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ЕЛЕКТРОФІЗИЧНІ ВЛАСТИВОСТІ ВОДНИХ РОЗЧИНІВ ЦИТРАТУ МАГНІЮ (3:2)

Мета: *Магній відіграє вагоме значення у процесах метаболізму людини. Існують різні форми його потрапляння до організму. Однією з найбільш ефективних є органічна форма саме у вигляді цитрату магнію. Активне використання цитрату магнію при виробництві харчових продуктів та при безпосередньому вживанні в якості фармакологічного препарату вимагає досконалих знань та досліджень його фізико-хімічних властивостей, а також дії на організм людини. У світовій науковій літературі описані два способи сполучення магнію із іоном лимонної кислоти. Перший , коли один катіон магнію приєднується до одного аніону лимонної кислоти (1:1). Другий, коли три катіони магнію сполучаються з двома аніонами цитрату - магній цитрат (3:2), тримагній дицитрат або тримагній цитрат. Поведінка таких сполук в розчинах не досліджена. Метою даної роботи було дослідження електрофізичних властивостей водного розчину цитрату магнію(3:2).* ***Методи дослідження****: Поведінка цитрату магнію у водних розчинах різної концентрації була досліджена методами атомно-абсорбційної спектроскопії, кондуктометрії та іонометрії. Для досліджень було взято порошок цитрату магнію, отриманий методом аквананотехнології із брутто-формулою* $C_{12}H_{10}Mg_3O_{14}\cdot 14H_2O$. ***Результати:*** *Встановлений вміст магнію у досліджуваному розчині склав 0,86 мг/л. що в результаті розрахунків підтверджує брутто-формулу даної речовини і означає, що в 1 г даного порошку цитрату магнію міститься 86 мг магнію (8,6%). Середовище всіх досліджених розчинів було слабко кислим, близьким до нейтрального. З розведенням вихідного розчину значення pH зростало, а потім зменшувалося, прямуючи до значення pH бідистильованої води. Визначене середнє значення молярної електропровідності при нескінченному розведенні для цитрату магнію склало 534.32 См*см*^{2}*/моль, що свідчить про існування в розчині великої кількості багатозаряджених часточок.* ***Обговорення****: В результаті проведеного дослідження методом атомно-абсорбційної спектроскопії була практично підтверджена брутто-формула цитрату магнію* $C_{12}H_{10}Mg_3O_{14}\cdot 14H_2O$*, який отриманий методом аквананотехнології. Встановлено, що ця сіль важкорозчинна і утворює розчини слабокислої реакції, дисоціюючи при цьому на велику кількість багатозарядних часточок.*

Ключові слова: *цитрат магнію, молярна електропровідність, pH; електролітична дисоціація****.***

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ELECTROPHYSICAL PROPERTIES OF MAGNESIUM CITRATE (3:2) AQUEOUS SOLUTION

Purpose: *The great importance for metabolic processes has such element as magnesium. There are different forms of ingress of magnesium to the human body. One of the most effective forms is magnesium citrate. Active using of magnesium citrate as food additive and pharmacological drug demands perfect knowledge and researches of its physicochemical properties and also the effect on human body. The world scientific literature describes two ways of combination of magnesium with citrate-ion. The first, when one magnesium cation is connected with one citrate-ion (1:1). The second one, when 3 magnesium cations are connected with 2 citrate-ions - magnesium citrate (3:2), trimagnesium dicitrate or trimagnesium citrate. The behavior of such compounds hasn't been researched. The purpose of this study has been to research electrophysical properties of magnesium citrate (3:2) aqueous solutions.* ***Methods:*** *The behavior of magnesium citrate in the aqueous solutions with different concentration has been by the methods of atomic absorption spectrometry (AAS), conductometry and ionometry researched. For the research has been used the powder of magnesium citrate, which has been obtained by the method of aquananotechnology with gross-formula* $C_{12}H_{10}Mg_3O_{14}\cdot 14H_2O$*.* ***Results:*** *Identified content of magnesium in analyzed solution has been 0,86 mg/l. In considering of dilution which has been made, it is ascertained the gross-formula of the substance and that 1g of given powder of magnesium citrate contains 86 mg of magnesium (8,6%). The medium of all researched solutions has been weak-acid, near-neutral. By the dilution of the initial solution pH value increases and then decreases to pH of bidistilled water. Value of molar conductivity at infinitely dilution for the magnesium citrate solution has been 534.32* $S\cdot cm^2/mol$*, that points at the presence of large quantity of multi-charged particles.* ***Discussion:*** *As the result of the experiment by the method of atomic absorption spectrometry (AAS) the gross-formula of magnesium citrate* $C_{12}H_{10}Mg_3O_{14}\cdot 14H_2O$*, which has been obtained by the method of aquananotechnology, has been corroborated in practice. It is ascertained, that the salt is not very soluble in water, forms weak-acid solutions and is dissociable into the large quantity of multi-charged particles*

Keywords: *magnesium citrate; molar conductivity; pH; electrolytic dissociation.*

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ЭЛЕКТРОФИЗИЧЕСКИЕ СВОЙСТВА ВОДНЫЙ РАСТВОРОВ ЦИТРАТА МАГНИЯ (3:2)

Цель*: Магний очень важен в процессах метаболизма человека. Существуют разные формы попадания его в организм. Одной из наиболее эффективных является органическая форма именно в виде цитрата магния. Активное применение цитрата магния в производстве пищевых продуктов, а так же при непосредственном употреблении в качестве фармакологического препарата требует совершенных знаний и исследований его физико-химических свойств, а так же действия на человеческий организм. В мировой литературе описаны два способа соединения магния с ионом лимонной кислоты. Первый, корда один катион магния присоединяется к одному аниону лимонной кислоты(1:1). Второй, когда три катиона магния соединяются с двумя анионами цитрата – магний цитрат (3:2), тримагний дицитрат или тримагний цитрат. Поведение таких соединений в растворе не было исследовано. Целью данной работы было исследование электрофизических свойств водного раствора цитрата магния (3:2).* ***Методы:*** *Поведение цитрата магния в водных растворах разной концентрации было исследовано Методами атомно-абсорбционной спектроскопии, кондуктометрии и ионометрии. Для исследования был взят порошок цитрата магния, который был получен методом аквананотехнологии с брутто-формулой* $C_{12}H_{10}Mg_3O_{14}\cdot 14H_2O$. ***Результаты****: Установленное содержание магния в исследуемом растворе составляло 0,86 мг/л, что по результатам расчетов подтверждает брутто-формулу данного вещества и означает, что в одном грамме порошка содержится 86 мг магния(8,6%). Среды всех изучаемых растворов были слабокислые, близкие к нейтральным. При разведении исходного раствора pH увеличивалось, а затем уменьшалось, приближаясь к значению pH бидистиллированой воды.Значение молярной электропроводности при бесконечном разбавлении для цитрата магния составляло 534.32 См*см*^{2}*/моль, что является свидетельством наличия в растворе большого количества многозаряженных частиц.* ***Обсуждение****: В результате проведенного исследования методом атомно-абсорбционной спектроскопии была практически подтверждена брутто-формула цитрата магния* $C_{12}H_{10}Mg_3O_{14}$ • $14H_2O$*, полученного методом аквананотехнологии. Установлено, что эта соль труднорастворима и образует растворы слабокислой реакции, дисоциируя при этом на большое количество многозарядных частиц.*

Ключевые слова: *цитрат магния, молярная электропроводность, pH, электролитическая диссоциация.*

Introduction. Microelements play a significant part in processes of human vital functions. The great importance for metabolic processes has such element as magnesium. Magnesium is essential for protein synthesis, keeping the normal function of nervous system and cardiac muscle, removing excess cholesterol from the body etc [1]. The deficiency of that element provokes such diseases as osteoporosis, arthritis, migraine etc [2]. That is why it is necessary to receive adequate dose of magnesium, which can be supplied with food products and/or food additives. As magnesium natural forms in the food products are either almost absent or hardly digestible, there is necessity of its (magnesium) alternative way of supply to the human body.

There are different forms of ingress of magnesium to the human body: mineral form as magnesium oxide, organic one as compounds of magnesium and organic acids. Certainly the most effective form is magnesium citrate [3].

The analysis of researches and publication. The researches of magnesium bioassimilability by the human organism have shown, that magnesium organic compound in the form of citrate had significantly higher bioavailability: 35-38% for organic form, 5% for inorganic [4]. Therewith magnesium citrate doesn't provoke irritation of gastrointestinal tract mucous membrane and citrate-ion fully transform into water and carbon dioxide by the human organism [5]. There is pharmacological preparation of magnesium in the form of the chelate compound with citric and malic acids, which called magnesium chelate [6]. In agriculture also used magnesium fertilizer in the form of chelate [7].

In food industry magnesium citrate is used as synergist of antioxidants, stabilizer, acidity regulator, color retention agent, salt substitute – food additive E345 [8].

Active using of magnesium citrate as food additive and pharmacological drug demands perfect knowledge and researches of its physicochemical properties and also the effect on human body.

However there aren't any systematic analyses of the magnesium citrate behavior in the solutions, namely, in this form it is absorbed by a living organism.

The world scientific literature describes two ways of combination of magnesium with citrate-ion. The first, when one magnesium cation is connected with one citrate-ion (1:1). That compound called magnesium citrate. It is white powder with weak sour taste. It is soluble in water (20g/100ml), better soluble in hot one. The solution of magnesium citrate smacks of citric acid. The content of pure (atomic) Mg^{2+} in magnesium citrate reaches to 11%. The second, when 3 magnesium cations are connected with 2 citrate-ions. The name of that compound is magnesium citrate (3:2), trimagnesium dicitrate or trimagnesium citrate. Also that compound often called just magnesium citrate. Magnesium citrate (3:2) – white powder, not very soluble in water and has a bitter taste [9].

The purpose of study. The purpose of this study has been to research electrophysical properties of magnesium citrate (3:2) aqueous solutions.

Objects and methods of research. For the research has been used the powder of magnesium citrate, which has been kindly given by "Avatar" firm (Kiev) and obtained by the method of aquananotechnology [10]. Preliminary X-ray analyses have ascertained, that given compound has had gross-formula $C_{12}H_{10}Mg_3O_{14}\cdot 14H_2O$. That means that it is crystalline hydrate, in which 3 magnesium-ions connected with 2 citric-ions.

The analysis of magnesium content in the solution has been conducted by the method of atomic absorption spectrometry (AAS) at atomic absorption spectrometer Perkin Elmer AAnalyst 400. The acidity of the solutions has been measured by HANNA pH meter "PICCOLO"

Specific conductance has been measured at conductometer HANNA EC214.

Results and Discussion. One gram of powder has been dissolved in one litre of bidistilled water. For the identification of magnesium content, obtained solution has been analyzed be the method of atomic absorption spectrometry (AAS) at atomic absorption spectrometer Perkin Elmer AAnalyst 400. As instrument readings have gone beyond the calibration curve, initial solution has been diluted with bidistilled water in a 1:100 ratio and analyzed again. Identified content of magnesium has been 0,86 mg/l. So, in considering of dilution which has been made, it is ascertained, that 1g of given powder of magnesium citrate contains 86 mg of magnesium (8,6%).

Theoretical calculation according to the gross-formula $C_{12}H_{10}Mg_3O_{14}\cdot 14H_2O$ (M=702,9 g/mol) shows, that the content of magnesium in 1 g of powder is 103,7 mg. So, X-ray analyzed gross-formula of magnesium citrate is close to real.

The acidity of initial solution of magnesium citrate has been measured by HANNA pH meter "PICCOLO" and has been pH= 5,78, so, the medium has been weak-acid. PH value of the solutions practically doesn't depend on its dilution.

The results of acidity measurement of solutions at temperature in the range 16,2-17,8 °C for 3 series of dilution shown in table 1.

The medium of all researched solutions is weak-acid, near-neutral. By the dilution of the initial solution pH value increases and then decreases to pH of bidistilled water. At 0,0000285 mole/l concentrations is observed abnormal deviation at dependence acidity of medium-concentration.

The electroconductivity of magnesium citrate solution has been researched at conductometer HANNA EC214 at 18 °C. For that the initial solution has been serially diluted with bidistilled water (Experiment 1).

Table 1

pH value of magnesium citrate solutions with different concentration

$C \cdot 10^5$, mol/l	pH		
	Experiment 1	Experiment 2	Experiment 3
0(H_2O)	6,16	5,98	6,09
0,143	-	6,25	6,23
0,285	-	6,18	6,18
0,713	-	6,38	6,38
1,425	6,40	6,44	6,45
2,850	6,89	6,88	6,85
3,563	6,40	6,40	6,38
4,750	6,41	6,42	6,43
7,125	6,34	6,35	6,35
14,250	6,27	6,29	6,31
142,500	5,69	5,75	5,77

At the same time has been prepared the series of solutions with multiple generally accepted values of magnesium citrate concentrations in the solutions (Experiment 2). The results of the researches are represented in table 2. Specific conductance of the solutions is represented without electroconductivity of water which are equal to 1,4 μS/cm(Experiment 1) and 1,8 μS/cm (Experiment 2).

Table 2

Specific conductance of magnesium citrate solutions with different concentration

	Experiment 1		Experiment 2	
№	$C \cdot 10^5$, mol/l	$\chi \cdot 10^6$, S/cm	$C \cdot 10^5$, mol/l	$\chi \cdot 10^6$, S/cm
1	0,143	0,7	0,200	1,2
2	0,285	2,8	0,400	2,8
3	0,713	3,0	0,800	3,0
4	1,425	4,2	1,000	3,6
5	2,850	7,3	2,000	6,3
6	4,453	11,1	4,000	10,5
7	8,906	18,2	8,000	17,2
8	17,813	29,4	10,000	20,2
9	35,625	51,4	20,000	34,3
10	71,250	90,9	25,000	41,6
11	142,500	168,0	50,000	73,7
12			100,000	130,1
13			200,000	123,45

According to experimental values of specific conductance have been calculated the values of molar conductivity of magnesium citrate solution. The results are shown in table 3.

Table 3

Molar conductivity of magnesium citrate solutions with different concentration

	Experiment 1		Experiment 2	
№	$C \cdot 10^5$, mol/l	λ, S·cm²/ mol	$C \cdot 10^5$, mol/l	λ, S·cm²/ mol
1	0,143	491,2	0,200	600,0
2	0,285	982,5	0,400	700,0
3	0,713	421,1	0,800	375,0
4	1,425	294,7	1,000	360,0
5	2,850	256,1	2,000	315,0
6	4,453	249,3	4,000	262,5
7	8,906	204,4	8,000	215,0
8	17,813	165,1	10,000	202,0
9	35,625	144,3	20,000	171,5
10	71,250	127,6	25,000	166,4
11	142,500	117,9	50,000	147,4
12			100,000	130,1
13			200,000	123,45

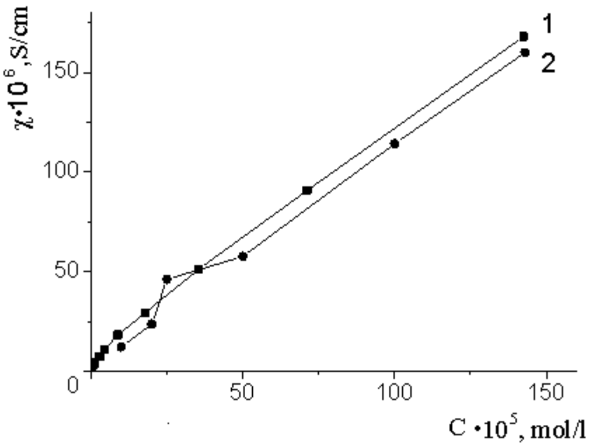
As electroconductivity has been abnormal high, it was agreed to carry out the control experiment with the reference substance – KCl at equal conditions in order to corroborate the correctness of the experiment. The results of the control experiment are represented without electroconductivity of water, which is 1,4 μS/cm (table 4).

Table 4

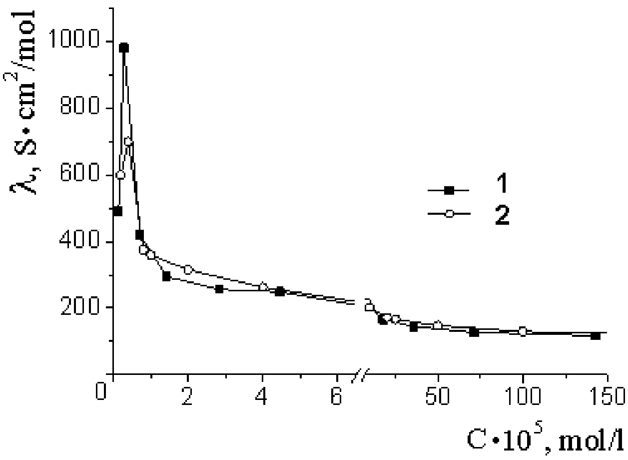
The electroconductivity of potassium chloride solutions with different concentration

	Concentration	Specific conductance	Molar conductivity
№	$C \cdot 10^3$, mol/l	$\chi \cdot 10^6$, S/cm	λ, S*cm²/mol
1	0,10	12,2	122
2	0,20	23,7	118,5
3	0,25	46,2	184,8
4	0,50	57,6	115,2
5	1,00	114,2	114,2
6	2,00	219	109,5
7	4,00	444,7	111,2
8	5,00	551,8	110,4
9	10,00	1083,6	108,4
10	12,50	1216,6	97,3
11	25,00	2338,6	93,5
12	50,00	4605,6	92,1
13	100,00	9981,6	99,8

The graphical display of the results is shown at pictures 1and 2.



Pic.1. Specific conductance-concentration relation of solutions: 1 – magnesium citrate (experiment 1); 2 – potassium chloride 5



Pic. 2. Molar conductivity-concentration relation of magnesium citrate solutions: 1 - experiment 1; 2 - experiment 2.

It can be seen from the graphs, that every experiment has one error value. It is rejected at further mathematical treatment of the results. Obtained curves of the results can be described by exponential equation which is correct for diluted solutions:

$$y = A_1 e^{\frac{-x}{t_1}} + A_2 e^{\frac{-x}{t_2}} + y_0$$

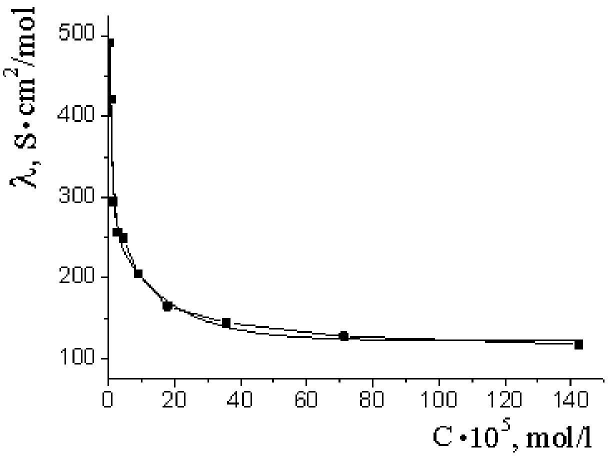
The parameters of the equation are represented in table 5.

The results of the mathematical treatment are shown at pictures 3 – 5.

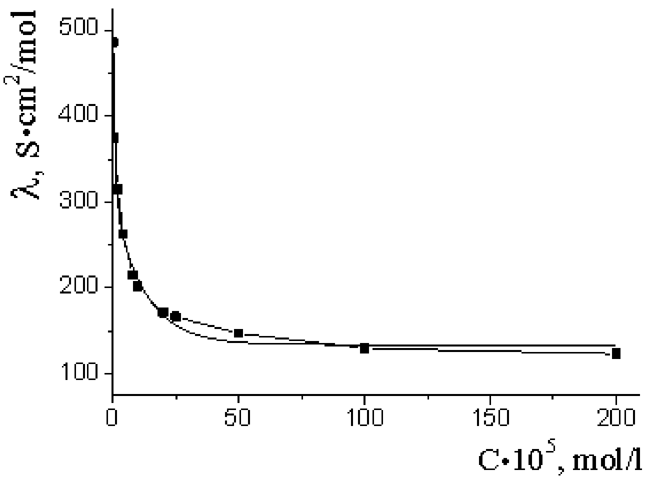
Table 5

The parameters of the equation of molar conductivity-concentration relation of magnesium citrate and potassium chloride solutions

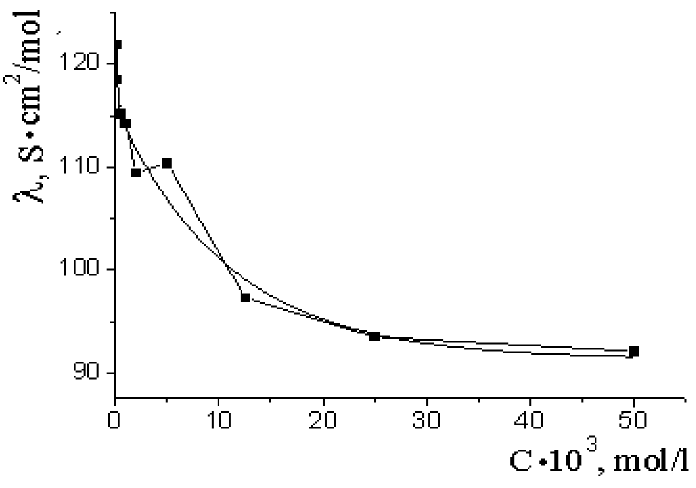
Parameters	Magnesium citrate		Potassium chloride
	Experiment 1	Experiment 2	
A_1	143,21	171,13	24,70
A_2	271,03	227,08	13,10
t_1	16,64	12,47	10,84
t_2	1,01	0,87	0,13
y_0	122,37	133,82	91,31
R^2	0,977	0,990	0,956



Pic. 3. Mathematical treatment of experimental molar conductivity-concentration relation of magnesium citrate solutions (experiment 1)



Pic. 4. Mathematical treatment of experimental molar conductivity-concentration relation of magnesium citrate solutions (experiment 2)



Pic. 5. Mathematical treatment of experimental molar conductivity-concentration relation of potassium chloride solutions

As confidence interval (R^2) verges towards 1, it is safe to say, that chosen type of function and mathematical treatment of the experimental results are correct.

According to derived equation, calculated value of molar conductivity for potassium chloride at infinitely dilution of the solution at 18 °C is 129,11 S·cm^2/mol, that almost agrees with tabulated value [11], which is calculated according to Kohlrausch's law - 129,9 S·cm^2/mol.
For magnesium citrate the value of molar conductivity is calculated according to approximation equations: for experiment 1 – 536.61 S·cm^2/mol; for experiment 2 – 532,03 S·cm^2/mol. Better reproducibility of the results couldn't be reached because of low values of the specific conductance of high-diluted solutions, which verges towards values of the bidistilled water. So, as a true value of the molar conductivity at infinitely dilution of the magnesium citrate solution should be taken the average value of two experiments, which is 534,32 S·cm^2/mol.
In any case, the molar conductivity at infinitely dilution of the magnesium citrate solution has really high value. That points at the presence of large quantity of multi-charged particles.

Conclusions

As the result of the experiment by the method of atomic absorption spectrometry (AAS) the gross-formula of magnesium citrate $C_{12}H_{10}Mg_3O_{14}\cdot 14H_2O$, which has been obtained by the method of aquananotechnology, has been corroborated in practice. It is ascertained, that the salt is not very soluble in water, forms weak-acid solutions and is dissociable into the large quantity of multi-charged particles

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