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DETERMINING A DEPENDENCE OF THE EFFECT OF INERT ELECTROLYTE ON A DIFFICULTLY SOLUBLE SALT UNDER DIFFERENT CONDITIONS

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Проаналізовано залежність впливу похідних розчинності (ПР) шести важкорозчинних неорганічних солей у воді і інших розчинниках при впливі на них інертним електролітом. Солі були обрані на підставі заряду аніона, який коливався від 1 до 6. Було встановлено вплив на цей процес як діелектричної проникності розчинника і величини заряду аніона, так і йонної сили розчину

Ключові слова: коефіцієнт активності, дисоціація, узагальнений момент, важкорозчинна сіль, інертний електроліт, солевой ефект

Проанализирована зависимость влияния произведения растворимости (ПР) шести труднорастворимых неорганических солей в воде и других растворителях при воздействии на них инертным электролитом. Соли были выбраны на основании заряда аниона, который колебался от 1 до 6. Было установлено влияние на этот процесс как диэлектрической проницаемости растворителя и величины заряда аниона, так и ионной силы раствора

Ключевые слова: коэффициент активности, диссоциация, обобщенный момент, труднорастворимая соль, инертный электролит, солевой эффект

1. Introduction

It is generally known that during melting of the electrolyte thermal motion of molecules is put above the energy of the crystal lattice and there occurs a transition into the liquid state. Liquids are similar in structure to a solid body, with the exception of the intramolecular vibrations that are virtually non-existent in a solid body [1].

When inorganic salt is dissolved in water or other polar solvent (ethyl alcohol, liquid ammonia or hydrogen fluoride), destruction of the crystal lattice is carried out due to the action of the solvent. This leads to the polarization of dissolved salt as a result of very high dipole moments, as well as the solvation of cations and anions by the solvent molecules.

The ions being formed possess a charge density Q, which depends on the ratio of the magnitude of size and charge values. The size of ion depends on the position of the atom in the periodic table, and the charge values – on the number of electrons lost or acquired by the atom.

The influence of the ionic atmosphere will lead to the inhibition of cations and anions, which results in a significant decrease in the mobility, which is called the coefficient of activity. Without considering the dielectric permittivity of electrolyte, activity coefficient is equal to:

$$lg\,\gamma = -0{,}51 \cdot z^2 \cdot \sqrt{I}, \qquad (1)$$

where z^2 is the charge of cation/anion, I is the ionic strength of solution (a measure of the total electric field intensity per unit volume of solution) [2].

In an infinitely diluted solution, the activity coefficient in the Debye-Hückel equation can be considered equal to unity. In an actually existing solution, there are effects of inter-ion interactions in the solution, and electrostatic forces of interactions in the solution lead to the fact that activity coefficient of cation and anion deviates from unity. Equilibrium is reached in a saturated solution (for example, for lithium orthophosphate it is):

$$Li_3PO_4 \leftrightarrow 3Li^+ + PO_4^{3-}. \qquad (2)$$

The solubility of different salts in the same solvent (for example, water) is quite different. It is measured in grams per 100 cm^3 of the solvent. There is a conditional division into practically insoluble substances, difficult-to-solve (or poorly soluble) substances, and soluble substances.

Thus, the soluble ones in the given solvent are considered to be the substances whose solubility exceeds 1 g/100 cm^3 of the solvent. The difficult-to-solve ones in the solvent are the substances whose solubility is less than 1 g/100 cm^3 of the solvent but higher than 0.01 g/100 cm^3 of solvent at 293 K.

2. Literature review and problem statement

One of the most important theoretical problems in physical chemistry is the mismatch between strong electrolytes and the Arrhenius theory [3]. Strong electrolytes constitute salts, strong bases and strong acids, whose solutions are wholly dissociated in water. Devising a theory of strong electrolytes has been one of the tasks of physical chemistry up to now [4]. This is being tackled by chemists and physicists in different countries, including Ukraine. Thus, the problem is investigated with the power of organic acids in different solvents (which are also the activity coefficient of weak electrolytes), as well as the problem is explored of the activity of ions in alloys and melts (which are actually solutions as well, only at high temperatures) [5–7].

The cause of all these problems is the difficulties in determining the activity of strong electrolytes. This can be done in various ways, for example, on the basis of determining real increasing activity coefficients of difficultly solved salts [8].

Specialists in physical chemistry from Russia are trying to solve these problems mainly through physical research into solutions – by conductometry, potentiometry, and other studies related to the study by physical procedure [9].

In the United States and the United Kingdom (as well as in other English-speaking countries of the world), generally accepted are theoretical studies based on known electrostatic laws (in particular, the Coulomb law). Specifically, this substantiated the application of the theoretical ideal model of Debye-Hückel; in this case, with deviations from a perfect solution. Both in Russia and other countries, the result is determining the dependence of deviations from the solution [10].

It is known that strong electrolytes do not comply with the Arrhenius equation. Studying them in terms of physical chemistry does not make sense as they wholly dissociate into ions. Weak electrolytes at the same time dissociate into ions in a relatively narrow assigned range, and, due to this reason, the theory of Debye-Hückel electrolytes holds for them in real solutions. This attracts considerable interest in them from theoretical studies on physical chemistry [11].

Such a separate position of weak electrolytes (which include difficultly solvedsalts) is due to the fact that the soluble salts experience extremely strong deviations because of other factors (depending on the nature of the salt). Salts that are insoluble in water practically do not change their solubility in the given solvent under any conditions.

For this reason, an additional unit to measure the solubility, in addition to a standard one, is applied for the difficult-to-solve salts. It is called the solubility product (SP). There is always an equilibrium in the saturated solution of a difficult-to-solve salt (2) [12].

In this case, the Debye-Hückel theory of strong electrolytes describes the behavior of ions and the magnitude of salt solubility not only for the solutions in water but in other polar solvents as well. An example of non-aqueous polar solvents is such liquids as anhydrous hydrofluoric acid, alcohols, acetone, as well as other substances.

This is linked to the fact that, similar to water, these and other polar solvents possess ionizing ability, that is, lead to the complete substance disintegration into ions. The ionizing ability of ethyl alcohol is analogous to that of water, but has a slightly less power because of the lower generalized momentum of ethanol and its having an electro-donor hydrocarbon radical.

$$\Pi_{\mathrm{p}}(\mathrm{MgSO_4}) = \{\mathrm{Mg}^{2+}(aq)\}\{\mathrm{SO}_4^{2-}(aq)\}. \tag{3}$$

Solubility of the salts, which are strongly polar substances (typically of the ionic structure) usually increases with increasing dielectric permittivity of the solvent, and falls at decrease.

However, the solubility does not depend directly on dielectric permittivity of the solvent. Solubility limit of any dissolved substance in any solvent, in line with the Semenchenko-Shakhporonova theory, is determined by the equality of the generalized momentum, which is a first approximation of the function of magnitude of dielectric permittivity of the solvent.

The solubility is maximal if the generalized momentum of the dissolved substance is equal to the generalized momentum of the solvent.

Generalized momentum for any substance is equal to the ratio of dipole momentum of the molecule to the volume, for example:

$$\mu_{об}=\mu/V. \tag{4}$$

where V is the volume of the molecule of the given substance.

Among the known solvents that have different dielectric permittivity, there are no those with such a high dielectric permittivity at which $\mu_{\text{genetalized moment (sol)}}$ would be equal to $\mu_{\text{genetalized moment (salt)}}$.

That is why diagrams of substance solubility in the solvents show that the growth curve of salt solubility does not reach a maximum with increasing dielectric permittivity of the known solvents [12].

Dielectric permittivity and the dipole momentum of solvents are closely related to the polarity of solvent molecules. The polarity of the solvent depends first of all on the magnitude of the degree of ionicity of its separate bonds. This explains, for example, good solubility of nonpolar substances in the non-polar solvents [13].

However, the solubility product of difficult-to-solve salts is substantially affected not only by a change in the temperature, but also by additionally dissolved electrolyte (which is actually salt, well-soluble in the given solvent). This electrolyte is called inert and the effect – salt effect.

This effect can lead to both the increasing action (the solubility of difficultly soluble salts will grow) and decreasing action (the solubility will fall) [14].

Solubility product of difficultly soluble salts in any polar solvent is determined by the reversible reaction – impact on the solid crystalline lattice of salt, solvent molecules. Polar solvent possesses a prominent part of its molecules not in the molecular but in the ionic state. Further, under the law of Coulomb, ions are attracted to the salt ions and cause its dissociation, due to the small share of covalent bond in the substances of typically ionic structure, such as inorganic salts. Solubility product of any salt in a polar solvent is determined in aggregate by equation:

$$\Pi_{\mathrm{P}}(K_A)=[\mathrm{K}^+]+[\mathrm{A}^-]\cdot f(\mathrm{K}^+)\cdot f(\mathrm{A}^-). \tag{5}$$

If the solution of a difficultly soluble salt consists of equally-charged cation and anion, regardless of the charge magnitude ($\mathrm{Li^+F^-}$, $\mathrm{Ca^{2+}CO_3^{2-}}$, $\mathrm{Al^{3+}PO_4^{3-}}$, $\mathrm{Zr^{4+}(P_2O_7)^{4-}}$), then there will be an equilibrium in the solution.

Activity coefficients with an increase in the degree of charge will fall the faster the larger the charge. However, in the presence of ions with different charge (for example, $\mathrm{Li_3PO_4}$) of molecule in the solution the solubility product will be derived based on the fact that the concentration of cation $\mathrm{Li^+}$ is actually three times higher than the concentration of phosphate anion $\mathrm{PO_4^{3-}}$. This follows from the starting composition of salt [15].

The activity of several identical ions will be identical as well, since there occurs a steady process of interaction between each other in the solution.

$$\Pi_P(K_3A)=3[K^+]\cdot[A^-]\cdot 3f(K^+)\cdot f(A^-). \tag{6}$$

It is also known that the strength of the impact of ion, having a greater absolute charge, has a stronger effect. This magnitude is equal to raising the power equal to the absolute magnitude of the charge (regardless of whether a charge is positive or negative).

It is of great interest to resolve the issue on determining a dependence of an increase in the solubility of difficultly soluble salt in various solvents with inert electrolyte under identical ionic forces.

The modern theory of electrolytic dissociation is based on the activity coefficients of electrolytes. The theory was created by the Swedish physicist and chemist Arrhenius in 1887 who assumed the disintegration into ions in solutions even without participation of external forces, such as electric current. Subsequently, P. Debye, G. Lewis and E. Hückel created the theory of strong electrolytes, which defined the problems of inter-ion interaction. The problems on determining the inter-ion interaction include the inability to take into account the interaction between all particles between themselves in solutions or melts, depending on the concentration of the solution.

Infinitely diluted, or the perfect solution, is the solution where the activity coefficient is equal to unity. In practice, activity coefficient varies by the type of solution, dielectric permittivity, and ionic strength.

The main problem is to determine the impact of the aforementioned factors on the real solutions, where there is both a weak electrolyte (difficultly soluble salt) and a strong one (inert electrolyte). This problem has remained unresolved so far, as it can only be determined experimentally, however, the theory of strong electrolytes allows us to assume the properties of such solutions, as well as activity coefficients in different media to determine the multiplying factor.

3. The aim and objectives of the study

The goal of present study is to establish the dependence of influence of inert electrolytes in the solutions with different total ionic strength, various dielectric permittivity under conditions of different solvents.

To accomplish the set goal, the following tasks have been set:

– to determine the multiplying factor for six difficultly soluble salts at a large number of different conditions of the experiment;

– to prepare solutions of 54 difficultly soluble salts for obtaining which different solvents and different ionic strength were employed, but with the same inert electrolyte for all substances;

– to determine the multiplying factor based on the ratio of magnitudes of solubility product (Solbulity Product 2/Solublity Product 1).

4. Materials and methods for examining the enhancing action of inert electrolyte at different ionic strength of solutions

We used the following materials in the course of research:

1. Six different examined inorganic salts.

– LiF (lithium fluoride);

– Li_2CO_3 (lithium carbonate);

– Li_3PO_4 (lithium orthophosphate);

– H_4ZrO_4 (ortho zirconium acid, related to the difficultly soluble salts due to its low solubility product);

– Na_5IO_6 (sodium orthoperiodate);

– Na_6TeO_6 (sodium orthotellurate).

2. Three polar solvents that have been selected by the degree of increasing the relative dielectric permittivity – ethyl alcohol (C_2H_5OH), acetonitrile ($CH_3{-}C{\equiv}N$) and water ($H{-}O{-}H$). Information on the relative dielectric permittivity is given in Table 1.

3. Inert electrolyte, which did not have common cations/anions with none of the selected salts. We selected cesium chloride (CsCl).

4. We prepared three solutions with varying ionic strength of cesium chloride whose calculation was performed based on its molar concentration. The influence of ionic strength of the difficultly soluble salts themselves is minimal due to the very low solubility products compared to such magnitude of cesium chloride, so it was decided to neglect it.

5. Qualitative analysis was conducted on a change in the dynamics of solubility product using chromatographic and spectroscopic analyses for determining the concentration of cations.

Theoretical substantiation of research techniques is that the salt effect, based on the theory of strong electrolytes, is explained by a decrease in the activity coefficients of electrolytes of difficultly soluble salt. This decrease leads to a decrease in the constant of transformation reaction of reversible reaction into the molecule of a difficultly soluble salt. The magnitude of this process depends on the magnitude of ionic strength of the solution [16].

One of the most important tasks is to determine actual values of the increase in solubility through the fall of activity coefficients for different salts [17].

In this regard, it is of interest how the basicity of acid residual affects an increase in the solubility of a difficultly soluble salt.

We selected in all salts a one-valent chemical element as a cation. This is linked to the fact that in line with the theory of Debye-Hückel, all cations of the same valence have equal activity coefficient, even if these are different chemical elements. In the Debye-Hückel theory, the size of ions is neglected, considering them to be the point ones.

Activity coefficients are expressed by default from the mean ion coefficient in the limiting law of Debye-Hückel [18].

$$\lg\gamma=-A\,\left|z_1z_2\right|\sqrt{I}, \tag{7}$$

where coefficient A is expressed by formula

$$A=\frac{e^3\sqrt{2000N_A}}{2{,}3\cdot 8\pi(\varepsilon\varepsilon_0 kT^{3/2})}. \tag{8}$$

Based on this equation, it follows that the ratios of actual activities at different dielectric permittivities correspond to $(A_2/A_1)^{3/2}$, where A_2 is the ultimate dielectric permittivity, A – elementary.

Ion activity implies a degree of interaction between the ions, the greater the dielectricpermittivity, the interaction of ions will be lower, and vice versa [19].

For a difficultly soluble salt the saturation of solution is achieved at a relatively low concentration of ions in the solution, which will contain only particles of difficultly soluble electrolyte. However, if the solution contains any other electrolyte, the total ion will be determined based on the sum of all ion strengths of individual components dissolved in it.

According to the Lewis formula (9), ionic strength of solution is equal to the half-sum of the concentrations of all ions per charge squared.

$$I = \frac{1}{2}\sum m_i \cdot z_i^2. \qquad (9)$$

If a difficultly soluble salt and other salt (for example, Li_3PO_4 and Li_2SO_4) have a common cation or anion, this reduces the solubility of the difficultly soluble salt. The reason is the offset of the equilibrium and dissociation in the opposite direction.

In order to measure the dependence of dielectric permittivity on the inert electrolyte solution, we applied three different electrolytes.

The measurement of values of relative dielectric permittivity of electrolytes was performed using the solution as a medium to separate the plates of the flat capacitor.

The scientific literature data on the dielectric permittivity of salt solutions indicate that the magnitude of relative dielectric permittivity typically in most cases is proportional to the molar share of solvent and the dissolved substance. The exception to the rule is certain solutions of ferroelectrics (for example, potassium-sodium tartrate).

In order to create the salt effect, we used cesium chloride (CsCl) as an inert electrolyte. Upon data processing, we calculated the experimental enhancing strength in each of the three solvents – ethyl alcohol (C_2H_5OH), acetonitrile (CH_3CN) and water.

Enhancement of dielectric permittivity typically contributes to increasing (as well as acceleration) the solubility of a polar substance (for example, salts), mostly due to such factors as [21]:

1. High dielectric permittivity facilitates the dissociation of the solvent itself into ions.
2. High dielectric permittivity both retains more ions in the solution (which increases solubility) and prevents the reverse reaction.
3. The perfect solubility, as mentioned above, is determined by the ratio of the generalized momentum of the dissolved substance and the solvent. Since the generalized momentum of salt is much higher than that of all known solvents, this would also enhance the solubility.
4. High dielectric permittivity inhibits solvation, which also improves solubility.
5. Activity of ions deteriorates due to electrostatic voltage.

However, the solubility is affected exactly by the ratio of generalized momentums, while dielectric permittivity is a relative magnitude that demonstrates by how many times the strength of interaction between two charges is less than in a vacuum. Hence it is of interest to determine in which way inert electrolyte increases the solubility of difficultly soluble salts in media with different dielectric permittivity.

We used as a solvent three different polar solvents with different values of dielectric permittivity whose data are given in Table 1.

Table 1

Data on dielectric permittivity of the selected solvents (in relative magnitudes relative to vacuum)

Solvent	Ethyl alcohol	Acetonitrile	Water
Solvent formula	$CH_3–CH_2–OH$	$CH_3–C≡N$	H–O–H
Relative dielectric permittivity (293 K)	27	39	81

Activity coefficient of the inert electrolyte during salt effect in non-aqueous polar solvent will be different from those values in water. But if one knows the magnitude of activity coefficient in the solvent with one dielectric permittivity, it is possible to determine its theoretical values in another. This can be done using the Lewis-Randall rule, based on data on the magnitude A in different solvents [22].

The base magnitude A is unique for any solvent (8). Knowing the activity coefficient, ionic strength of the solution and the value of relative dielectric permittivities for one solvent, one can easily find activity coefficients of the same ions in another solvent. The condition for it is the identical ionic strength created by these ions.

In equation (8), product $\varepsilon\varepsilon_0$ also represents the value of relative dielectric permittivity. T is the absolute temperature (in Kelvin).

In order to study the enhancement of solubility of the difficultly soluble salts, we applied three different solvents. Their dielectric permittivity was measured by employing a solution as a medium to separate the plates of the flat capacitor.

It was decided to neglect the influence on the dielectric permittivity, because the difficultly soluble salts in all cases demonstrate low solubility product and the influence on the dielectric permittivity is negligible. Thus, the scientific literature data indicate that the dielectric permittivities of solutions in the vast majority of cases are proportional to the molar shares of components during formation of the solution.

In the course of conducting a series of experiments, we performed agitation using a magnetic agitator. Next, the solution was discharged and we measured a drop in the weight of sediment of the difficultly soluble salt, which testified to the resulting solubility and, as a consequence, to a change in the solubility product. sodium orthotellurate and potassium orthoperiodate were selected due to the fact that they are the difficultly soluble salts, while similar lithium salts are well-soluble in water. The choice was justified on the grounds that, according to the theory of Debye-Hückel, activity coefficients of one and the same cation/anion in the ionic form will be the same. Note that this happens regardless of the composition of salt, from which they were formed.

Theoretically, the activity coefficient of all ions is the same, but in practice the coefficient of activity also depends on the size of the cation, and in a series of alkali metal elements and hydrogen decays from H^+ and Li^+ to Cs^+. Given this, we took from the scientific literature data on the experimental activity coefficients of ions, which are given in Table 2 [8, 24].

Table 2

Experimental activity coefficients of ions used in the experiment at different ionic strengths (*I*=ionic strength of the solution)

I	Anion valency of a difficultly soluble salt								
	1				2	3	4	5	6
	H^+	Li^+	Na^+	F^-	CO_3^{2-}	PO_4^{3-}	ZrO_4^{4-}	IO_6^{5-}	TeO_6^{6-}
0.1	0.85	0.865	0.780	0.79	0.44	0.16	0.037	0.0058	0.00060
0.2	0.83	0.8	0.775	0.76	0.41	0.14	0.028	0.0038	0.00033
0.5	0.87	0.84	0.807	0.81	0.5	0.21	0.062	0.013	0.0020

5. Results of examining an enhancing factor of the inert electrolyte

Research results are given in the form of Table 3–5. They present the following data:

1. The scientific literature data on solubility of the selected difficultly soluble salts in pure solvents.
2. Experimentally derived data on solubility in the solution of inert electrolytes, where the "salt effect" manifests itself.
3. We calculated ratios of solubilities in the pure solvent, and considering the inert electrolyte with assigned degree of ionic strength.

Table 3

Dependence of salt solubility in the distilled water and the electrolyte solution used for the salt effect (caesium chloride) at ionic strength *I*=0.1

Salt	Solubility, g/cm³, 20 °C, in pure solvents			Solubility, g/100 cm³, in the solution of inert electrolytes at *I*=0.1, 20 °C			Solubility ratio		
	Solvent			Dielectric permittivity of pure solvent					
	Et	AcN	H_2O	27	39	81	27	39	81
LiF	0.038	0.105	0.134	0.038	0.105	0.134	≈1	≈1	≈1
Li_2CO_3	0.377	0.98	1.33	0.421	1.046	1.8	1.12	1.07	1.35
Li_3PO_4	0.006	0.02	0.022	0.0082	0.024	0.046	1.36	1.21	2.09
H_4ZrO_4	0.005	0.015	0.02	0.0092	0.022	0.07	1.84	1.48	3.5
Na_5IO_6	0.042	0.11	0.15	0.144	0.264	1.24	3.43	2.40	8.27
Na_6TeO_6	0.227	0.59	0.8	0.780	1.42	6.65	3.44	2.41	8.3

Data from Table 3–5 demonstrate that with an increase in the ionic strength of solution the "salt effect" initially grows to ionic strength *I*=0.2, and then begins to decline. At very high ionic strengths the activity coefficient of electrolytes grows, which contradicts the theory of Debye-Hückel.

The reason is that at high concentrations of ions they begin to interact through the attraction of charges with different signs. In the solutions of well-soluble salts with very high ionic strength, the activity coefficient of electrolytes may even exceed unity and larger, that is activity in the infinitely diluted solution.

This agrees with the Debye-Hückel third approximation for strong electrolytes, activity coefficient can be found by the following equation:

$$-\lg f_i = \frac{0,5z_i^2 \cdot \sqrt{\mu}}{1+\sqrt{\mu}} + 0,1z^2\mu \text{ at } 0.1<\mu<1. \qquad (11)$$

Dut to this reason, there are no equations for very concentrated solutions (where the ionic strength is accepted *I*>1), capable to adequately describe the processes occurring there. Therefore, the Debye-Hückel equation does not apply to describe such concentrated solutions. Experimental analysis of solubilities is appied exclusively.

Table 4

Dependence of salt solubility in the distilled water and the electrolyte solution used for the salt effect (caesium chloride) at ionic strength *I*=0.2

Salt	Solubility, g/cm³, 20 °C, in pure solvents			Solubility, g/100 cm³, in the solution of inert electrolytes at *I*=0.2, 20 °C			Solubility ratio		
	Solvent			Dielectric permittivity of pure solvent					
	Et	AcN	H_2O	27	39	81	27	39	81
LiF	0.038	0.1	0.134	0.039	0.102	0.141	1.01	1.02	1.05
Li_2CO_3	0.377	0.98	1.33	0.407	1.112	1.89	1.08	1.13	1.42
Li_3PO_4	0.006	0.02	0.022	0.0093	0.039	0.086	1.56	1.93	3.9
H_4ZrO_4	0.005	0.015	0.02	0.0076	0.028	0.073	1.52	1.87	3.7
Na_5IO_6	0.042	0.11	0.15	0.1034	0.378	1.29	2.46	3.44	8.6
Na_6TeO_6	0.227	0.59	0.8	0.5765	2.11	7.2	2.54	3.57	9.0

Table 5

Dependence of salt solubility in the distilled water and the electrolyte solution used for the salt effect (caesium chloride) at ionic strength *I*=0.5

Salt	Solubility, g/cm³, 20 °C, in pure solvents			Solubility, g/100 cm³, in the solution of inert electrolytes at *I*=0.5, 20 °C			Solubility ratio		
	Solvent			Dielectric permittivity of pure solvent					
	Et	AcN	H_2O	27	39	81	27	39	81
LiF	0.038	0.1	0.134	0.038	0.1	0.13	≈1	≈1	0.99
Li_2CO_3	0.377	0.98	1.33	0.395	1.0682	1.7	1.05	1.09	1.27
Li_3PO_4	0.006	0.02	0.022	0.011	0.044	0.077	1.83	2.20	3.5
H_4ZrO_4	0.005	0.015	0.02	0.0085	0.030	0.062	1.7	2.01	3.1
Na_5IO_6	0.042	0.11	0.15	0.126	0.4279	1.05	3	3.89	7.0
Na_6TeO_6	0.227	0.59	0.8	0.677	2.277	5.55	2.98	3.86	6.95

6. Discussion of results of examining enhancement of solubility products of difficultly soluble inorganic salts under different conditions

Results of the study showed that the increased solubility of a difficultly soluble salt directly depends not only on the dielectric permittivity, but also on the magnitude of charges on them. A deviation from the Debye-Hückel equation is also affected by the type of a particular cation.

Sodium orthotellurate and potassium sodium orthoiodate in all solvents demonstrated the greatest increase in solubility due to the “salt effect”. This is directly connected with the largest charges of anions (5 and 6, respectively).

Ortho zirconium acid at high ionic strengths of I=0.2 became inferior to other salts (even lithium orthophosphate), which is linked to deviations from the Debye-Hückel equation. The causes are lower ionicity of the bond O–H compared with O–Li or O–Na.

An analysis of experimental data revealed that if it is required to select such a difficultly solved salt to act with the salt effect, then it is desirable to use the one that possesses the largest anion charge anion (acid basicity).

Such task can be set when designing the adsorbent, where multibase acids with the same cation have potential benefits.

An example is lithium orthophosphate Li_3PO_4 – potentially more efficient dryer than LiCl, it has, however, lower solubility in water and, therefore, low rate of its absorption.

It is also known that a decrease in the activity coefficient occurs to a certain value of ionic strength. Further increase in the ionic strength leads, in contrast, to the accelerated growth in the activity coefficient, which is due to the fact that the Debye-Hückel theory displays the ions as point charges. The deviation of the ideal solution model from reality predetermines such ionic strength at which the salt effect is maximal because with further growth the ionic strength will fall [25].

The difficultly solved salt, consisting of two monovalent cations, demonstrates solubility enhancement using the salt effect, for which purpose the inert electrolyte is applied, or considerable excess of eponymous exelectrolyte, is the least significant, which is evidenced by results of the research, in this case, the least significant impact is observed in all solvents.

When reaching certain ionic strength, solubility gradually begins to fall, and at the ion strength equal to unity, solubility will drop below the solubility in pure distilled water.

The results obtained unambiguously demonstrate that an increase in the charge in the composition of salt leads to enhanced solubility through the exposure to inert electrolyte. The maximum effect will be achieved at minimal activity coefficient, which in theory, according to the Debye-Hückel equation, is the same.

In other dielectric permittivities, an increase in the salt effect will vary from the magnitude of dielectric permittivity. The higher dielectric permittivity of the solvent, the stronger the enhancement of the action of inert electrolyte. This is explained by the stronger polarization of a difficultly soluble salt.

If one applies as an inert electrolyte a ferroelectric material (for example, potassium-sodium tartrate), then this will dramatically improve the permittivity of a standard solvent (for example, water). As a consequence, to increase solubility by times due to the enhanced activity coefficients, which grow proportionally to the increase in dielectric permittivity of the medium.

7. Conclusions

1. We established dependence of the impact of the salt effect at the same ionic strength on various difficultly solved inorganic salts, which are based on acids with different basicity. An increase in the acid basicity (from 1 to 6) leads to the natural growth in the magnitude of the salt effect.
2. We determined influence of dielectric permittivity of the solvent effect on the magnitude of salt and confirmed that the salt effect grows larger proportionally to the growth of dielectric permittivity of the solvent.
3. We determined dependence of the salt effect for all difficultly solved salts based on the ionic strength as well. Maximum strength of the salt effect roughly corresponds to the ionic strength I=0.2, which approximately corresponds to the activity coefficients, based on data reported in the scientific literature.
4. It was found that the ionic strength of solution and the inflection point of the salt effect does not depend directly on the dielectric permittivity of the solvent.
5. In order to enhance the salt effect, it is expedient to employ a solvent with the largest dielectric permittivity, salt – with the highest valency of cation or anion.

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