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The effect of electromagnetic field on silver iodide sols stability

It is shown that the influence of the ultrahigh-frequency electromagnetic field on purified water leads to a significant increase in its electrical conductivity and pH. The effect can be interpreted as a change in the supramolecular organization of water. The kinetics of the formation of nuclei of the crystalline phase in irradiated water by the example of silver iodide sols was studied by turbidimetry. It is shown that in the irradiated water the growth of AgI crystals slows down, which is noticed as a slower decrease in the light transmission of the sol in time. The effectiveness of electromagnetic influence depends on the frequency and time of irradiation so that the maximum effect is achieved at the field frequency of 170 MHz and at the irradiation time of 3 hours. Destruction of the sols prepared with irradiated water takes place on the 4th day, while in the control samples it begins after 24 hours. It is assumed that in the irradiated water the growth of crystalline nuclei slows down due to a change in the surface tension and a decrease in AgI solubility.

Keywords: water, silver iodide, sol, light transmission, stability, electromagnetic field, frequency, irradiation time.

Introduction

The problem of the disperse systems stability is one of the most important in colloid chemistry. It is of great importance in many processes occurring in nature and used in the national economy. Ensuring the free-disperse systems stability is necessary in the production of various products, coatings, binders, medicines, aerosols, etc. Destruction of stability is required to cause structure formation in materials, to obtain precipitation during phase separation, to purify industrial emissions. The stability of hydrosols is affected by various factors, namely, heating and cooling, mechanical stirring, the introduction of electrolytes into the system [1]. Another possibility to control the disperse systems stability is the effect of physical fields of various nature as ultrasonic, permanent magnetic and electric, electromagnetic field, as evidenced by numerous publications [2–8].

In recent years, the scientific interest in the problems of the interaction of electromagnetic fields with matter has increased, and the particular interest is the study of the effect of high-frequency and ultrahigh-frequency electromagnetic fields (HF and UHF EMF) on various environments. This interest is due to the perspective of using electromagnetic interference in scientific industries to intensify technological and physical-chemical processes and manage them by directly influencing the working environment. HF and UHF technological processes have been widely used and distributed in various fields of industry such as chemical, mechanical engineering, food industry, woodworking industry, pulp and paper industry, medicine, etc. Examples of such electric and magnetic fields applications are technologies for separating constituents of an inhomogeneous medium, as well as a variety of applications HF and UHF EMF in the technological processes of heating and heat treatment, drying, thawing, etc. [9].

Unlike the methods of influence on the continuous media, the effect of HF and UHF EMF has a number of advantages. So, firstly, electromagnetic waves extend over sufficiently large distances into the object until complete attenuation, and we can talk about various electro-hydrodynamic phenomena and control them in the depths of the dispersion medium. Secondly, under the influence of HF and UHF EMFs in the medium due to the dissipation of the electromagnetic field energy into heat, distributed heat sources arise. The value of the density of thermal sources is determined by the type (geometry) of the electromagnetic wave extending in the dispersion medium and the dielectric properties of the dispersion medium. Thus, for a given wave geometry for a given medium, with use of changed frequency HF and UHF EMF it is possible to carry out controlled processes of interaction of EMF with the medium (for example, heating to a given depth) [10, 11].

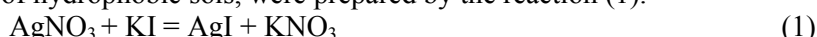
Smaller applications so far low-intensity fields have been found, although numerous studies in this area also make it possible to conclude that they are promising for use in various technological processes associated with the use of disperse systems.

Previous studies [12–16] have shown that as a result of the action of the ultrahigh frequencies electromagnetic field (30–300 MHz), the optical and electrical properties of the silver halides, iron and aluminum

hydroxides sols are changed. It was found that the effectiveness of electromagnetic influence depended on the frequency, field strength, exposure time and concentration of the dispersed phase of the sol. Each disperse system is sensitive to the action of a field of strictly defined frequencies. It is possible to significantly change the stability of these disperse systems by varying the field frequency and the exposure time. All previous experiments were carried out when the field affected directly on the sol [16]. At the same time, in our studies and studies of other authors, it is asserted that electromagnetic fields primarily affect water, changing its supramolecular organization [17–19]. Therefore, it was of interest to study the processes of formation of a dispersed phase particles in a medium with a modified field structure. As an object of study, an AgI sol with a negative charge of particles was chosen. The purpose of the study is to evaluate the influence of the electromagnetic field on the kinetics of formation and stability of silver iodide sols, based on the measurement of their optical properties.

Method

The AgI sols, as a classic example of hydrophobic sols, were prepared by the reaction (1):



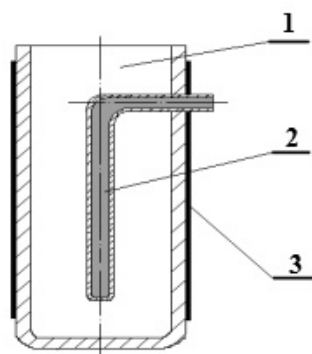
Schematically, the micelle structure of the silver iodide sol obtained with an excess of KI can be represented as follows (2):



AgNO₃ (99 % pure) and KI (99 % pure) were used as a reagents. To prepare the sol 5 mL of a 0.1 M KI solution was added to 25 mL of water purified by reverse osmosis. With stirring, a 0.1 M of AgNO₃ solution was gradually added in an amount necessary to produce a sol of the desired concentration. The concentration of the obtained sol was calculated with use of the reaction equation, taking into account the 100 % yield of AgI (solubility product of AgI is 8.3×10^{-17}).

The light transmission measurements were carried out with use of a CPC-2 colorimetric spectrometer at a wavelength of 440 nm and a temperature of 22–24 °C. Water was used as a standard solution. The length of the cuvette was 5 cm.

A high-frequency (HF) signal generator G3–19A, allowing to vary the frequency of the EM field in the range 30–200 MHz, was used to irradiate water. The voltage at the HF electrodes was 20–22 V. The generator power was 1 W. Irradiation of water was carried out in a 50 mL capacitive cell made of glass (Fig. 1). The cell consisted of a glass cup with a volume of 50 mL with an internal HF Wood's alloy electrode and an external electrode made of aluminum foil closely adhering to the outer surface of the cell. HF-electrodes were connected to the HF-generator with the help of a RF connector RC-75.



1 — glass cup; 2 — internal electrode; 3 — external electrode

Figure 1. HF cell structure

Water with a specific electric conductivity of 1.4×10^{-4} S/cm was used. The water was irradiated with a field of 170 and 180 MHz for 1–3 hours. The choice of frequencies is due to the fact that it was shown earlier that the maximum change in the properties of water is observed as a result of the action of the field at a frequency of 170 MHz, and the maximum change in the properties of the sol is at 180 MHz [5, 4]. After irradiating the water, the change in its electrical conductivity and pH was recorded (Table 1). In our experiments, a more noticed change in the water properties corresponded to $f = 180$ MHz so that the electrical conductivity changed almost 3 times, and the pH was changed more than one.

Table 1

Change in the electrical conductivity of water as a result of electromagnetic interference

f, MHz	0	170	180
$\kappa \cdot 10^4$, S/cm	1.4±0.2	3.0±0.3	4.1±0.6
pH	6.5±0.1	7.4±0.3	7.6±0.2

Sols with a concentration of 0.1 and 0.2 % were prepared by pouring the reagent solutions either to the non-irradiated control sample or to irradiated water ($f = 170$ or 180 MHz). Their light transmission was measured every 20 minutes. The Table 1 data indicate that as a result of the influence of the electromagnetic field, the water properties changed, so that the properties of the sols prepared with irradiated water could also be expected to change.

Results and discussion

Silver iodide sols are formed almost immediately after mixing the reagents, as evidenced by a lower light transmission of the resulting system compared to the light transmission of water. They are metastable and over time, auto-coagulation processes occur in them, which can be noticed in a fairly rapid decrease in light transmission. With increasing sol concentration, the rate of the auto-coagulation process increases (Table 2). For further studies, 0.1 and 0.2 % of AgI sol was chosen, because the auto-coagulation proceeds rapidly enough in them, which makes it possible to compare the kinetics of this process for irradiated and non-irradiated systems.

Table 2

Change in light transmission (T , %) of AgI sols of different concentrations with time

t , days	T , %			
	$C = 0.01$ %	$C = 0.02$ %	$C = 0.1$ %	$C = 0.2$ %
0	97±2	94±2	83±2	75±3
1	51±2	50±5	Precipitate	Precipitate
2	38±3	39±4		
3	34±6	32±2		
4	24±2	22±1		
5	19±2	18±2		
6	Precipitate	Precipitate		

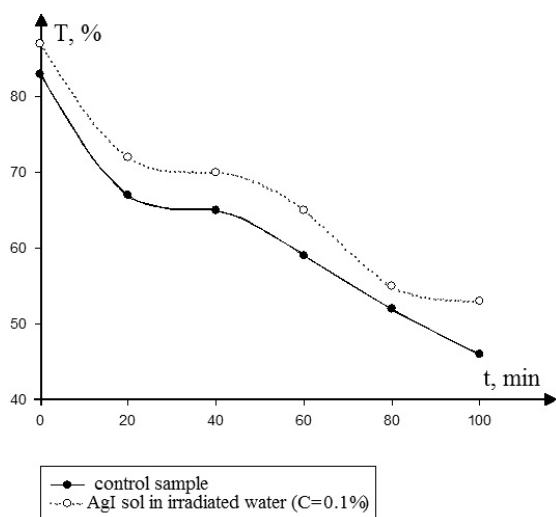
Studies have shown that the sols prepared in irradiated water (170 MHz) initially have a higher light transmission: 87 ± 1 % (0.1 % sol) and 80 ± 2 % (0.2 % sol). For control samples, these values were 83 ± 2 % and 75 ± 3 %, respectively (Table 2). Over time, the light transmission in all disperse systems decreased, but in the samples prepared in irradiated water it decreased to a much lesser extent. This is especially true for 0.2 % sols so as at the end of the experiment, the difference in light transmission of the sol was 9 ± 2 % (Fig. 2, 3).

The values of light transmission and its time variation for 0.2 % of AgI sols prepared in irradiated water with a field of 180 MHz are given in Table 3. In this case, the field effect proved to be ineffective. Thus, the AgI sols prepared in irradiated water with a field of 170 MHz were more susceptible to field action than those prepared on water irradiated at a 180 MHz field. Thus, it can be affirmed that the influence of an electromagnetic field on water dispersions is selective. The determining parameter is a frequency of an applied field.

Table 3

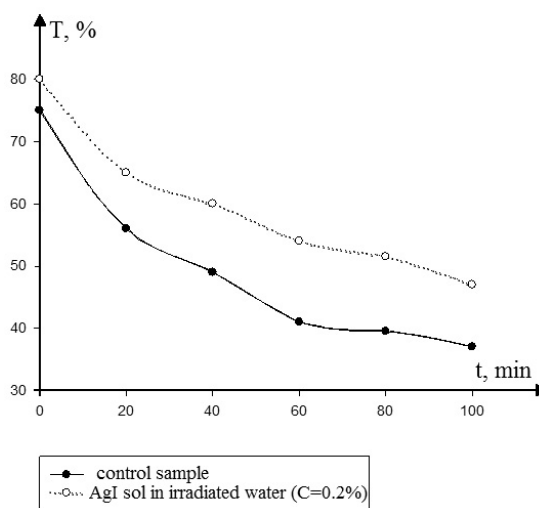
Change in time of light transmission of 0.2 % AgI sols prepared in irradiated water with a field of 180 MHz

t , min	T , % control sample	T , % AgI sol in irradiated water
0	58	59
30	46	47
60	39	41
90	34	35
120	27	28



$f = 170 \text{ MHz}$, $t_{\text{irr}} = 1 \text{ h}$, $\lambda = 440 \text{ nm}$, $C = 0.1 \%$

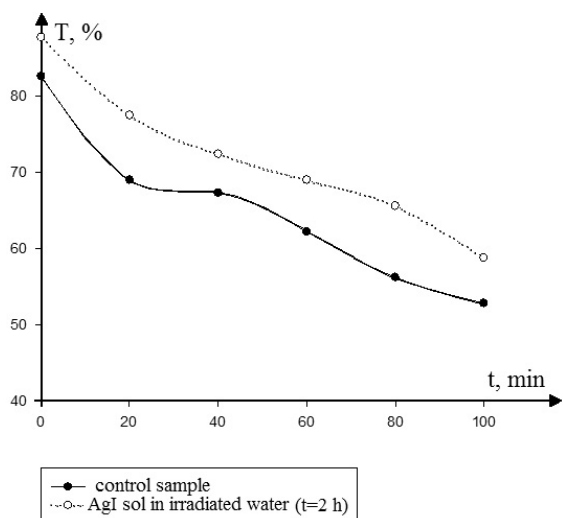
Figure 2. Change in time of light transmission of AgI sols prepared in irradiated and non-irradiated water



$f = 170 \text{ MHz}$, $t_{\text{irr}} = 1 \text{ h}$, $\lambda = 440 \text{ nm}$, $C = 0.2 \%$

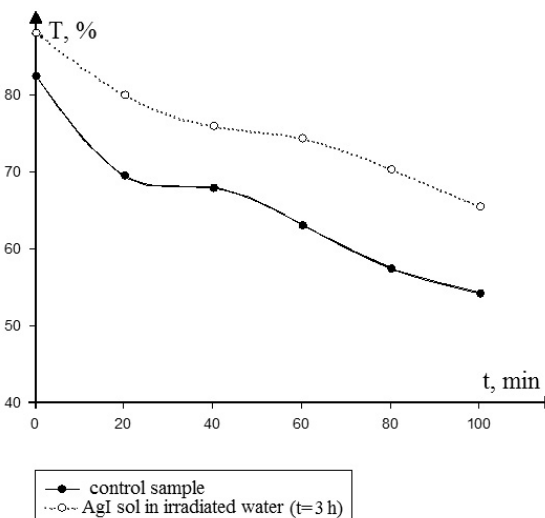
Figure 3. Change in time of light transmission of AgI sols prepared in irradiated and non-irradiated water

The dependence of the effectiveness of the electromagnetic effect on its duration was studied. The increase in time of irradiation of water, which was then used to prepare the sols, increased their stability to 3 hours (Fig. 4, 5).



$f = 170 \text{ MHz}$, $t_{\text{irr}} = 2 \text{ h}$, $\lambda = 440 \text{ nm}$

Figure 4. Change in time of light transmission of 0.1 % AgI sols prepared in irradiated and non-irradiated water



$f = 170 \text{ MHz}$, $t_{\text{irr}} = 3 \text{ h}$, $\lambda = 440 \text{ nm}$

Figure 5. Change in time of light transmission of 0.1 % AgI sols prepared in irradiated and non-irradiated water

Table 4 shows the initial light transmission values of 0.1 % of AgI sols prepared in non-irradiated and irradiated ($f = 170 \text{ MHz}$) for 1–3 hours with water. The initial value of light transmittance (T_{in} , %) increased with increasing time of electromagnetic influence on water. Table 4 also gives the final light transmission values (T_{f} , %) after the end of the experiment (100 min). The transmission of light by irradiated systems during this time was reduced, as well as by non-irradiated systems, but had higher values. At the end of the experiment, it was higher by 3, 7 and 14 %, depending on the time of field influence.

The initial and final (after 100 min) light transmission values of 0.1 % of AgI sols prepared in non-irradiated and irradiated ($f = 170$ MHz) water title

	Control sample	Irradiation time		
		1h	2h	3h
$T_{in}, \%$	83 ± 2	87 ± 2	89 ± 1	91 ± 2
$T_f, \%$	48 ± 1	51 ± 2	55 ± 2	62 ± 1
$\Delta T, \%$	–	3	7	14

If a solution of AgNO_3 is added to the KI solution in small portions, then, when the AgI solubility product is reached, the crystals of the new phase begin to form. Since KI is taken in excess, the particles are charged negatively due to the selective adsorption of iodide ions. However, as AgNO_3 is added, the negative charge of the particles will decrease down to zero (the neutralizing mechanism of coagulation). With further addition of the electrolyte, the surface is recharged so as the particles acquire a positive charge due to adsorption of potential-determining ions of silver. Thus, the light transmission curve of a given system as a function of the AgNO_3 concentration should be characterized by a sufficiently deep minimum, which was confirmed in practice (Fig. 6).

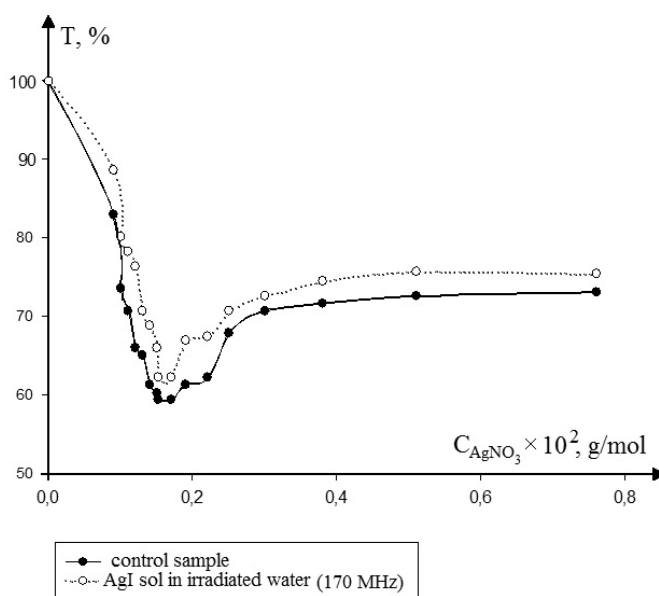


Figure 6. Change in the light transmission of 0.01 M KI solution with the addition of a 0.01 M AgNO_3 solution

A similar experiment was carried out with a KI solution prepared in irradiated water: 0.01M AgNO_3 solution was added to 0.1 M KI solution in 0.1 mL of each one and the light transmission was recorded. The shape of the obtained curves is the same, but all points of the curve for the irradiated system are located higher. Moreover, on the descending part of the curve (negatively charged particles), the ΔT value is 6–8 %, and on the ascending one (positively charged particles) is 2–3 %, which indicates that the field effect has a greater effect on sols with a negative particle charge. Because the minimum of the light transmittance curves (Figure 6) corresponds to the same AgNO_3 concentration, it can be assumed that the charges of colloidal particles in irradiated and non-irradiated water coincide, and the higher light transmission of the sols in irradiated water is due to the smaller particle size of their particles.

About an increase in the stability of 0.1 % AgI sols prepared in water irradiated with an electromagnetic field of 170 MHz for 3 hours we can know by the fact that the destruction of the sol and the formation of the precipitate occurred on the 4th day, while in the control sample the precipitate formed after a day. With a shorter exposure time, the precipitates in the irradiated systems formed on the third day.

The observed phenomena may be caused by the formation of smaller colloid particles in sols prepared in irradiated water. The size of the formed crystals of the dispersed phase is determined by the ratio between

the rate of nucleation of the solid phase and the rate of their growth. The condition for the formation of nuclei of the solid phase is expressed by the equation (3) [20]:

$$r = \frac{2\sigma V_M}{RT \ln(C_1 / C_2)}, \quad (3)$$

where r — is the radius of the particles; σ — is the surface tension at the solid-liquid interface; V_M — is the molar volume of the dispersed phase; R — is the gas constant; T — is the temperature; C_1 — is the concentration of supersaturated solution; C_2 — is the concentration of saturated solution.

Analysis of this equation allows us to state that the reduction of surface tension at the solid-solution interface and the increase in the degree of supersaturation $\gamma = C_1/C_2$ facilitates the production of smaller crystals. It can be assumed that the electromagnetic action causes a decrease in the surface tension due to a change in the energy of interaction between solvent and solid phase as a result of reorganization of the supramolecular structure of water. In addition, an increase in the degree of supersaturation of the solution can be observed due to a decrease in the solubility of AgI in the reorganized solvent as a result of a decrease in the energy and degree of hydration of the silver ions and iodine ions.

The rate of precipitation of the dispersed phase particles in the gravitational field is proportional to the square of their radius, therefore, even a small change in particle size leads to a significant slowing of sedimentation and to an increase in the stability of the disperse system. In irradiated sols, the increase in light scattering (decrease in light transmission) with time is slower than in non-irradiated ones, which indicates a slowing of the rate of crystalline solid-phase nuclei growth.

Conclusions

The research has shown that during the exchange reactions accompanied by the formation of a slightly soluble compound (AgI) in an aqueous medium at an electromagnetic field, a slowdown in the growth of crystalline nucleus is observed. This leads to an increase in the stability of the silver iodide sols, as evidenced by higher light transmission values compared to the light transmission values of the control samples. Sedimentation occurred on the 4th day, while in the control samples it happened after a day. The influence of the electromagnetic field is selective and the effect is noticed only as a result of the action of a field of a certain frequency on the water. With increasing irradiation time, the efficiency of electromagnetic influence increases.

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И.Е. Стась

Электрмагниттік өрістің күміс йодиді зольінің тұрақтылығына әсері

Аса жоғары жиіліктегі электрмагниттік өрістің тазартылған суға әсерінен оның электрөткізгіштігі мен рН көрсеткіші мәнінің жоғарлауы байқалған, ол молекулалық деңгейден жоғары судың өзгерісімен түсіндіріледі. Турбидиметрия әдісімен сәулеленген суда күміс йодиді мысалында кристалдық фаза түзінділерінің түзілу кинетикасы зерттелді. Сәулеленген суда AgI кристалдарының өсуі баяулайтыны байқалған. Электрмагниттік әсер ету тиімділігі сәулеленудің жиілігі мен уақытына тәуелді болады, сонда сәулелену уақыты 3 сағ, ал жиілігі 170 МГц болатын өріс әсері тиімдірек екені анықталды. Сәулелену әсеріне ұшыраған сумен дайындалған зольдің ыдырауы 4-ші күні, ал бақылау үлгілерінде 24 сағ кейін жүретіні белгілі болды. Сәулеленген суда кристалдық түзінділердің өсуі аралық кернеудің өзгеруінен және AgI тұзының ерігіштігінің азаюынан болуы мүмкін деп түсіндірілді.

Кілт сөздер: су, күміс йодиді зольі, жарықөткізу, тұрақтылық, электрмагниттік өріс, жиілік, сәулелену уақыты.

И.Е. Стась

Влияние электромагнитного поля на устойчивость зольей йодида серебра

Показано, что воздействие электромагнитного поля ультравысоких частот на очищенную воду приводит к значительному увеличению ее электропроводности и рН, что интерпретировано как изменение надмолекулярной организации воды. Методом турбидиметрии изучена кинетика образования зародышей кристаллической фазы в облученной воде на примере йодида серебра. Доказано, что в облученной воде замедляется рост кристаллов AgI, что проявляется в более медленном снижении светопропускания золя во времени. Эффективность электромагнитного воздействия зависит от частоты и времени облучения — максимальный эффект достигается при воздействии поля частотой 170 МГц и времени облучения, равном 3 ч. Разрушение зольей, приготовленных с помощью облученной воды, происходит на 4-е сутки, в то время как в контрольных образцах — через 24 ч. Отмечено, что в облученной воде замедляется рост кристаллических зародышей вследствие изменения пограничного натяжения и снижения растворимости AgI.

Ключевые слова: вода, золь йодида серебра, светопропускание, устойчивость, электромагнитное поле, частота, время облучения.

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