current intensity in case of KOH concentration of 50.9 g/l, at temperature of 25°C and the current frequency of 50 Hz. The alternating electric current with intensity of 200 - 550 mA, voltage of 1.0 - 3.2 V and various frequencies was overlaid on two electrodes made of metal molybdenum (diameter is 1.3 mm). Molybdenum dissolving rate is 0.5 - 4.3 mg/min. It is significantly that molybdenum was dissolved only in case of potassium hydroxide concentration of 10% and less. Dissolving rate of molybdenum is disproportional to current intensity, and dissolving process stops in case of increase in current frequency and electrodes passivation by molybdenum oxides; electrodes passivation rate decreases with increase in current intensity, and electrodes passivation is not observed at 500 mA and low current frequency; electrodes passivation rate increases at temperatures 25 - 45°C, and in some cases, it increases by 10 times; at temperature over 75°C, molybdenum is not dissolved at any electric current frequencies and current intensity.

It is established that with sequential increase of current intensity, the current frequency, at which the reaction stops completely: at temperature 25°C and current intensity of 90 mA, the reaction stops with a current frequency of 66 Hz, in case of 200 mA - 130 Hz, in case of 360 mA - 350 Hz, in case of 450 mA - 400 Hz; at temperature 75°C and current intensity of 200 mA, the reaction stops in case of 160 Hz, 300 mA - 330 Hz, 500 mA - 700 Hz. The reaction beginning was fixed according to beginning of gas bubbles evolution.

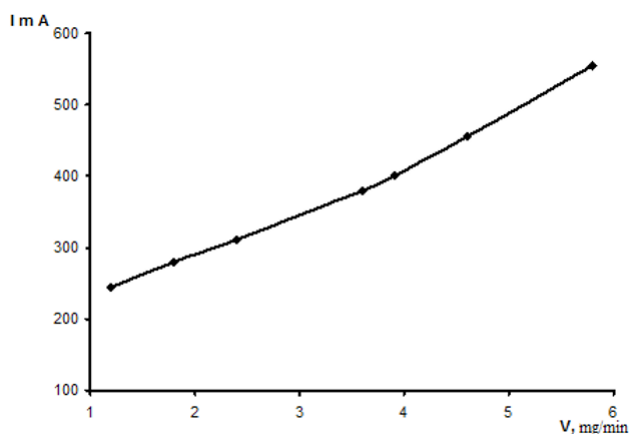


Figure 3. Dependence of rate of metal molybdenum transition to solution on current intensity at frequency of 50 Hz (50.9 g/l KOH), $t = 25^\circ\text{C}$

Depending on current intensity, the reaction of molybdenum dissolving was activated in case of reduction of current frequency to the following values:

100 mA - 20 Hz, 225 mA - 30 Hz, 325 mA - 50 Hz, 420 mA - 70 Hz, 500 mA - 90 Hz. When using of new electrodes with current frequency higher than 140 Hz for specified values of current intensity, molybdenum was not dissolved.

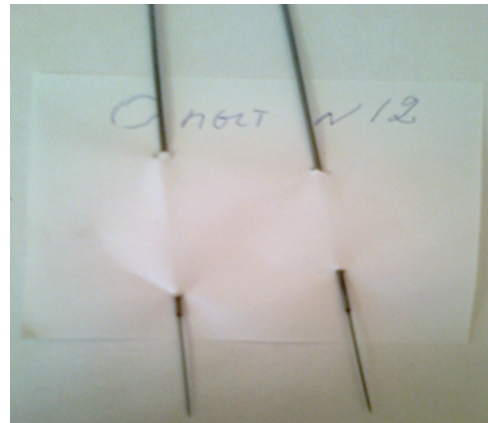


Figure 4. Configuration of a molybdenum electrode after dissolving

In a Figure 4, the form of molybdenum electrode after dissolving is presented.

Data on different metals dissolving with the use of non-stationary currents can serve as the basis for development of the new ecologically acceptable etching methods of metal products in mechanical engineering without obtaining of etching reagents requiring complex recovering technology. In particular, the opportunity of metals dissolving in alkaline solutions by means of non-stationary electric currents can be used for development of non-waste technology of metals etching.

As pointed out above [5], I.E. Suleymenov Doctor of Chemistry set up direct experiment on microstructure determination of aqueous solution of vanadium pentoxide. The experimental technique was very simple. The probe of various materials was put into aqueous solution of vanadium pentoxide. The gel precipitated on this probe. In Figure 5, vanadium pentoxide hydrogel precipitated on copper probe is shown (in this case, gel of composition $12\text{V}_2\text{O}_5 \times 480\text{H}_2\text{O}$ was evolved).

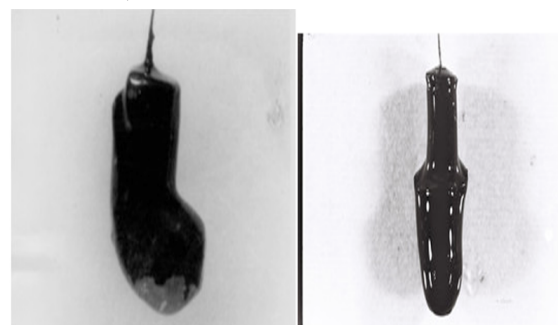
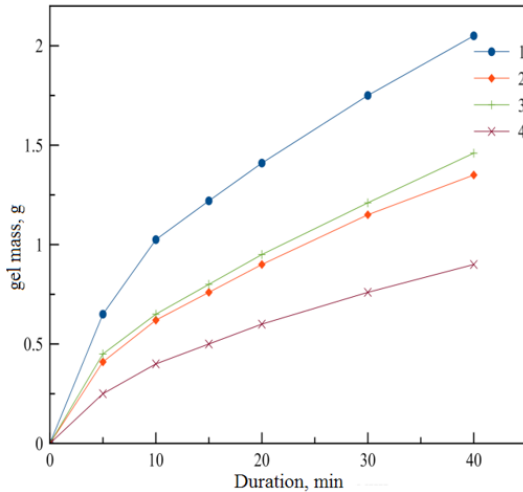


Figure 5. Vanadium pentoxide hydrogel on a copper probe

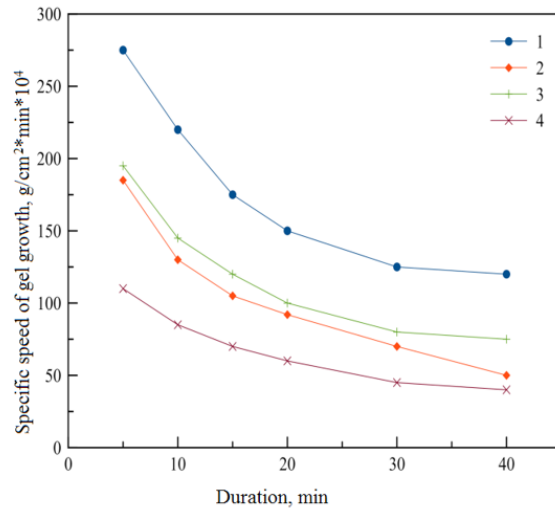
The electrochemical nature of precipitation of pentoxide vanadium hydrogel on a metal probe [9] is determined experimentally. As the molecular nature of solution is obvious, the experiments on mechanical oscillations impact on aqueous solution of vanadium pentoxide were conducted. It was established that distribution density of substance of hydrogel by volume is non-uniform; this served as the basis for these

experiments. The impact of ultrasonic vibrations on the process of mesogels formation was determined. Solution of vanadium pentoxide was processed by ultrasonic vibrations of various frequencies. After that, the copper probe was put into solution, and the process of mesogel formation was recorded.

The experiments results are given in Figure 6.



(a)



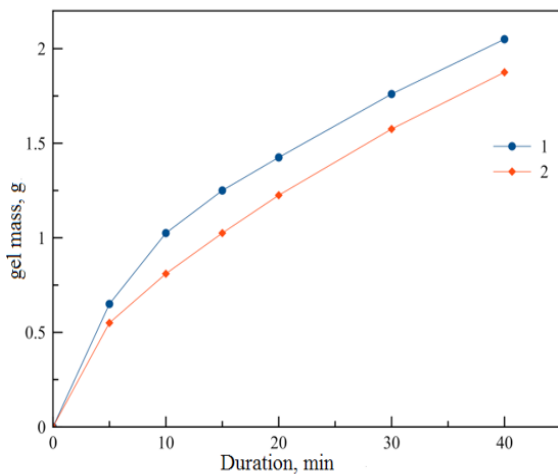
(b)

Frequency kHz: 1 - 15; 2 - 22; 3 - 35; 4 - without processing

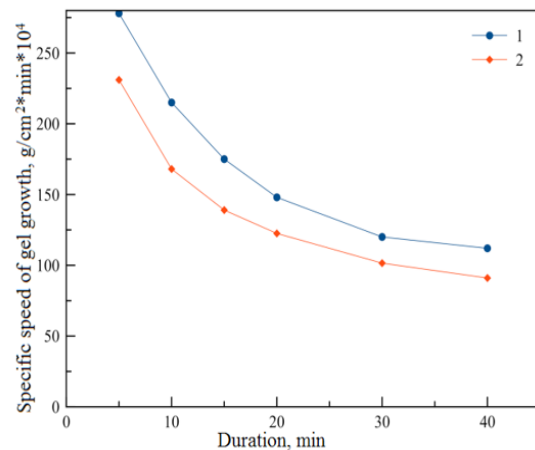
Figure 6. Dependence of gel mass growth on time after solution processing by ultrasonic vibrations, kHz (a) and dependence of specific speed of gel growth on time after solution processing by ultrasonic oscillations, kHz (b)

According to data of Figure 8, it is obvious that solution processing by vibrations of various frequencies intensifies the process of gel formation. The lower vibration frequency is, the higher gel formation process speed is. It can be a consequence of reduction

of the solvation shell round a molecule of hydrated vanadium pentoxide. The frequency 15 kHz should be considered as optimum in the range under investigation.



(a)



(b)

Figure 7. Dependence of gel mass growth on time (a) and dependence of specific speed of gel growth on time (b): initial (1) and in case of repeated processing of solution after 21 hours of holding (2). Vibration frequency is 15 kHz.

It is obvious that influence of mechanical oscillations on aqueous solution of vanadium pentoxide causes changes in structure of solutions. I.e., it is shown that any energetic impact on liquid can significantly affect its microstructure.

Conclusions

The researches have shown that conductivity value of inorganic aqueous solutions in case of change of temperature and electric current frequency cannot be explained by anions and cations transport in liquid volume. The experiments have proved that electrolytic dissociation cannot explain a series of abnormal phenomena when passing through inorganic aqueous solution of an electric current. It is shown that any energetic impact on inorganic aqueous solutions can influence significantly their microstructure.

Ideas of molecular nature of inorganic aqueous solutions and a series of found phenomena taking place in solutions under the influence of non-stationary energetic impacts can be used for improvement of chemical and hydrometallurgical technologies.

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