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D.I. Mendeleev's concentration decrement in lucigenin aqueous solutions

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Abstract. The article discusses the results of study for the optical properties (luminescence) of aqueous solutions with low concentrations of lucigenin. One new methodology for the mathematical processing of luminescence spectra is presented. The method to prepare the solutions, which can be used to identify critical points (D.I. Mendeleev's decrement) in the physicochemical properties of aqueous solutions, is considered.

Keywords: lucigenin aqueous solutions, relaxation, D.I. Mendeleev's decrement

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1. INTRODUCTION

D.I. Mendeleev was the first researcher who pointed that solutions weren't the mechanical mixture of components but special chemical compounds. He found the compression phenomenon of alcohol aqueous solutions when increasing alcohol concentration. It is accompanied by the appearance of jumps and gaps in the concentration density derivatives of the solution [1]. D.I. Mendeleev explained this property with the formation of hydrated compounds in the solution in the vicinity of the special alcohol concentrations. Many famous

scientists made significant contribution in studying of the physicochemical solution properties and the creation of theoretical dynamics and structure bases. We could mention the of famous scientist names: N.S. Kurnakov, I.I. Frenkel I.Z. Fisher, M.I. Shakhparonov, A.V. Voronel, O.Ya. Samoilov, M.N. Rodnikova, N.A. Bulienkov, G.A. Martynov, G.G. Malenkov, Yu.I. Naberukhin, A.K. Lyashchenko and many others. J. Bernal and R. Fowler were the pioneers in the science of the water structure and ionic solutions. Now A. Geiger and J. Pollack are updating structural ideas for water solutions.

Our studies of optical absorption, dynamic light scattering (**DLS**) and luminescence of aqueous solutions are reason to write this article. L_c is chemical marker of the chemical silver nanoparticles synthesis finishing in reverse micelles. The reverse micelles contain small amount of water and it is in the form of bound water. So it is very difficult to measure the L_c concentration in of reverse micelles water. In order to

simplify the problem, it was decided only to estimate the concentration boundary of the L_c content in distilled water, when at low L_c concentrations the luminescence bands L_c characteristic of could be still recorded.

The article considers new approaches to study low L_c concentrations aqueous solutions and proposes mathematical methods to analysis the optical properties for aqueous solutions (e.g. luminescence) which have not been currently almost considered. The features of the behavior for aqueous solutions with low substances concentration are usually attributed to the lability of the solution. In this case one could only speak about equilibrium in aqueous solutions conditionally. Thermodynamic methods are not sufficient to describe aqueous solutions and it is necessary to create a number of new methods and models to understand properties of aqueous solutions in infinity systems. The article presents the results of brief study for the high dilutions aqueous solutions luminescence and some discrete models to analyze the relaxation characteristics of solutions based on D. I. Mendeleev's decrement.

2. MATERIALS AND METHODS

Lucigenin (10,10'-dimethyl-9,9'-biacridinium dinitrate, L_c , MW 512.51 is golden yellow crystals ($T_{\text{melt}} = 330^\circ\text{C}$), readily soluble in water and poorly soluble in ethanol. The green fluorescence could be observed when exposed to UV light in acidic and neutral environments. The bright green-blue chemiluminescence arises under the action of O_2 or in the presence of H_2O_2 ($\lambda_{\text{exc}} = 360 \text{ nm}$, $\lambda_{\text{max}} = 510 \text{ nm}$) and in an alkaline environment or in addition various reducing agents (hydrazine, hydroquinone, hydroxylamine, etc.).

In all experiments for the preparation of L_c solutions the distilled water of single distillation was used with the following parameters:

- 1) the mass concentration of the residue after evaporation of 4 mg/dm^3 ;
- 2) the mass concentration of sulfates (SO_4) 0.45 mg/dm^3 ;
- 3) the mass concentration of chlorides (Cl) 0.015 mg/dm^3 ;
- 4) $\text{pH} = 5.6$;
- 5) conductivity at 20°C $\sigma = 4.8 \cdot 10^{-4} \text{ Cm/m}$.

The initial L_c aqueous solution with concentration ($C_{L_c} = 44 \text{ mg/dm}^3$) was prepared. Then it was tested by the DLS method for the presence of L_c molecules aggregates. The correct identification of L_c aggregates by the DLS method is impossible because of the nanobubble phase of atmospheric gas [2-5] (Fig. 1) exists constantly in the aqueous solution. The sizes of atmospheric gas nanobubbles depend on internal and external factors and they can reach several hundred nanometers. Therefore the method of fluorimetry was adopted in further study in which the luminescence bands L_c (high resolution fluorimeter "Hitachi F 7000") are recorded in the luminescence spectra of aqueous solutions in wide range of concentrations up to high dilutions.

Before conducting luminescence experiments in aqueous L_c solutions the optical absorption spectra (OAS, "Hitachi-3310") were recorded for the solution with different L_c concentration ($C_{L_c} = 0.7 \text{ mg/dm}^3$). The quartz corvette with optical path length (OPL) of 10 mm was used in all experiments and OAS were recorded relative to distilled water. In the OAS of aqueous solution L_c , two maximums of light absorption at wavelengths are clearly shown: $\lambda = 260$ and 367 nm (Fig. 2).

"Hitachi F 7000" fluorimeter (quartz cuvette, OPL 10 mm) was used to measure the luminescence spectra. The luminescence spectrum of the sample ($C_{L_c} = 0.7 \text{ mg/dm}^3$) was recorded at excitation

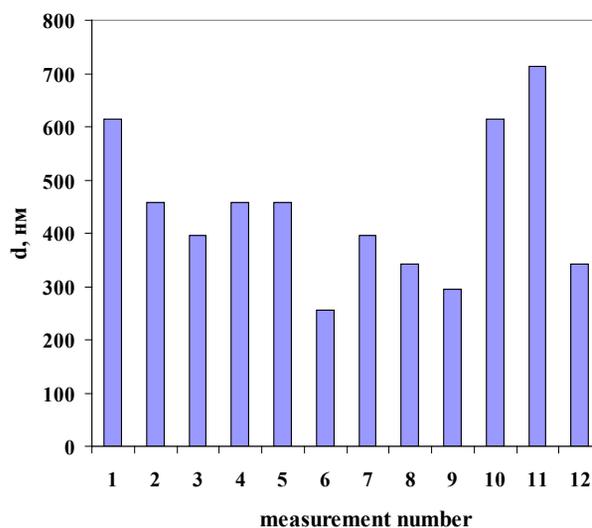


Fig. 1. DLS data on particle sizes in an aqueous solution of L_c ($C_{L_c} = 44 \text{ mg/dm}^3$).

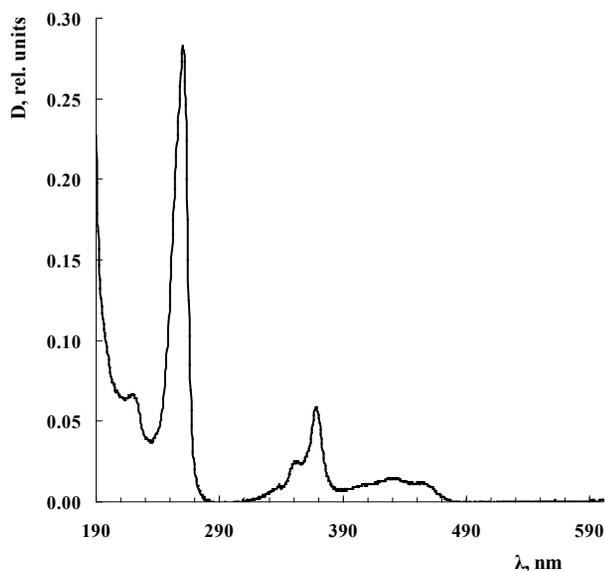


Fig. 2. Optical absorption spectrum of *Lc* aqueous solution ($C_{Lc} = 0.7 \text{ mg/dm}^3$). Light absorption maxima at wavelengths ($\lambda = 260$ and 367 nm).

wavelength ($\lambda_{exc} = 360 \text{ nm}$) with luminescence maxima $\lambda = 480$ and 510 nm (**Fig. 3**). When processing the luminescence spectra the built-in program filters were used and corrections parameters of the xenon lamp were taken into account. It was found that these corrections affect only the shape of the spectrum and not the position of the luminescence maxima for the *Lc* aqueous solution. Therefore in further study the main parameters in assessing the change in the optical properties of aqueous solutions of different

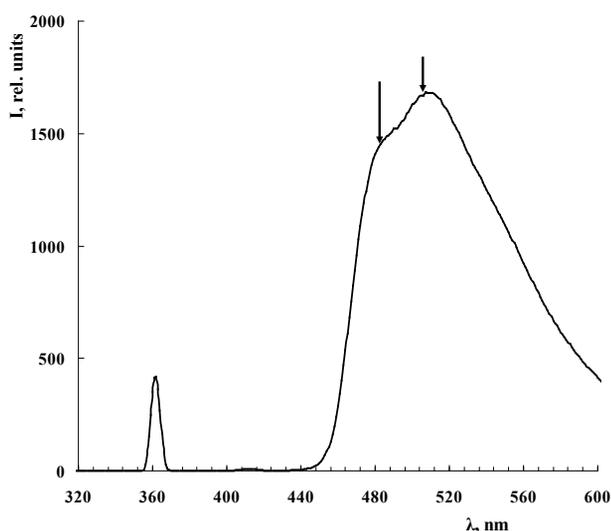


Fig. 3. The luminescence spectrum of *Lc* aqueous solution ($C_{Lc} = 0.7 \text{ mg/dm}^3$). Excitation at wavelength $\lambda = 360 \text{ nm}$, the arrows point the maxima of the *Lc* luminescence bands ($\lambda = 480$ and 510 nm).

dilutions were the position of these maxima and their intensity.

The initial solution was obtained by diluting *Lc* in distilled water according to the following scheme: distilled water (90 cm^3 volume) was poured into glass tube (volume 250 cm^3) in which sample of 8 mg *Lc* was dissolved. After dissolving *Lc* the volume of the aqueous solution was increased to 180 cm^3 (the solution was manually mixed with glass stick 20 times stirring clockwise). Thus the concentration of the *Lc* aqueous solution of the first dilution was $C_{L1} = 44 \text{ mg/dm}^3$.

Subsequent dilutions were obtained according to the scheme [6]. The second glass was filled with 90 cm^3 of distilled water and then 7.5 cm^3 of the solution from the first glassful was added to it by using glass pipette. After increasing the volume of the *Lc* aqueous solution to 180 cm^3 it was manually mixed with glass stick 20 times stirring clockwise. This was *Lc* aqueous solution of the 2nd dilution. The each solution container was covered with glass plate after each dilution. The glass stick and the glass pipette were washed with distilled water. The same dilution procedure was repeated up to 23d dilution.

The estimated concentration of the *Lc* solute at 10th dilution is equal ($C_{L10} = 1.7 \cdot 10^{-11} \text{ mg/dm}^3$) by the analytical chemistry formulas [7]. This concentration corresponds to the presence of several *Lc* molecules in aqueous solution. *Lc* molecules should be absent in an aqueous solution at 11th dilution. Nevertheless, if the dissolution of *Lc* solid occurs according to the cluster mechanism then *Lc* molecules can be detected at higher dilutions apparently. It is always difficult to prove that the soluble substance has decomposed into individual molecules and is not in solution in the form of dimers, trimers, or *n*-mers (clusters). The preparation of high dilution aqueous solutions has certain physicochemical meaning and it will become apparent soon. The properties change of aqueous solution has deeper character at dissolution of substances apparently. It is confirmed according to the luminescence data up to high dilutions. The reason for the abnormal behavior of the solution is the relaxation. The relaxation mechanisms base on many physical and chemical processes and effects in aqueous solutions apparently. The relaxation

mechanisms determine various quasi-equilibrium states of the aqueous solutions. They can be detected by optical instruments (e.g. by luminescence).

The aqueous solutions are labile systems that are change under the influence external and internal factors. The pressure and temperature were continuous change in during the registration of the luminescence for 23th aqueous solutions samples (approximately 2 h). These factors can affect change in the pH of aqueous solutions for example. One should not expect "reproducibility" of the data in the generally accepted sense because the experiment includes the series of samples (23 dilutions) under different environment parameters. So the environment parameters will be any different for another series of aqueous solutions samples. Therefore it isn't possible comparative analysis the data or it is very difficult and requires special mathematical methods.

In 1892 D.I. Mendeleev was headed the Main Chamber of Measures and Scales in St. Petersburg and he was made great contribution into chemical metrology. "Experimental study of the oscillations of scales" [8] is one of his famous works in the metrology field. It is model to study the quasi-equilibrium processes by registration decrement for the measured in experiment values¹. Mendeleev's decrement is widely used in many fields of science to process the results of experiment. Mendeleev's decrement is important practical method to identify the characteristics of periodic physical and chemical processes, e.g., for the phenomenon "Liesegang rings" [9-11]. The Mendeleev's decrement was used in the article to process the data of luminescence spectra for labile aqueous solutions (Appendix 1).

The aqueous solutions samples (2 cm³) were poured into quartz cuvette (OPL 10 mm) by using glass pipette and then the luminescence spectra were recorded. The luminescence spectra ($\lambda_{exc} = 360$ nm) were recorded in sequence in the reverse order of dilution and that was from 23rd down to the 1st sample. The glass pipette and quartz cuvette were washed with distilled water after the completion of the another measurement. The atmospheric

¹By definition, D.I. Mendeleev's decrement

$$D = \frac{X_{n+1} - X_n}{X_n - X_{n-1}} \text{ (where } n \text{ is the measurement number, } X_n \text{ is the measured value).}$$

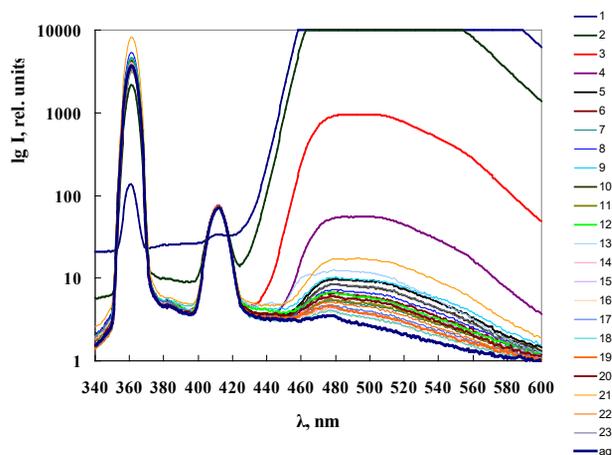


Fig. 4. The luminescence spectra of aqueous solutions from the 1st up to the 23rd dilution. The logarithm of the luminescence intensity is used along the ordinate axis.

pressure varied from 735 to 738 mmHg during the experiment, the temperature of 21°C remained approximately constant.

The luminescence spectra of all samples (from the 1st to the 23rd dilution) is showing in Fig. 4. The digits indicate dilutions and the lower graph is the luminescence spectrum of initial distilled water. If we plot the dependence graph of the luminescence intensity (at wavelength $\lambda = 480$ nm) on the dilution number (Fig. 5), then the data are divided into two groups. At the beginning the luminescence intensity decrease monotonously down to the 5th dilution and then it has oscillations

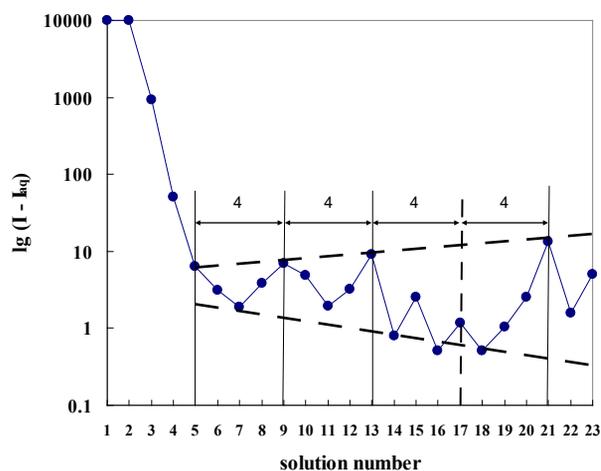


Fig. 5. It is plotting the depending luminescence intensity (at wavelength $\lambda = 480$ nm) of Lc aqueous solutions on the solution numbers. The logarithm of the intensity is plotted along the ordinate (the luminescence intensity for distilled water was subtracted).

with anomalously increasing amplitude down to the 23d dilution (Fig. 5). So the solutions down to 4th dilution can be attributed to "ordinary" aqueous solutions and the solutions down to 23rd dilutions can be assigned to the aqueous solutions with "high" dilution conditionally. It should note the concentration of the Lc aqueous solution is ($C_{Lc5} = 1.4 \cdot 10^{-4} \text{ mg/dm}^3$) at the 5th dilution according to the estimate. It is corresponds to approximately $4.0 \cdot 10^7$ molecules/dm³. The vertical lines indicate the main local luminescence maxima. Note they indicate the regularity also in character on the dilution numbers. The vertical dashed line marks the "local dip" in the vicinity of the 17th dilution.

The depending luminescence intensity of "high dilution" aqueous solutions (at wavelengths $\lambda = 480$ and 510 nm) on the solution number is shown in Fig. 6. The set of local maxima of the aqueous solutions luminescence intensity is shown in Fig. 6. When turn our attention to the maxima at 5th, 9th, 13th, and the 21st solutions. They are manifested well but in the vicinity of the 17th aqueous solution "local dip" is founded. The maximum luminescence occurs at the 21st solution both at wavelength of $\lambda = 480 \text{ nm}$ and 510 nm in this case. There should not be Lc molecules in solution according to estimate.

The special mathematical methods are used (Appendix 1) to analysis those data based on the concept of decrement ($D = \frac{X_{n+1} - X_n}{X_n - X_{n-1}}$). It was introduced by D.I. Mendeleev to study dynamic properties of physical and chemical systems [8]. Here n determines the action of the extensive factors for the dilution process and X_n determines the action of the intensive factors. If the decrement is integer then it is special situation. The characteristics both

the extensive process (arithmetic progression) and the intensive process (geometric progression) are agreed.

The oscillations intensities luminescence indicates to unstable the aqueous solutions behavior during sequential dilutions (after the 5th dilution). The local maxima of the luminescence intensity are located regularly (from the 5th down to the 23rd aqueous solution) and distance 4 units apart. In the vicinity of the 17th diluting "local dip" is founded (Fig. 6). Note the first local maximum intensity according to the 9th dilution of aqueous solution then there are practically no molecules in the solution (about 100 molecules/dm³) on estimate. The peculiarity of changing the luminescence intensity of aqueous solutions, for example, the appearance of a "local dip" is natural in systems with a "memory" as a manifestation of relaxation mechanisms that affect subsequent states of the solution (Appendix 2).

It should be noted that when modeling various physical and chemical processes in the relaxation system, it is necessary to apply a generalized decrement ($D = \frac{X_{n+1} - X_n}{X_n - X_{n-1}}$) in which the difference $X_n - X_{n-2}$ takes into account the "memory" of the system. This relation is easily transformed into a difference equation, and its solution determines the denominator of the geometric progression, of which X_n is a member (Appendix 2). In this case, two segments $X_n - X_{n-2}$ fit on the segment $X_{n+1} - X_n$. As a result, the processes of the extensive and intensive types are coordinated at points X_{n-2} , X_n and X_{n+1} (Fig. 7), and the first maximum (Fig. 6) falls on the 9th dilution (the 17th dilution does not correspond to this agreement) (Appendix 2).

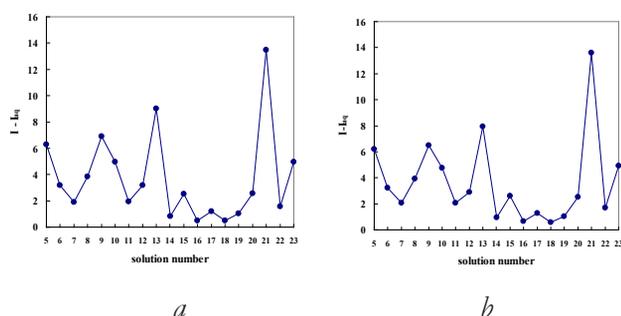


Fig. 6. The values for the luminescence maxima of aqueous solutions (the luminescence intensities for distilled water were subtracted) at wavelengths $\lambda = 480 \text{ nm}$ (a) and $\lambda = 510 \text{ nm}$ (b) depending on the dilution number.

The using of the decrement (or generalized decrement) and the corresponding difference equation is the basis for modeling physicochemical technologies [12]. They are usually presented as

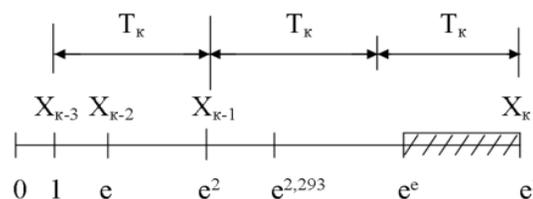


Fig. 7. A development cell [24,25] for matching parameters of arithmetic and geometric progressions. The shading indicates the transition zone.

models of parallel and sequential reaction stages, including those taking into account their relaxation properties [13].

Thus, the relationship of the physicochemical extensive and intense factors at the dilution stages with the practically absent starting material (L_c) is apparently determined by their coordination according to the relaxation mechanism. This leads to the appearance of both regular local luminescence intensity maxima of aqueous solutions at high dilutions, and to the regular "local dip" (Fig. 6).

3. RESULTS AND DISCUSSION

In a first approximation, the ability of chemical compounds to dissolve in water is characterized by the different type molecular interaction of the molecules of the soluble substance with water molecules, causing the division into hydrophobic and hydrophilic substances.

According to modern theoretical concepts, the number of physicochemical properties of liquid water and its structure are rather fully described by the random network model of hydrogen bonds (NHB) or its expansion — an of hydrogen bonds elastic network (ENHB) [14]. There are many ways to represent interparticle interaction in aqueous solutions, the most popular of which is pair interaction (pair interaction potential or its modifications). In addition the three-particle potential and more complex potentials are used, for example, the potential of an immersed atom [15]. Such variety of potentials indicates the search for adequate models to describe the physicochemical properties of water systems.

The hydrogen bond network model is productive because it allows us to discuss the real "chemistry of aqueous solutions on weak hydrogen bonds" and expands the understanding of the causes of the manifestation of anomalous physicochemical properties in them. When discussing the causes of various anomalies in aqueous solutions, it is necessary to take into account the nature of the molecular bonds in the aqueous solution (hydrogen bonds). In this case, an additive increase/decrease in the mass of the solution components due to the transformation of the hydrogen bond network leads to a multiplicative increase/decrease in the number

of bonds. This effect apparently determines the aqueous solution anomalous properties.

This approach is accepted in physical chemistry when in thermodynamic calculations distinguish between extensive and intensive properties of aqueous solutions. At the molecular level of consideration, the extensive properties of the system depend on the number of elements in the system and their change (for example, an increase) is accompanied by the addition of elements to the system (arithmetic progression). That leads to an increase in the "connectivity" between the elements in the system and the appearance of intense properties determined by the number of bonds (for example, the energy of the system). It is important to keep in mind that a linear increase in the number of elements in the system leads to an exponentially growing number of "bonds" between them, described by a geometric progression. Of course, the basis and the exponent are different for each system and are interconnected.

Molecular interaction during the dissolution of one substance in water leads to the transformation (sometimes significant) of NHB and an increase (on average) in the system with the "strong"² hydrogen fraction. As a rule the strong hydrogen bonds also have long lifetimes [16], which leads to the appearance of partially ordered associations water molecules or groups of molecules at the "boundary" with dissolved molecules. In our opinion this fact leads to a problem not quite well indicated by the term "memory" of water. The "memory" of water corresponds either to the stable hydrate formation of the dissolved hydrophilic substance with "strong" hydrogen bonds, or to the formation of interphase region [17] (from water molecules, according to [18], "3-4 molecules" are thick) between a hydrophobic substance and bulk water with NHB. The relaxation of the network of hydrogen bonds in water when interacting with hydrophilic/hydrophobic molecules of the solute, apparently, determines the physicochemical processes, which are understood as the "memory" of water.

It should be noted that the phenomenon of hydrophobic interaction upon contact of water ²A strong hydrogen bond suggests that the hydrogen atom is (on average) practically on the line connecting two oxygen atoms of two water molecules.

with the atmosphere causes the formation of the "nanobubble gas phase" with predominant nanobubble sizes in the range of 100 - 200 nm [4]. The average sizes of nanobubbles formed in water under identical conditions in the atmosphere from pure components (nitrogen, oxygen, carbon dioxide) are stable [19]. The average sizes of nitrogen and oxygen bubbles are close to each other and have the above values, and for carbon dioxide the average size of the bubbles differs by three orders of magnitude. This difference is apparently determined by the solubility of carbon dioxide in water with the formation of the carbonic acid. According to L. Pauling, under normal conditions, approximately 19 cm³ of atmospheric gas dissolves in 1 dm³ clear water [20]. If we assume that the gas is dissolved in the form of nanobubbles with an average nanobubble diameter of 150 nm, then this volume (19 cm³) corresponds to a concentration of nanobubbles of approximately 10¹² dm³/cm³. According to [4.21], the "real" concentration of nanobubbles in this size range is estimated at about 10⁹ dm³/cm³. This result shows that, apparently, part of the molecules of the atmospheric gas is either located in bubbles much smaller (< 100 nm) or in clathrates [22, 23].

When analyzing the physicochemical properties of aqueous solutions in contact with the atmosphere, it is necessary to take into account the constant presence of the quasi-equilibrium "nanobubble phase" in atmospheric gas. Many physicochemical properties of aqueous solutions are apparently determined by the constant presence of this phase, the state of which strongly depends on pT conditions (and not only) during the experiments. The most important factor is the inner surface of nanobubble, the estimated volume of which at an average size of 150 nm and the concentration of 4·10⁹ bubbles/cm³ is nearly 3000 cm²/dm³ ($S = \pi D^2 \times 4 \cdot 10^9 \text{ bubbles/cm}^3 \approx 2826 \text{ cm}^2/\text{dm}^3$) [21]. In addition, the interphase region of nanobubbles appears to be bound (polarized) water, the properties of which and the effect it has on the character of physicochemical processes in aqueous solutions have yet to be studied.

Above was considered only one of the constantly acting factors in aqueous solutions (nanobubble gas phase), without touching on the specific mechanisms of intermolecular interaction of the molecules

of the solute and the solvent (water). In turn, this interaction is an equally important factor in the dissolution of solids in water and could determine the presence of the part of the substance in the cluster state (dimers, trimers, ..., *n*-mers), which composition depends on the volume of the solvent. It should be noted that at least two physicochemical processes compete in the process of dissolving one substance in water, which determine the elasticity of the solution and the osmotic pressure in the solution, which ultimately determines the quasi-equilibrium concentration of the molecules of the dissolved substance in it. Apparently, many physicochemical properties of aqueous solutions could be determined by the type of connectivity (for example, a system of strong hydrogen bonds near the surface, dissolved molecules) and, in general, the number of "strong" hydrogen bonds.

Thus, the basis for constructing the model of physicochemical processes in an aqueous solution should be based on the principle of the relationship between the type of accumulation of elements in the system (arithmetic progression) and the growth of "connectivity" in the system (solution) according to a power law (geometric progression). For example apparently this effect determines the of the optical properties change of the solution. This allowed us to expand our understanding of modeling the aqueous solutions properties with high dilutions. Instead of assuming that the properties of the solution are determined by the presence of solute molecules after each dilution, it is proposed to consider the change in the system of the number of moles with "strong bonds" (for example, hydrogen bonds) after each dilution. So, the "memory" of water with a large number of dilutions apparently does not depend on the number of molecules of the initial dissolved substance (arithmetic progression), but on the degree ("depth") of the NHB transformation under the influence of the dissolved substance in the initial concentration (geometric progression) and further from breeding to breeding.

4. CONCLUSION

Summarizing the results of the study of the aqueous solutions luminescence of with L_c high dilutions, it should be noted that, apparently, there is the boundary in the concentration of L_c (estimated

at about 10^{-4} mg/dm³), when the nature of the luminescence changes significantly. In addition, in the case when, according to the estimate, there are no Lc molecules at all in the aqueous solution, the luminescence intensity amplitude at wavelengths $\lambda = 480$ and $\lambda = 510$ nm has the growing tendency, which is apparently a consequence of unstable type physicochemical processes occurring in an aqueous solution.

Using the decrement of D.I. Mendeleev and its generalized version (taking into account relaxation) made it possible to evaluate the regular nature of the arrangement of the local maxima luminescence intensity as corresponding to the coordination of extensive and intensive mechanisms for changing the characteristics of solutions during successive dilutions.

Finally, one general methodology for the study of labile aqueous solutions is proposed, which with appropriate standardization of the procedure for their preparation, can be used to verify the anomalous properties of high dilution aqueous solutions.

APPENDIX 1

From the decrement of D.I. Mendeleev for a number of experimental points

$$D = \frac{X_{n+1} - X_n}{X_n - X_{n-1}} \quad (1)$$

follows the corresponding difference equation of the form.

$$X_{n+1} - (D + 1)X_n + DX_{n-1} = 0. \quad (2)$$

The solution to equation (2) is sought in the form of $X_n = \lambda^n$, which leads to the characteristic equation $\lambda^2 - (D + 1)\lambda + D = 0$, whose roots are equal $\lambda_1 = 1, \lambda_2 = D$.

As a result, the solution of equation (2) has the form

$$X_n = C_1 + C_2 D^n \quad (3)$$

which corresponds to an exponential function of a fixed level C_1 , where D is the denominator of geometric progression (decrement).

APPENDIX 2

Consider a generalized version of the decrement of D.I. Mendeleev (1), taking into account the possible relaxation characteristics of the breeding process.

They determine the "memory" parameters of the state, which leads to a generalized decrement of the form

$$D_1 = \frac{X_{n+1} - X_n}{X_n - X_{n-2}} \quad (4)$$

and reproduces the solution (3) of the previous equation, but it allows one to synchronize the members of arithmetic and geometric progressions. For him, the difference equation has the form

$$X_{n+1} - (D_1 + 1)X_n + D_1 X_{n-2} = 0, \quad (5)$$

and his characteristic equation

$$\lambda^3 - (D_1 + 1)\lambda^2 + D_1 = 0. \quad (6)$$

When we rewrite (6) in the $(\lambda - 1)(\lambda^2 - D_1\lambda - D_1) = 0$ form, we obtain the obvious first root, as a result of which we have two more roots $(\lambda_{2,3})$.

$$\text{Then } \lambda_{2,3} = \frac{D_1}{2} \pm \sqrt{\frac{D_1^2 + 4D_1}{4}}.$$

in this case the solution of equation (5) has the form

$$X_n = C_1 + C_2 \lambda_2^n + C_3 \lambda_3^n.$$

Then, at $C_3 = 0$, the solution (3) of the difference equation corresponding to the decrement of D.I. Mendeleev [8] is reproduced.

In this case, it is possible to determine the conditions for matching the extensive and intensive characteristics of the solution using the synchronization model of arithmetic and geometric progressions.

The relationship between the intervals representing the arithmetic progression (T_n) and the terms of the geometric progression (X_n) is determined by the equation

$$X_{n+1} - X_n = D_1 T_n. \quad (7)$$

$$\text{Then } X_{n+1} \left(1 - \frac{1}{\lambda}\right) = D_1 T_n \text{ and } X_n = \frac{\lambda(D_1 - 1)}{\lambda - 1} T_n.$$

This ratio determines the relationship between the members of the arithmetic progression with difference and geometric progression with the denominator λ .

When the value is

$$D_1 = 2, \quad \lambda = 1 \pm \sqrt{3}.$$

Here the positive root $\lambda = 1 + \sqrt{3} = 2.7320\dots$, is close to the Neper number $e = 2.71828\dots$, and the difference equation has the form

$$X_{n+1} = 2(X_n + X_{n-1})$$

$$X_{n+1} = \frac{2e}{e-1} T_n = 3.164 T_n.$$

In general, the synchronization of boundaries represented by arithmetic and geometric progressions is shown in **Fig. 7**.

Moreover, $e^2 = 7.39\dots$ and $e^3 = 20.085\dots$ and therefore the dilution ratio represented by this structure is 7.4 in the first case, and in the second case it is 20.

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