

The Effect of Concentration on the Optical Properties of Solutions of 3, 6 - Diaminoacridine

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The effect of concentration of 3, 6 - diaminoacridine solution on absorption spectra, luminescence spectra, intensity of glow, average lifetime of excited state and polarization spectra was studied. It was shown that the changes in the optical properties due to increase of concentration of a solution are the result of dimerization of molecules in the solution. Optical properties of dimers were established, and the degrees of association of the solutes at various concentrations were determined. Study of the effect of solvent and temperature on the association of 3, 6 - diaminoacridine molecules were carried out.

AN increase in the concentration of solutions of complicated organic compounds usually causes essential changes in the optical properties of the solute. These changes are: depolarization of luminescence, increase of extinction, and decrease in average lifetime of excited state τ of luminescent material. In cases of large increases in concentration one often observes significant changes in absorption spectra and sometimes also in luminescence spectra.

The above-mentioned effects of concentration were known long ago and different hypotheses were offered as explanations. Most of them were abandoned for one reason or another. At present only two basic concepts remain in favor. One of them associates the concentration changes with the inductive transfer of excitation energy from an excited molecule to a non-excited one¹. Another considers the association of molecules of solute as the main reason for concentration effects².

The theory of inductive migration of energy is well developed at present. It has been proved many times experimentally. The theory of molecular association is in fact not yet created. Only some computations were made, which later were confirmed by experiment. It should be mentioned that none of these notions can explain all known experimental facts without making some special assumptions. Hence the theory of inductive migration of excitation energy generally omits consideration and explanation of the significant

changes in absorption spectra, and sometimes also in luminescence spectra, which occur in concentrated solutions. On the other hand, starting from the notion of molecular association, one cannot explain, without making some special assumptions, the parallel decrease in emission of light and in τ when the concentration of the solution increases.

The change in optical properties due to the increase in concentration is different for different materials. Some cases can be better explained by migration of energy, others by association. Thus, apparently, both notions are based on correct assumptions, but each of them has its own domain of application. In some cases operation of both mentioned kinds of interaction between the molecules seems to be probable.

In this work the effect of concentration of solution on optical properties of acridine and of nine of its derivatives was studied³. The data obtained lead us to the conclusion that the concentration effects of acridine solutions are the results of the association of the molecules of these materials. Formation of associated molecules was explained by some authors as a result of the action of dispersion forces⁴. Association is a reversible process. The molecules return to the monomeric state as a result of dilution of the solution.

The increase of concentration has different effects on solutions of different compounds. Apparently association can occur in different ways depending on the structure of the molecules in question. With respect to the type of effect of concentration on ab-

¹ F. E. Vavilov, *Microstructure of Light*, Publishing House of Academy of Sciences of USSR (1950)

² V. L. Levshin, *Photoluminescence of Liquid and Solids*, State Publishing House of Technical Literature Moscow-Leningrad (1952)

³ V. L. Levshin, *Doklady Akad. Nauk SSSR* **96**, 473 (1954)

⁴ E. Rabinowitch and L. Epstein, *J. Amer. Chem. Soc.* **63**, 69 (1941)

sorption spectra the investigated compounds can be grouped in the following manner. To the first group belongs 3, 6 - diaminoacridine. This article is devoted to the effect of concentration on its optical properties. The changes in optical characteristics due to changes in concentration of 3, 6 - diaminoacridine are strong and unique. The data on the effects of concentration on the optical properties of other acridine compounds we have investigated, which belong to the second group, and also considerations concerning the character of their association, will be described in the next article. The measurements were made by photoelectric methods. The absorption spectra were obtained by means of spectrophotometer SF - 4. The luminescence spectra were measured with photoelectric apparatus, arranged on the principle of the monochromator UM - 2 connected to the photoamplifier FEU - 19. The average lifetime of the excited state of the molecules was measured with phase fluorometer designed by Galanin⁵. The polarization spectra were obtained by means of the photoelectric arrangement of N. D. Zhevandrov which was wired according to Spektorov's circuit diagram⁶.

1. THE EFFECT OF CONCENTRATION ON THE ABSORPTION SPECTRUM OF 3, 6 - DIAMINOACRIDINE

The absorption spectrum of 3, 6 - diaminoacridine consists of two wide bands, located in the visible and the ultraviolet ranges of the spectrum. Fig. 1 shows the results of measurements on 3, 6 - diaminoacridine solutions in ethyl alcohol*. In the long wave band the increase in concentration causes a sharp decrease of the absorption maximum at $\lambda = 460 \text{ m}\mu$. At the same time a new absorption maximum appears at $\lambda = 405 \text{ m}\mu$. At a concentration of $2 \times 10^{-3} \text{ gm/cm}^3$ the $460 \text{ m}\mu$ band absorption maximum decreases almost by a factor of three and becomes equal in absolute value to the absorption in the new maximum at $405 \text{ m}\mu$. Analogous changes are observed in the ultraviolet absorption band. At a concentration $c = 2 \times 10^{-5} \text{ gm/cm}^3$, in addition to the maximum at $\lambda = 260 \text{ m}\mu$, a shoulder absorption (secondary maximum) appears at λ

$= 285 \text{ m}\mu$. As concentration increases the main absorption maximum becomes lower, and the shoulder absorption increases markedly.

The above-described changes in absorption spectra of 3, 6 - diaminoacridine have previously been found in the long wave absorption bands of some compounds in water solutions. Thus Levshin discovered similar changes in the spectrum of rhodamine 6G^{7,8}, and Rabinowitch and Epstein observed them in thionine and methylene blue⁴, etc.⁹⁻¹². Significant changes in the absorption spectrum, such as the appearance of new maxima and disappearance of the old ones, can be explained at high concentrations by formation of associated groups of 3, 6 - diaminoacridine molecules having absorption spectra which are different from the spectrum of molecules in the monomer state. Also the absorption spectra of associated molecules consist of two bands which are located closer to each other than the corresponding bands of the monomers.

From the fact that the spectral curves obtained at different concentrations cross at one point ($\lambda = 417 \text{ m}\mu$) one can consider the concentrated solutions as binary mixtures consisting of molecules in monomer and associated conditions^{7,1}. From the absorption spectrum of 3, 6 - diaminoacridine one can see that at increased concentration all associated groups of molecules must have a common spectrum. Hence it is natural to consider that in a concentrated solution of 3, 6 - diaminoacridine only monomers and dimers are present. If, however, some groups of higher aggregation are formed, their spectrum must coincide with the absorption spectrum of the dimer. The absorption spectrum of 3, 6 - diaminoacridine changes markedly with increase of concentration, which can be explained by a strong interaction of molecules in the process of dimerization. Assuming that the molecules of 3, 6 - diaminoacridine aggregate in a "pile", the distance between the components of associated molecules in this case will be very small and interaction between them large. A similar conclusion is drawn by the previous workers⁴ whose computations for

⁵ M. D. Galanin, Doklady Akad. Nauk SSSR **73**, 925 (1950)

⁶ L. A. Spektorov, Doklady Akad. Nauk SSSR **65**, 485 (1949)

* Ordinate shows absorption coefficients. Concentrations are computed in grams per cm^3 .

⁷ V. L. Levshin, Zh. Fiz. Khim. **6**, 1 (1935)

⁸ V. L. Levshin and T. M. Tarasova, Izv. Acad. Nauk SSSR, Ser. Fiz. **15**, 573 (1951)

⁹ V. Söderberg, Ann. Physik. **41**, 381 (1913)

¹⁰ B. Van der Plaats, Ann. Physik **47**, 424 (1915)

¹¹ T. P. Kravets, A. L. Peshkina and Z. V. Zhidkova, Izv. Acad. Nauk SSSR, Ser. Fiz. **14**, 493 (1950)

¹² V. Zauker, Z. Phys. Chem. **199**, 225 (1952)

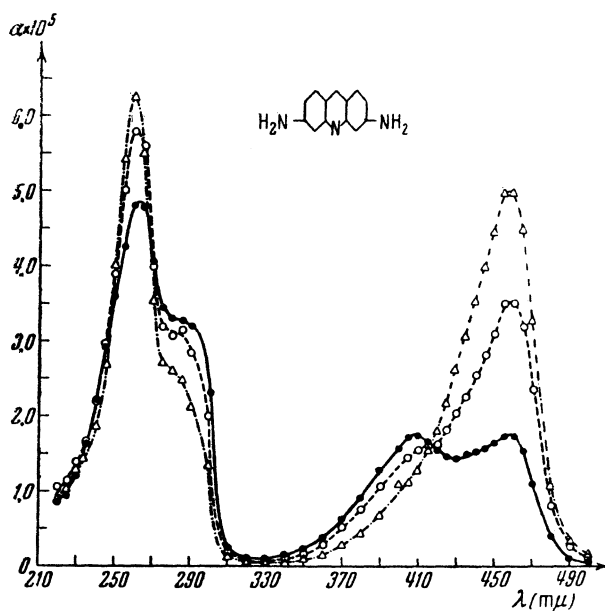


Fig. 1. Dependence of absorption spectrum of 3, 6 - diaminoacridine in ethyl alcohol on concentration of the solution.

● - 2×10^{-3} , ○ - 2×10^{-4} , △ - 2×10^{-5} gm/cm³.

thionine solutions show that the distance is only 3.12 Å.

The comparison of structural formulas of materials for which changes in absorption spectra similar to that of 3, 6 - diaminoacridine were observed, shows that all of them, in spite of different composition have substituents symmetrically located on both sides of the molecular skeleton. The compound 3, 6 - diaminoacridine has this type of structure (Fig. 1). It is possible that the aggregation of associated molecules may take place by means of these groups.

The determination of areas of absorption spectra of 3, 6 - diaminoacridine shows that with an increase of concentration the absorption ability of the molecules decreases markedly. This decrease takes place because of an absorption drop in long wave band. In the ultraviolet range of the spectrum the increase in concentration causes the redistribution of absorption inside the band only. The total value of absorption in the ultraviolet region remains unchanged.

Physical-chemical properties of the solvent must have a significant effect on the association of molecules of the solute. In this work the effect of concentration on absorption spectra of 3, 6 - diaminoacridine in various solvents was investigated. Identical

spectra were observed in both glycerin and ethyl alcohol (Fig. 1), which is natural, since the two solvents are related to each other. However, this shows that the viscosity of a medium has an insignificant effect on the association of 3, 6 - diaminoacridine molecules. In acetone (Fig. 2a), even at $c = 5 \times 10^{-6}$ gm/cm³, most of the 3, 6 - diaminoacridine molecules are in an associated state. At $c = 2 \times 10^{-3}$ gm/cm³, the process of dimerization is completed, which is expressed by the complete disappearance of a monomeric maximum. In a pyridine solution the most active association of 3, 6 - diaminoacridine molecules takes place. At $c = 2 \times 10^{-5}$ gm/cm³, practically all the molecules are in an associated state. With a further increase of concentration, the absorption spectrum remains unchanged (Fig. 2b). Similar phenomena can be observed in water solutions of hydrochloric 3, 6 - diaminoacridine.

Hence, from experiments with various solvents, one observes that the 3, 6 - diaminoacridine molecules associate most actively in media (such as pyridine, acetone, glycerin, alcohol) which hinder the development of association of dyestuffs. Here with one cannot relate the association phenomena either to dielectric constant or to dipole moment of the investigated solvent.

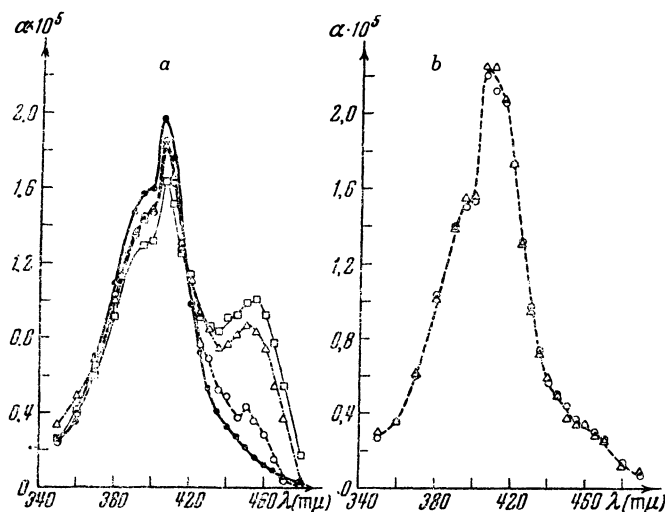


Fig. 2. The effect of solvent on the absorption spectrum of 3, 6 - diaminoacridine, *a* - solution in acetone, *b* - solution in pyridine, ● - 2×10^{-3} , ○ - 2×10^{-4} , △ - 2×10^{-5} , □ - 5×10^{-6} gm/cm³

To compute a degree of association of solvents with different concentration one can separate the dimer bands from monomeric bands in their absorption spectra. From Fig. 1 ($c = 2 \times 10^{-5}$ gm/cm³) it follows that the monomeric absorption maximum corresponds to $\lambda = 460$ m μ and the absorption band is more or less symmetrical. Assuming that the long wave band edge is caused purely by a monomeric absorption, one can draw the short wave part of the monomeric band according to it. By subtraction of the monomeric part from the total band, one can determine the absorption which is characteristic for the dimeric state of molecules. This enables one to determine how the absorption strength is distributed between monomers and dimers as the concentration of the solution increases. Performed computation has shown that during a transition from the monomeric state to a dimeric state the absorption strength of the molecules decreases by a factor of approximately 2.3. Knowing this and also the absorption strength of monomers and dimers at different concentrations of the solution, one can calculate the percentage of the monomers and dimers for each of the concentrations investigated. This calculation can also be made by some other methods.

It was mentioned above that, in concentrated acetone or pyridine solutions of 3, 6 - diaminoacridine, the dimeric band appears in its pure form. By comparing these bands with the monomeric band obtained for low concentration solutions in alcohol, one can determine the content of monomers and di-

mers in alcohol solutions of different concentrations. The result of computations by three methods are shown in Table I*.

It is evident that in spite of the approximations made in the computations all three methods give results which are in good agreement.

As one can see from Fig. 1, the maximum at $\lambda = 285$ m μ in the ultraviolet absorption band does not vanish completely even at considerable dilution of the solution. From this it follows that dimers as well as monomers show absorption in this region. By use of the results shown in Table I, the true absorption bands of molecules in monomeric and dimeric conditions were calculated.

Monomeric bands $\lambda_{\max} = 260, 285; 460$ m μ

Dimeric bands $\lambda_{\max} = 270, 290; 405$ m μ

Hence the dimers of 3, 6 - diaminoacridine molecules have two absorption bands which are located somewhat closer to each other as compared with the absorption bands of the monomers.

* First method - direct analysis of absorption bands of the alcohol solutions.

Second method - analysis by use of the band from acetone solutions.

Third method - analysis by use of the band from pyridine solutions.

TABLE I

Concentration of the alcohol solution of gm/cm ³	First Method		Second Method		Third Method		Average Value	
	Monomers	Dimers	Monomers	Dimers	Monomers	Dimers	Monomers	Dimers
2×10^{-5}	0.88	0.12	0.89	0.11	0.86	0.14	0.88	0.12
2×10^{-4}	0.63	0.37	0.64	0.36	0.59	0.41	0.62	0.38
2×10^{-3}	0.31	0.69	0.32	0.68	0.28	0.72	0.30	0.70

2. THE EFFECT OF CONCENTRATION ON LUMINESCENCE SPECTRA OF 3, 6 - DIAMINOACRIDINE SOLUTIONS

The dimers which are formed due to the increase of concentration can either retain some luminescence intensity¹³ or lose it completely.

In the case of 3, 6 - diaminoacridine the dimers retain the luminescence intensity. The luminescence spectra of 3, 6 - diaminoacridine are shown in Fig. 3 *a* and 3 *b* as functions of concentrations of the solutions for two different wavelengths of exciting light. These wavelengths were chosen in such a way that in one case mainly the monomers and in the other case mainly the dimers were excited*.

From the graphs on Fig. 3 one can see that the transition from a dilute solution to a concentrated one results in a small shift of the luminescence spectrum toward longer wavelengths and makes the emission band wider on account of development of the long wave part of the spectra. Decrease in the wavelength of the exciting light also causes some shift of the spectrum toward longer wavelengths and widens the emission band. This is clearly seen in Fig. 3 *c* where the dependence of the luminescence spectrum of the concentrated 3, 6 - diaminoacridine solution on the wavelength of exciting light is shown. Thus either an increase in concentration or a change of excitation wavelength in the region of a dimeric maximum yields approximately the same results with respect to the luminescence spectra. The noticeable change in the shape and location of the emission band, which takes place either upon increase in concentration of the solu-

tion or upon a decrease of wavelength of the exciting light gives additional confirmation of the association of 3, 6 - diaminoacridine molecules. The changes in luminescence spectra can be explained in the following way: the dimers, formed as concentration increases, have their own luminescence intensity, and their spectrum is shifted somewhat in the long wave direction and differs in shape from the monomeric spectrum. With the increase in concentration, the dimers take a larger and larger part in the emission, which results in the observed change in the luminescence spectrum.

We mentioned above that different absorption bands correspond to monomers and dimers. Decreasing the wavelength of the exciting light and going over from $\lambda_{\text{excitation}} = 436 \text{ m}\mu$ to $\lambda_{\text{excitation}} = 365 \text{ m}\mu$ we change the relative degree of excitation of the monomeric and dimeric fractions of the molecules. In the first case (Fig. 1), mainly the monomers and in the second case mainly the dimers will be excited. Correspondingly, the luminescence spectra will belong either to the monomers or to dimers, or to the mixture of both in certain proportion. By proper choice of the excitation and the concentration of the solution, one can get the monomeric and dimeric spectra in pure form. Thus, in Fig. 3 *a* there is shown a monomeric luminescence spectrum ($c = 5 \times 10^{-6} \text{ gm/cm}^3$) and in Fig. 3 *b*, a dimeric spectrum ($c = 2.2 \times 10^{-3} \text{ gm/cm}^3$).

If the above-mentioned line of reasoning is correct, one can represent any of the experimentally obtained spectra by superposition of a monomeric and a dimeric luminescence spectrum taken in the proper proportions. In the Figs. 4 *a* and 4 *b* is shown a comparison of experimental data with the computed data for two of the luminescence spectra obtained. In the first case one has to assume that 0.7 of the emission is by dimers and only 0.3 by the monomers (Fig. 4 *a*): in the second case the dimeric emission is 0.2 and the monomeric emission is 0.8 (Fig. 4 *b*). As one can see from the plotted curves, agreement between experiment and computation is

¹³V. L. Levshin, Z. Physik 43, 230 (1927)

* The necessary corrections with respect to secondary absorption were introduced according to the formula suggested in reference 2, page 51. However, because of the small superposition of the absorption spectra and the luminescence spectra of 3, 6 - diaminoacridine, these corrections were small.

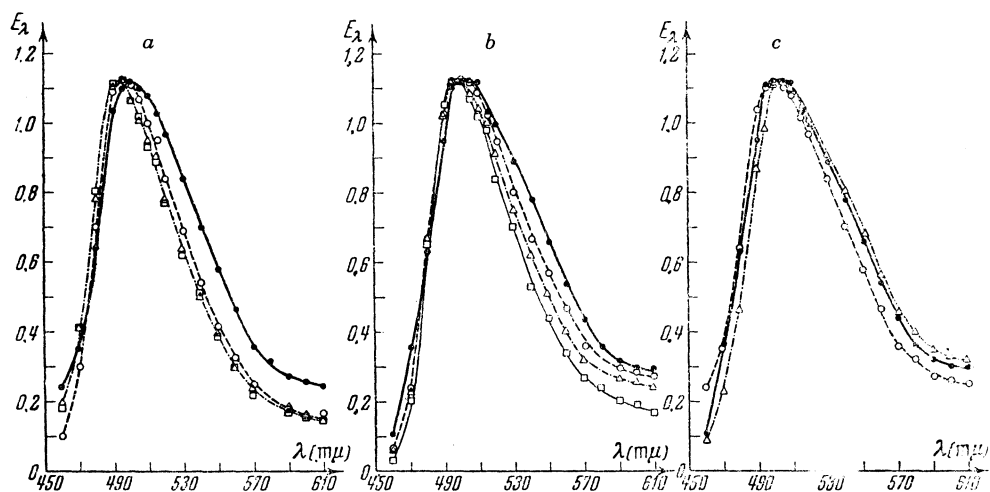


Fig. 3. Dependence of the luminescence spectra of alcohol solutions of 3, 6 - diaminoacridine on concentration and wavelength of exciting light. *a* - $\lambda_{\text{excitation}} = 436 \text{ m}\mu$; *b* - $\lambda_{\text{excitation}} = 365 \text{ m}\mu$, $\bullet - 2.2 \times 10^{-3}$, $\circ - 2 \times 10^{-5}$, $\Delta - 2 \times 10^{-5}$, $\square - 5 \times 10^{-6} \text{ gm/cm}^3$, *c* - $c = 2.2 \times 10^{-3} \text{ gm/cm}^3$, $\circ - \lambda_{\text{excitation}} = 436$, $\bullet - \lambda_{\text{excitation}} = 365$, $\Delta - \lambda_{\text{exc}} = 303 + 313 \text{ m}\mu$

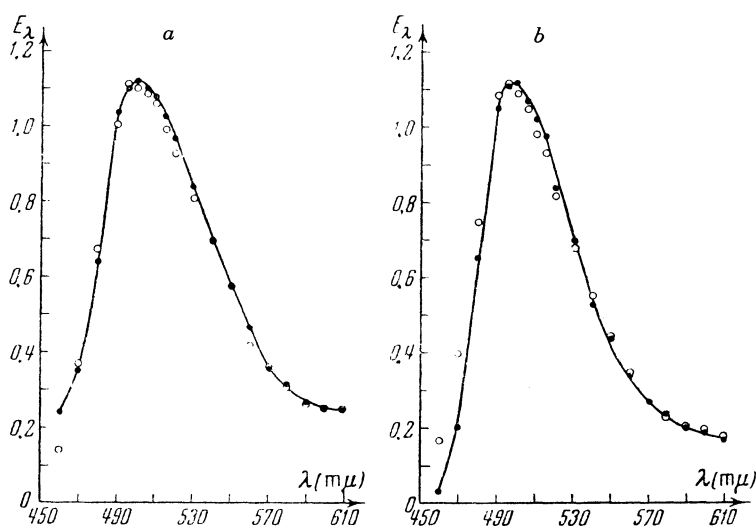


Fig. 4. Comparison of the shape of luminescence spectra for 3, 6 - diaminoacridine, obtained by calculation and by experiment: *a* - $\lambda_{\text{excitation}} = 436 \text{ m}\mu$, $c = 2.2 \times 10^{-3} \text{ gm/cm}^3$; *b* - $\lambda_{\text{excitation}} = 365 \text{ m}\mu$, $c = 5 \times 10^{-6} \text{ gm/cm}^3$; \bullet — experiment; \circ — calculation

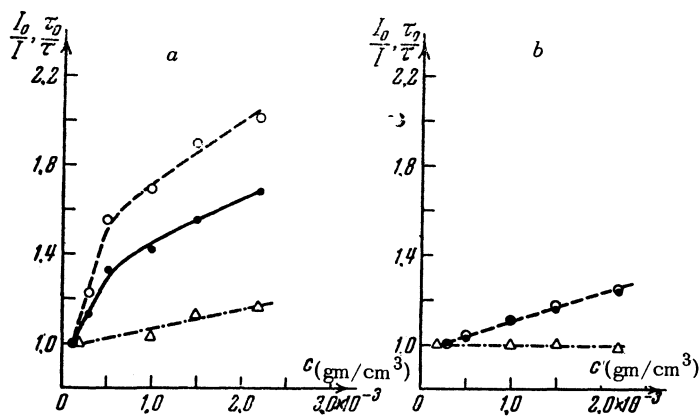


Fig. 5. The change of intensity of luminescence and of τ at increase of concentration of the 3, 6 - diaminoacridine solution in alcohol: a - $\lambda_{exc} = 436 \text{ m}\mu$; b - $\lambda_{exc} = 365 \text{ m}\mu$;

● I_0/I ($\lambda_{obs} = 530 \text{ m}\mu$), ○ I_0/I ($\lambda_{obs} = 490 \text{ m}\mu$), Δ - τ_0/τ

fairly good.

Marked divergence between the experimental and computed curves in the short wave part of the spectrum (Fig. 4b) apparently can be explained by the errors in measurements, which are to be expected at such small concentrations and (correspondingly) very low intensity of luminescence.

3. EXTINCTION OF LUMINESCENCE DUE TO CHANGE IN CONCENTRATION AND VARIATION OF τ

The increase in concentration results in extinction of luminescence and in variation of the average lifetime of the excited state of the 3, 6 - diaminoacridine molecules. The experiments have shown that the process of extinction depends on the wavelength of the exciting light and on the wavelength of the emission. In Fig. 5 the curves which describe the change of luminescence intensity due to increase of concentration of the solution are shown.

Strong extinction is observed at $\lambda_{excitation} = 436 \text{ m}\mu$ (Fig. 5). In this connection its observed behavior is different in regions of $\lambda_{observation} = 490$ and $530 \text{ m}\mu$. The extinction is markedly weaker at $\lambda_{excitation} = 365 \text{ m}\mu$. In this case the extinction curve is linear, and its concentration dependence is the same for both of the observation wavelengths chosen (Fig. 5b).

The changes of τ due to changes in concentration also depend on the wavelength of the exciting light. At the $\lambda_{excitation} = 436 \text{ m}\mu$, τ markedly de-

creases as the concentration increases (Fig. 5a). As we go over to $\lambda_{exc} = 365 \text{ m}\mu$, τ remains unchanged in the entire interval of concentrations investigated (Fig. 5b).

The above-described extinction due to change in concentration and variation of τ can be explained with the help of the notion of dimerization of the molecules of 3, 6 - diaminoacridine. In the case of excitation of luminescence by the mercury line $436 \text{ m}\mu$ (Fig. 5a), the majority of the excited molecules are monomers. With increase of concentration the intensity of luminescence of the monomers becomes weaker, partly because of extinction due to change in concentration and partly because of the transition of the molecules from the monomeric state to a dimeric one. Although the dimers also have luminescence intensity, the chosen excitation conditions are not favorable for the appearance of their luminescence. For this reason only a small fraction of the dimers will take part in emission. The majority of them will not become excited, thus contributing to the extinction. The difference in the shape of the extinction curves resulting from observation of luminescence at different wavelengths is explained by the fact that $\lambda_{obs} = 490 \text{ m}\mu$ lies in the region of the monomeric maximum and $\lambda_{obs} = 530 \text{ m}\mu$ is located closer to the dimeric maximum. In the first case the extinction curve represents mainly the decrease in luminescence of the monomeric part of the molecules, while in the second case the participation of the monomer in the emission decreases and the extinction is less in-

tense. Upon excitation of luminescence by the line 365 m μ (Fig. 5b) the participation of the monomer in the emission is not large. Therefore the drop in intensity of luminescence with increase in concentration does not depend on the choice of the wavelength of observation.

There was mentioned above the difference in variation of τ due to concentration upon excitation of luminescence by mercury lines 436 and 365 m μ . On that basis, apparently, one can consider that with increase in concentration, the τ of the monomers decreases, and the τ of the dimers remains unchanged. The absolute values for τ of the monomers and dimers obtained at low concentrations of the solution at which the extinction does not occur are similar within the limits of the errors of the experiment ($\tau_{\text{monomers}} = \tau_{\text{dimers}} \approx 5.3 \times 10^{-9}$ sec).

Since τ of the monomers decreases upon increase in concentration, the extinction of the monomers, apparently, must be ascribed to migration of the excitation energy from an excited monomer to the neighboring non-excited monomers. Migration of energy from a monomer to a dimer is improbable, since the luminescence spectrum of the monomers practically never superimposes on the absorption spectrum of the dimers.

A weak extinction, which one observes when excitation of the dimeric fraction of the molecules prevails (Fig. 5b), cannot be explained by migration of energy from the excited dimers to the non-excited dimers or to the monomers. Indeed, one cannot expect a transfer of energy from one dimer to another dimer, since their luminescence and absorption spectra never superimpose. The transfer of energy from a dimer to a monomer is also improbable since τ remains unchanged upon increase of concentration. Most likely this weak extinction can be explained by the smaller emission of dimers compared to the emission of monomers.

4. THE EFFECT OF CONCENTRATION ON THE POLARIZATION SPECTRA OF 3, 6 - DIAMINOACRIDINE SOLUTIONS

Dimerization of 3, 6 - diaminoacridine molecules, which causes considerable changes in the absorption spectrum, can affect the mutual arrangement of the absorbing oscillators of these molecules. These changes can be detected by changes in the polarization spectrum of 3, 6 - diaminoacridine

upon increase of concentration of the solution*.

On Fig. 6 are shown the results of the measurements. From this Figure it follows that the 3, 6 - diaminoacridine molecules have positive polarization throughout the entire polarization spectrum. The increase in concentration markedly decreases the polarization maximum and leaves the polarization almost unchanged between the maximums. At $c = 1 \times 10^{-3}$ gm/cm³ the polarization spectrum degenerates into an almost straight line.

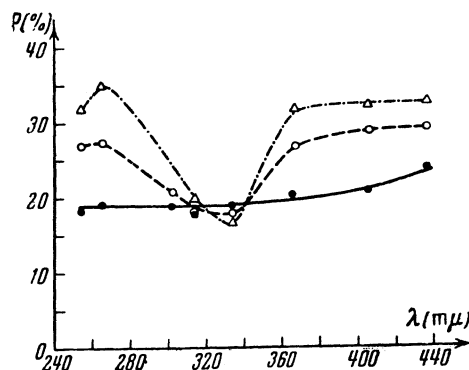


Fig. 6. The dependence of the polarization spectrum of 3, 6 - diaminoacridine in glycerin on concentration of the solution.

● - 1×10^{-3} ; ○ - 2×10^{-4} ; △ - 2×10^{-5} gm/cm³.

Significant changes of the polarization spectrum cannot be explained by depolarization due to change in concentration alone, since this depolarization only results in the decrease in absolute value of the degree of polarization throughout the spectrum¹⁴.

The changes indicate the formation of new bonds between molecules. Therefore it is their aggregation which yields the changes in mutual arrangement of the absorbing oscillators.

Apparently the curve for $c = 2 \times 10^{-5}$ gm/cm³ characterizes the polarization spectrum of the monomers and the curve $c = 1 \times 10^{-3}$ gm/cm³ characterizes the polarization spectrum of the dimers. It is probable that upon increase of concen-

¹⁴ P. P. Feofilov, Izv. Akad. Nauk SSSR, Ser. Fiz. 9, 317 (1945)

* The superposition of the absorption and luminescence spectrum of 3, 6 - diaminoacridine was small. Because of this, the effect of reabsorption on the degree of polarization was insignificant.

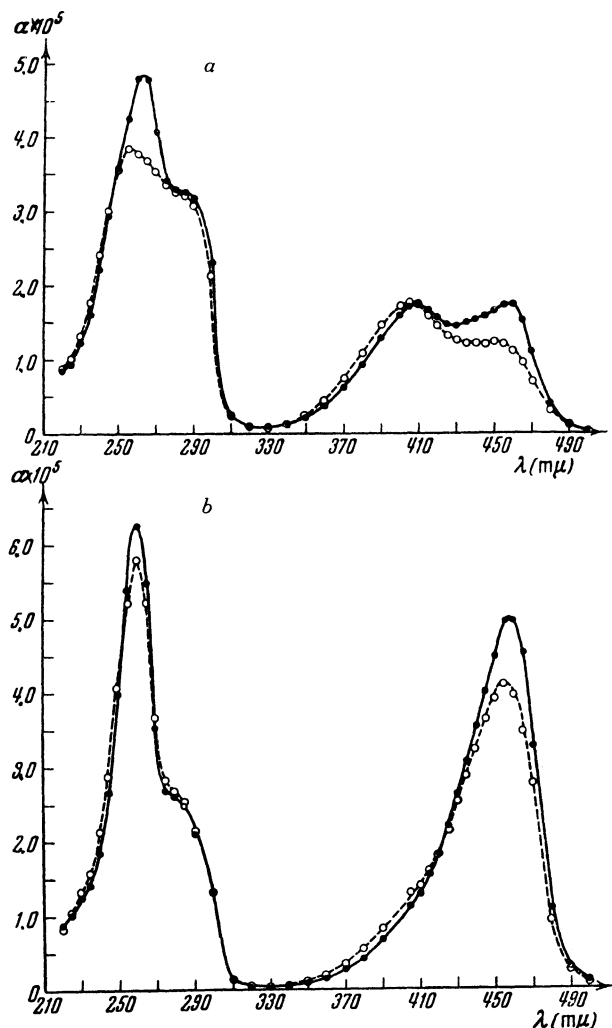


Fig. 7. Temperature dependence of the absorption spectra of 3, 6 - diaminoacridine:
 $a - c = 2 \times 10^{-3} \text{ gm/cm}^3$; $b - c = 2 \times 10^{-5} \text{ gm/cm}^3$;
 ● — 20°C, ○ — 73°C

tration in regions of spectral maxima, the depolarization due to change of concentration, as well as the process of passing over to the polarization spectrum of the dimers, are acting in the same direction. This results in the decrease of degree of polarization. In the region between the maxima, these two processes are acting in opposite directions, which results in the approximate stability of the degree of polarization in this part of the spectrum.

5. THE EFFECT OF THE TEMPERATURE ON THE ABSORPTIVE POWER OF THE MOLECULES OF 3, 6 - DIAMINOACRIDINE

Absorption and emission spectra as a rule de-

pend strongly on temperature¹⁵. Upon increase of temperature the absorption spectrum of the concentrated solution of a dye usually changes in the direction of the restoration of the spectrum of the diluted solution^{4,12}. A different picture is observed in the case of 3, 6 - diaminoacridine. In Fig. 7a is shown the dependence of the absorption spectrum of the concentrated solution of 3, 6 - diaminoacridine upon temperature. From this Figure one can see that in this case the warming from 20°C to 73°C does not restore the original form of the spectrum (Fig. 1). On the

¹⁵T. M. Tarasova, J. Exper. Theoret. Phys. USSR 21, 189 (1951)

contrary, the long wave absorption maximum markedly decreases, while there is almost complete stability in the shortwave maximum. The warming also results in the decrease in absorption in the ultraviolet band. It is particularly noticeable in the region of the monomeric maximum. The warming of the diluted solution ($c = 2 \times 10^{-5}$ gm/cm³) also results in some decrease of both absorption bands (Fig. 7b). Thus a decrease of the long wave maximum of a concentrated solution can be explained by considering the experimentally observed decrease in absorption power of the monomers upon increase of temperature.

The degree of association of 3, 6 - diaminoacridine solutions at various concentrations (at room temperature) was established above, and monomeric and dimeric absorption bands were obtained. Similarly, analysis of the bands observed for a heated solution resulted in the separation of the absorption due to the monomers from that of the dimers. Computation showed that the increase in temperature results in some decrease of absorption power of the dimers as well as of the monomers. Decrease of dimeric absorption can take place on account of decreasing number of dimers, due to their destruction. However, possible destruction of dimers is small and proceeds much more slowly than in the case of dye solutions. Analogous results are obtained from experiments with glycerin solutions of 3, 6 - diaminoacridine upon warming to 97° C.

It should be mentioned that even in the case of dyes a complete restoration of the absorption spectrum (of the dilute solution) was not achieved by warming the concentrated solutions⁷. The unusual stability of 3, 6 - diaminoacridine dimers is probably explained by the fact that for their formation the coupling monomers must be given some energy. In this case the increase in temperature will not only cause the dissociation of dimers but also simultaneously will increase the probability of coupling of monomers into dimers. Since the absorption spectrum does not change much upon the increase of temperature, one can assume that these two processes counterbalance each other. The necessity of an activation energy for the dimerization of molecules has been brought out by other authors⁴.

The effect of temperature on the association is very important; therefore the further experiments carried out in a wider range of temperatures are very interesting.

6. CONCLUSIONS

1. An increase in concentration of 3, 6 - diaminoacridine solution results in significant changes in the absorption spectrum, which can be explained by formation of dimers of molecules of this compound with a different absorption spectrum than the monomers.

2. Association of 3, 6 - diaminoacridine molecules proceeds differently in different solutions. It is most extreme in pyridine, acetone, alcohol, glycerin. These are media which usually counteract association in dye solutions. In addition the association can be related neither to viscosity, nor to dielectric constant, nor to the value of the dipole moment of the solvent.

3. The dimers are luminescent. Their spectrum differs somewhat in shape from the spectrum of monomers. It is also shifted in the long wave direction, as compared to the monomeric spectrum.

4. The extinction due to change in concentration is considerable. It can be explained by migration of excitation energy from an excited monomer to a non-excited one. The observed weak extinction when excitation of dimers prevails is explained by the smaller yield of luminescence of dimers as compared to the luminescence yield of monomers.

5. The average life time of the excited state of the monomer decreases upon increase of concentration. At the same time τ of the dimers remains insensitive to changes of concentration. At low concentrations, at which extinction does not yet occur, τ of monomers and dimers are equal within the limits of the error of the experiment.

6. The increase in concentration results in substantial changes in the form of the polarization spectrum, which indicates the aggregation of 3, 6 - diaminoacridine molecules, and with this a resulting change in the mutual orientation of absorbing dipoles.

7. The 3, 6 - diaminoacridine dimers are stable with respect to increase of temperature and apparently require a certain activation energy for their formation.

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