The Effect of Concentration on the Optical Properties of Solutions of Acridine Compounds

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The effect of concentration of nine acridine compounds on absorption spectra (in the range of 500 to 220 mμ), luminescence spectra, polarization spectra, yield of luminescence and average lifetime of the excited state was studied. It was shown that many effects produced by change in concentration are the results of association of molecules of the solute. Molecular association annihilates the luminescence power in some compounds and changes the spectral composition of the others.

IN previous work[1] the effect of concentration on optical properties of 3, 6 - diaminoacridine solutions was studied and significant action of molecular association on development of effects due to change in concentration was indicated.

The assumption was made that the significant change in the shape of the absorption spectrum of 3, 6 - diaminoacridine solutions is the result of a "pileshaped" aggregation of the molecules in process of association.

In this paper the effect of concentration on the optical properties of acridine and its eight derivatives is considered[2].

In Fig. 1 the names and structural formulas of investigated compounds are given. The experimental investigation was done by means of the same equipment as in the previous work[1].

The experiments showed that for most compounds the association of the molecules of the solute is of great importance for the development of the effects due to change in concentration. In some cases, particularly at not very high concentrations, the migration of excitation energy between neighboring molecules is an essential factor. Both kinds of interaction are coexistent.

No significant changes in shape of absorption spectra of the investigated compounds result upon increase in concentration. As the concentration increases, only uniform decrease or increase of absorption over the entire spectrum takes place. Apparently the aggregation of molecules here must be different from that of 3, 6 - diaminoacridine. One can assume that in this case the molecules aggregate in the form of a "chain". The possibility of bonds of this kind is indicated by the existence of two-ring acridine molecules, separated rings of which aggregate with each other in the form of a "chain"[3]. This assumption gets some confirmation when one compares the absorption spectrum of the concentrated acridine solution with the absorption spectrum of 9, 9′ - biacridyl. The biacridyl molecule consists of two acridine rings connected with each other by a single bond (Fig. 1). The absorption spectrum of pyridine solution of 9, 9′- biacridyl is shown in Fig. 2*a*, and the absorption spectrum of ethyl alcohol solution of acridine is shown in Fig. 2*b**.

The comparison of these spectra show that as we go from acridine to biacridyl the form of the absorption spectrum does not change much. However, some increase in absorption power of the molecules was observed in this case.

The increase in concentration from a dilute acridine solution to a concentrated one changes the shape of the spectrum even less. Increase of absorption due to change of concentration of acridine solution is somewhat smaller than the difference between absorption of acridine and 9, 9′- biacridyl (Fig. 2*b*)**.

[1] L. V. Levshin, J. Exper. Theoret. Phys. USSR **28**, 201 (1955); Soviet Phys. **1**, 244 (1955)

[2] L. V. Levshin, Doklady Akad. Nauk SSSR **96**, 473 (1954)

[3] V. L. Levshin and T. M. Tarasova, Izv. Akad. Nauk SSSR, Ser. Fiz. **15**, 573 (1951)

* In this Figure and in all further analogous figures the ordinate shows the absorption coefficients. The concentrations are given in gm/cm^3. The change of absorption coefficient upon concentration (measured in these units) defines the change in absorption power of coupled molecules, which takes place as a result of association. The absorption power of a single associated molecule is equal to the observed variation in absorption coefficient multiplied by the number of molecules of which it is composed.

** Comparison of only first absorption bands was made, since we could not obtain the second band of 9, 9′- biacridyl (because of the strong absorption of the pyridine in this part of the spectrum).

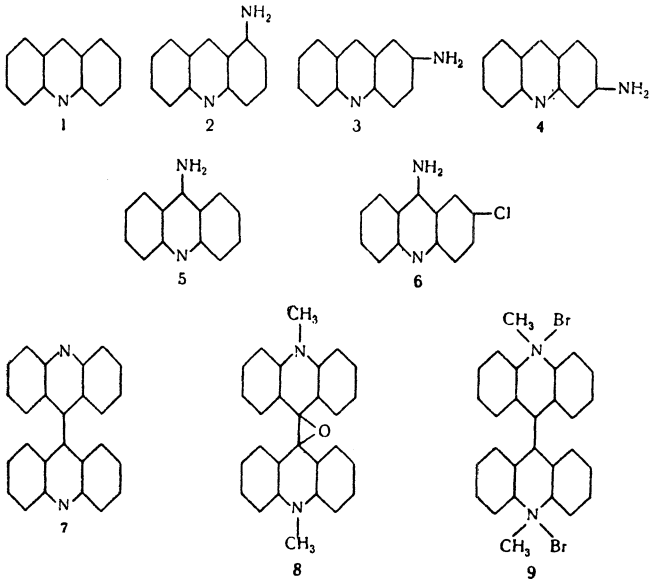

Fig. 1. Structural formulas of the acridine compounds: *1.* acridine; *2.* 1-aminoacridine; *3.* 2-aminoacridine; *4.* 3-aminoacridine; *5.* 9-aminoacridine; *6.* 2-chloric-9-aminoacridine; *7.* 9, 9′-biacridyl; *8.* 10, 10′-dimethyl-9, 9′-biacridine-oxide; *9.* dibrommethylate of 9, 9′-biacridyl

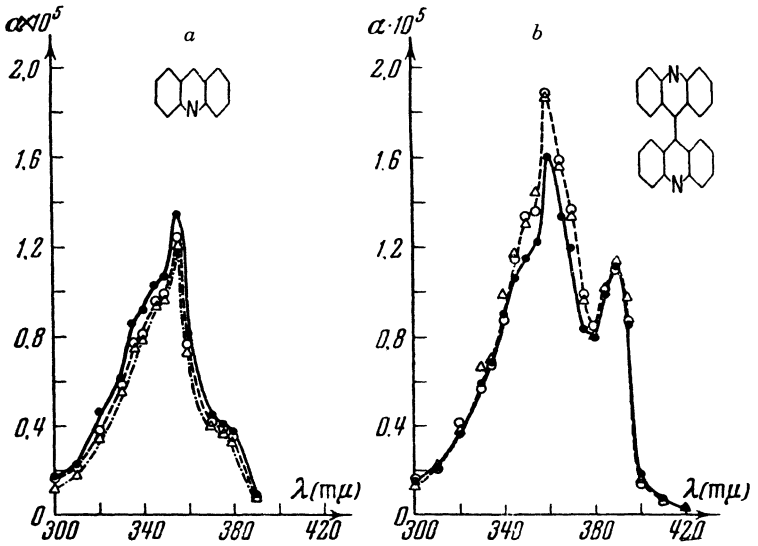

Fig. 2. Comparison of acridine and 9, 9′-biacridyl absorption spectra. *a.* Absorption spectra of ethyl alcohol solution of acridine, ● = 5×10^{-4}, ○ = 1×10^{-4}, △ = 1×10^{-5} gm/cm^3. *b.* Absorption spectra of pyridine solution of 9, 9′-biacridyl, ● = 8×10^{-4}, ○ = 1×10^{-4}, △ = 1×10^{-5} gm/cm^3.

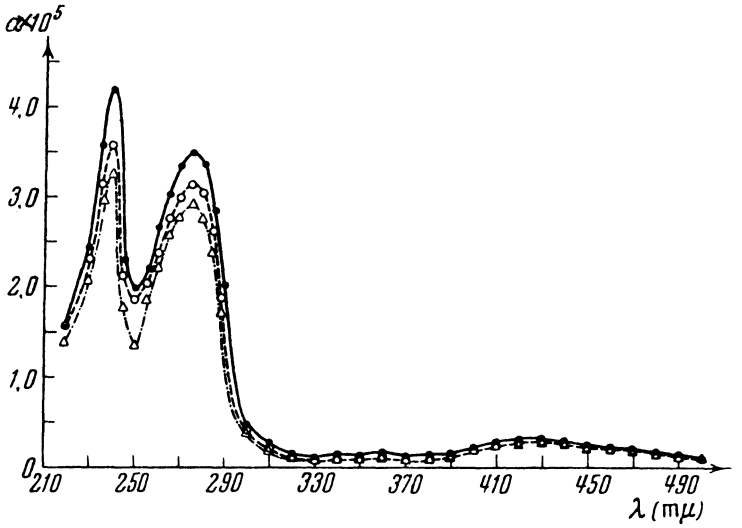

Fig. 3. Dependence of absorption spectrum of an ethyl alcohol solution of 1-aminoacridine on the concentration.
● = 1×10^{-3}, ○ = 1×10^{-4}, △ = 1×10^{-5} gm/cm^3

Hence, at least in an optical sense, there is no significant difference between the association of acridine molecules and the coupling of them by means of single chemical bonds. However, in the case of a chemical bond, the compound must be more stable. Apparently this explains the somewhat greater difference in absorption spectra observed in the transition from acridine to biacridyl in comparison with the spectra of the concentrated acridine solutions.

The increase in absorption power upon increase in concentration was found also in the case of alcohol solutions of 1-aminoacridine (Fig. 3). where the spectral form also remains without any significant changes. The luminescence spectra of acridine as well as of 1 - aminoacridine do not depend on concentration.

The absorption and luminescence spectra of alcohol solutions of 2 - aminoacridines and 3 - aminoacridines remain practically unchanged in a wide interval of concentrations (Fig. 4*a*). At the same time one observes a significant extinction of luminescence and a decrease in the average lifetime of the excited state τ of the molecules (Fig. 4*b*). The decrease in yield of luminescence is more rapid than the decrease in τ. Hence, for these compounds, the extinction due to change in concentration is apparently caused mainly by migration of the excitation energy. This conclusion is confirmed by the noticeable decrease of τ upon an increase of concentration of the solution.

The polarization spectrum of glycerin solution of 2 - aminoacridine was obtained and its dependence on concentration was studied (Fig. 5). The abscissa represents the wavelength of the exciting light, and the ordinate shows the percent values of degree of polarization. From Fig. 5 one can see that the polarization caused by 2 - aminoacridine molecules is positive over the whole polarization spectrum.

The increase in the concentration of the solution up to $c = 1 \times 10^{-3}$ gm/cm^3 does not change the polarization spectrum of 2-aminoacridine*. The explanation of this phenomenon will be given below.

In ethyl alcohol solutions of 9 - and 2 - chloric-9 - aminoacridines, increase in concentration results in a significant decrease of the absorption power of the molecules (Fig. 6). The main changes are observed here in the ultraviolet absorption band where the spectral form does not change very much.

The effect of concentration on molecular absorption of a solute was studied previously for the visible part of the spectrum**[4,5].

* The effect of reabsorption must be insignificant because of very little superposition of the luminescence and absorption spectra of 2 - aminoacridine.

** The only exception known to us is the work done by Kravetz and his coworkers, in which the ultraviolet absorption band of crystallic violet was studied as a function of concentration of the solution[6].

[4] V. L. Levshin, Zh. Fiz. Khim. **6**, 1 (1935)

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

[6] G. P. Kravetz, A. L. Pes'kina and Z. V. Zhidkova, Izv. Akad. Nauk SSSR, Ser. Fiz. **14**, 493 (1950)

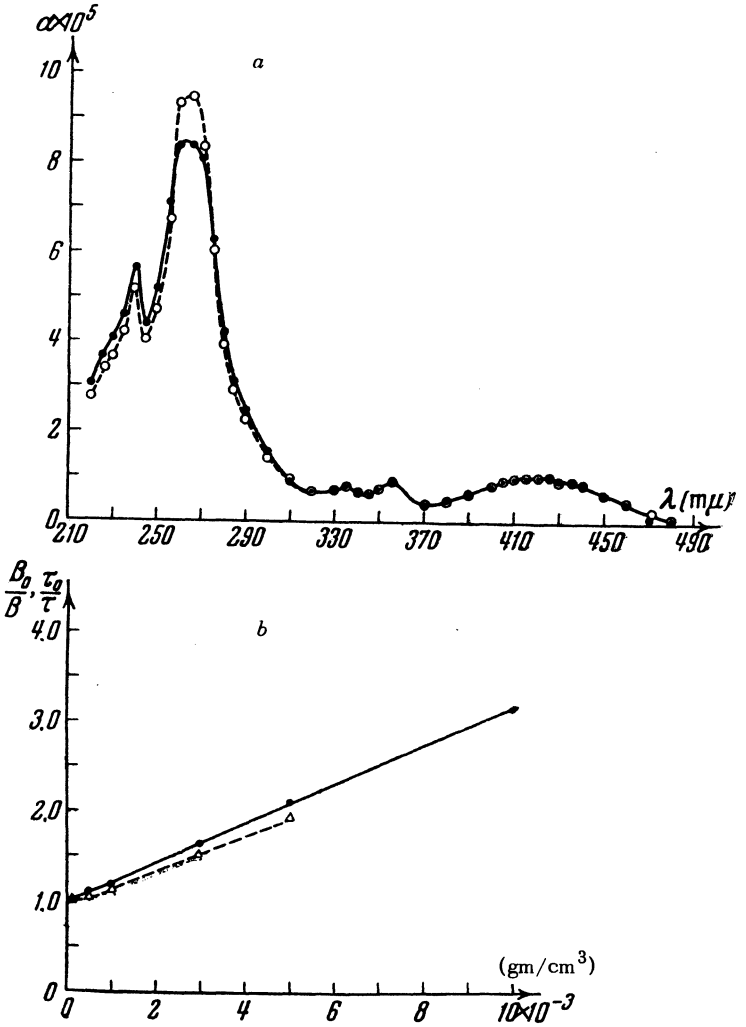

Fig. 4. Ethyl alcohol solution of 2-aminoacridine.

a. Dependence of absorption spectrum on the concentration of the solution,

● = 1×10^{-3}, O = 1×10^{-5} gm/cm^3.

b. The extinction of luminescence and variation of τ,

● = B_0/B, Δ = τ_0/τ.

In this work, as also in the work described in reference 1, the study of the effects due to change in concentration also was extended to the ultraviolet part of the absorption spectrum. In the case of 9 - aminoacridine one can see that the ultraviolet band is often more sensitive to the increase in concentration than the absorption in the long wave part of the spectrum.

The associated molecules can either retain their luminescence power[7] or lose it completely. For many acridine compounds, such as acridine, 1 - aminoacridine, 2 - and 3 - aminoacridine and others, the luminescence spectrum remains unchanged over a wide range of concentrations. However, in the case of some of them (9 - and 2 chloric - 9 - aminoacridine, 3, 6 - aminoacridine) the emission spectrum changes significantly in a concentrated solution. In case of 9 - aminoacridine, the luminescence spectrum changes markedly in form, and shifts in the long wave direction upon the increase in concentration (Fig. 7)*.

Apparently, in the diluted solution ($c = 2 \times 10^{-5}$ gm/cm^3) the emission is entirely caused by the

[7] V. L. Levshin, Z. Physik **43**, 230 (1927)

* In the luminescence spectra of all investigated materials reabsorption corrections were made.

molecules in monomeric state. The change of luminescence spectrum observed upon increase in concentration indicates the formation of the associated molecules, which have luminescence power. Their luminescence spectrum differs in form and location from that of monomers. At $c = 1 \times 10^{-3}$ gm/cm^3 the association is completed and the spectrum remains stable with respect to increase in concentration. At this concentration of the solution the luminescence spectrum belongs completely to the associated molecules.

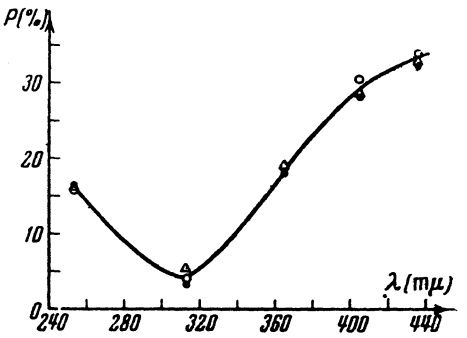

Fig. 5. Dependence of the polarization spectrum of glycerin solution of 2-aminoacridine upon the concentration.
● = 1×10^{-3}, ○ = 1×10^{-4}, △ = 1×10^{-5} gm/cm^3

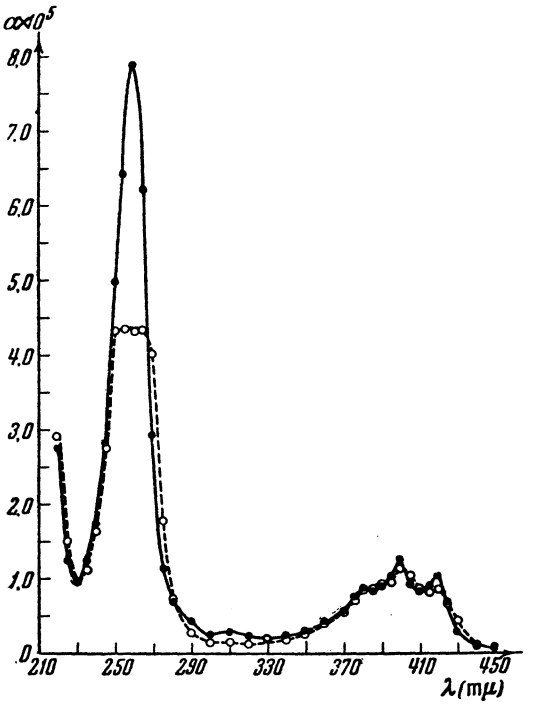

Fig. 6. Dependence of absorption spectrum of ethyl alcohol solution of 9-aminoacridine upon the concentration of the solution.
● = 2×10^{-5}, ○ = 1×10^{-3} gm/cm^3

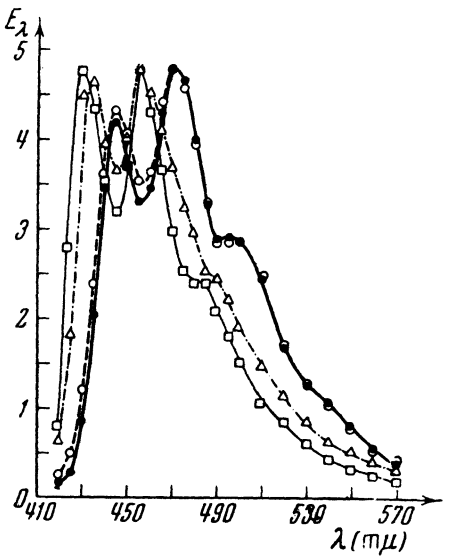

Fig. 7. Dependence of luminescence spectrum of ethyl alcohol solution of 9-aminoacridine on concentration of the solution. ● = 1×10^{-2}, ○ = 1×10^{-3}, △ = 1×10^{-4}, □ = 2×10^{-5} gm/cm^3

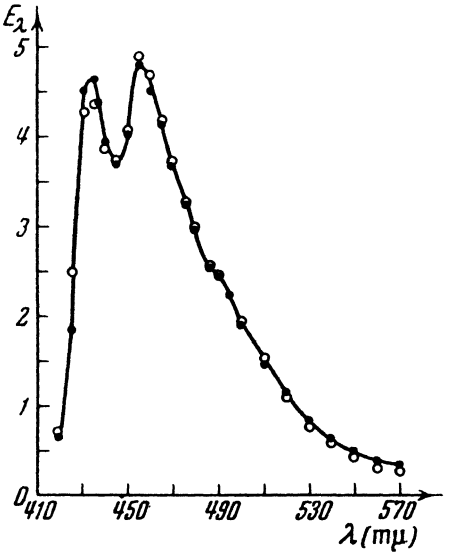

Fig. 8. The comparison of experimental and computed luminescence spectra of 9-aminoacridine.
● = experimental
○ = computed

If the above reasonings are correct, then, by superposition of a dimeric and a monomeric spectra, and taking into account the degree of participation of monomers and dimers in emission, one can obtain the spectrum of the solution with the intermediate concentration ($c = 1 \times 10^{-4}$ gm/cm^3).

Figure 8 shows the comparison of experimental and computed curves for luminescence spectrum of 9 - aminoacridine ($c = 1 \times 10^{-4}$ gm/cm^3). The computations are made by considering that 80% of the emission was caused by monomers and 20% by dimers. One can see that the experimental and computed curves are in good agreement. Analogous changes in luminescence spectrum were also discovered for alcohol solutions of 2 chloric - 9 - aminoacridine.

The increase in concentration results in significant extinction of luminescence and the decrease of the average lifetime of the excited state of the 9 - aminoacridine molecules (Fig. 9*a*). At the same time the polarization spectrum of 9 - aminoacridine does not depend on concentration, within the limits of experimental errors (Fig. 9*b*).

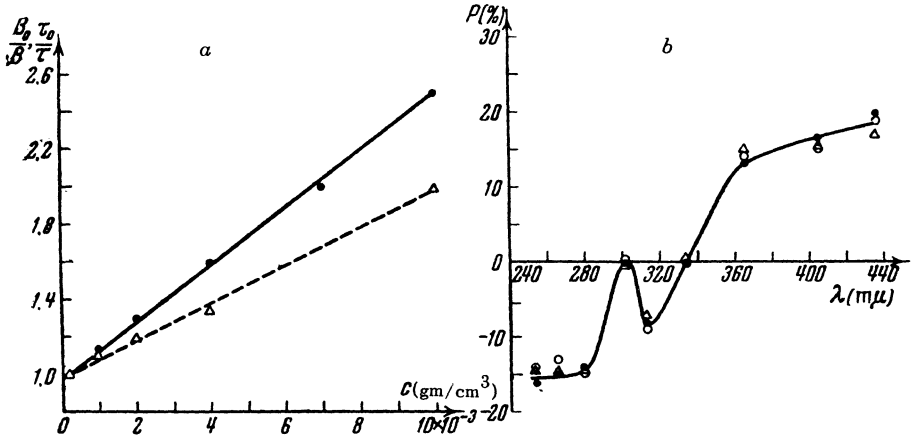

Fig. 9. 9-aminoacridine. *a*. ethyl alcohol solution. *b*. glycerin solution
a. extinction of luminescence and variation of τ.
● $= B_0/B$, △ $= \tau_0/\tau$;
b. dependence of polarization spectrum on the concentration of the solution.
● $= 5 \times 10^{-4}$, ○ $= 1 \times 10^{-4}$, △ $= 1 \times 10^{-5}$ gm/cm^3.

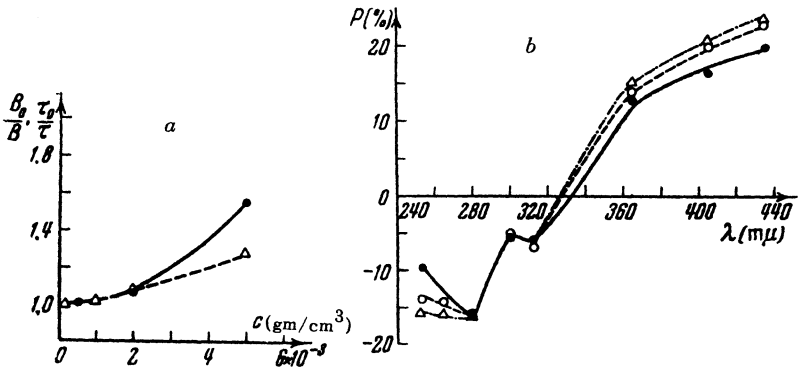

Fig. 10. 2-chloro-9-aminoacridine: *a*. in ethyl alcohol; *b*. in glycerine.
a. extinction of luminescence and variation of τ, ● $= B_0/B$, △ $= \tau_0/\tau$;
b. dependence of polarization spectrum in the concentration of the solution:
● $= 5 \times 10^{-4}$, ○ $= 1 \times 10^{-4}$, △ $= 1 \times 10^{-5}$ gm/cm^3

Meanwhile, it is known that the changes in degree of polarization usually occur much more rapidly than the extinction of the luminescence can develop and increase of τ can take place[8].

Lack of depolarization due to change in concentration apparently can be explained by competition of two counteracting processes. On one hand the degree of polarization decreases upon increase in concentration because of migration of the excitation energy between the neighboring molecules. On the other hand the migration of energy results in development of extinction of luminescence and decrease of τ (Fig. 9*a*). The decrease of τ leads to increase of polarization of luminescence. In our case both effects apparently cancel each other, and the polarization spectrum remains unchanged*. There is no cancellation in case of 2 chloric - 9 - aminoacridine, and the polarization spectrum changes markedly upon increase in concentration (Fig. 10*b*). This is in agreement with insignificant extinction and small variation of τ, observed in case of solutions of this compound (Fig. 10*a*).

The association must result in an increase of molecular volumes, which can be determined from experiments with polarization. The theory of polarized luminescence gives the relationship as follows[8]:

$$\frac{1}{P} = \frac{1}{P_0} + \left(\frac{1}{P_0} - \frac{1}{3}\right)\frac{TR\tau}{\eta V},$$

Here P is degree of polarization, P_0 = limit polarization, T = temperature, η = viscosity of the solution, R = universal gas constant, τ = average lifetime of the excited state of molecules, V = their volume. If ordinate represents $1/P$ and abscissa = T/η, then $1/P$ as a function of T/η will be a straight line. Intersection of this line with the ordinate gives us $1/P_0$, and its slope determines the value of $\left(\frac{1}{P_0} - \frac{1}{3}\right)\frac{R\tau}{V}$. The value of τ can be measured with a fluorometer. Then, from the last relationship, one can determine the average molecular volume and study its variation upon increase of concentration.

By this method the gram molecular volumes of two glycerin solutions of 9 - aminoacridine ($c_1 = 1 \times 10^{-5}$ gm/cm^3 and $c_2 = 5 \times 10^{-4}$ gm/cm^3) were determined. It turns out that an increase of concentration in this range approximately doubles the average volume of 9 - aminoacridine molecules. The results are not identical to the true volumes of luminescent molecules since the presence of a solvation envelope complicates the real situation. However, it is important that the volume increases, which is a direct proof of association of the 9 - aminoacridine molecules[7].

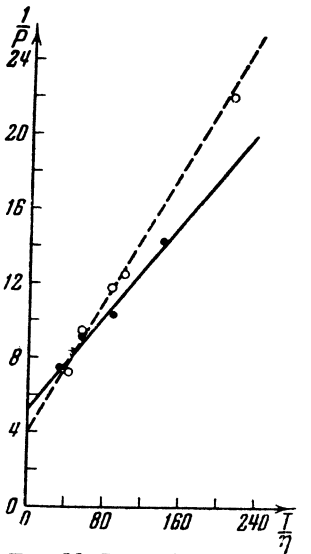

Fig. 11. Dependence of the limiting polarization of 9 - aminoacridine in glycerine on the concentration of the solution. ● = 5×10^{-4}, ○ = 1×10^{-5} gm/cm^3.

In Fig. 11 the experimental results are shown. Here one can see that the increase in concentration markedly changes the slope of the straight line and considerably decreases the value of the limit polarization (at $c_1 = 1 \times 10^{-5}$ gm/cm^3, $P_0 = 25\%$; at $c_2 = 5 \times 10^{-4}$ gm/cm^3, $P_0 = 19\%$). The value of the limit polarization of the diluted 9 - aminoacridine solution is close to that obtained by Feofilov[9].

An increase in concentration changes the optical properties of the solution of two-ring acridine compounds significantly. In Fig. 12*a* the dependence of absorption spectra of alcohol solutions of dibromethylate - 9, 9′- biacridyl on the concentration is shown. From Fig. 12 one can see that the shape of absorption spectrum does not change significantly. The absorption power in-

[8] V. L. Levshin, *Photoluminescence in Liquids and Solids*, State Publishing House of the Technical Literature, Moscow - Leningrad, 1951

* An analogous explanation can be suggested for the above described stability of polarization spectrum of 2 - aminoacridine (Fig. 5).

[9] P. P. Feofilov, Izv. Akad. Nauk SSSR, Ser. Fiz. **13**, 254 (1949)

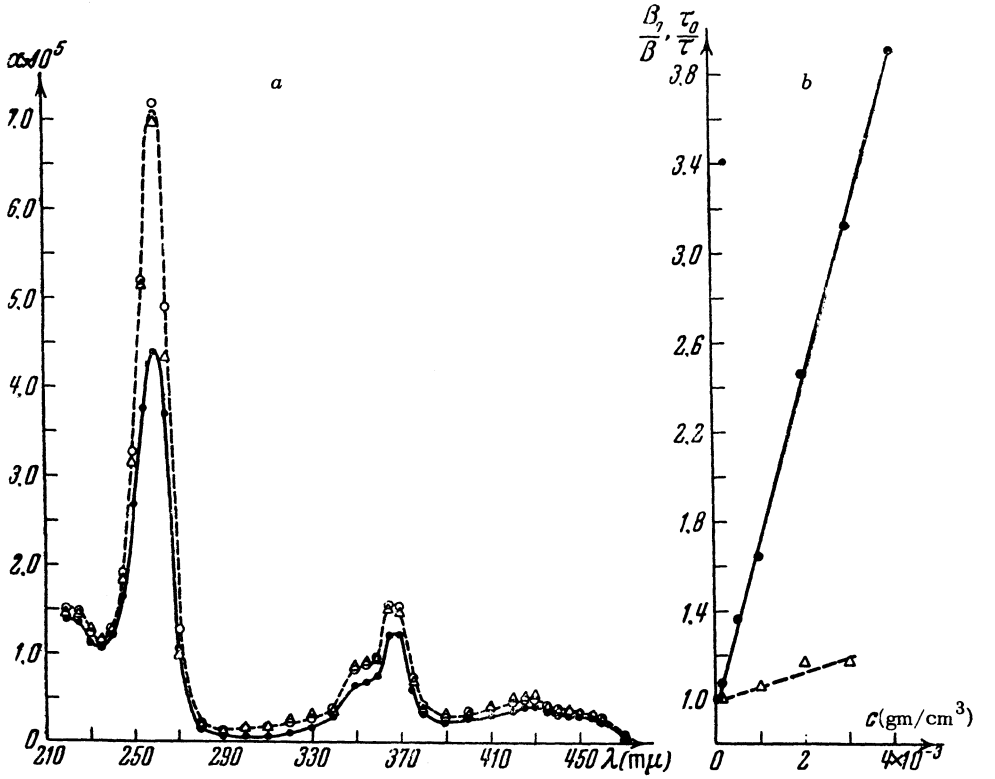

Fig. 12. Ethyl alcohol solution of dibromethylate-9, 9′-biacridyl.
a. dependence of absorption spectrum on concentration,
● = 2×10^{-3}, ○ = 2×10^{-4}, △ = 2×10^{-5};
b. extinction of luminescence and variation of τ,
● = B_0 / B, △ = τ_0 / τ.

creases uniformly along the whole absorption spectrum. The increase in concentration causes extremely strong extinction of luminescence, which is accompanied by small change of τ (Fig. 12*b*). Luminescence spectrum remains unchanged. The changes of the absorption spectrum support the assumption that association takes place in this compound also. Moreover, the changes of τ indicate the migration of excitation energy, which apparently is the reason for some fraction of observed extinction of luminescence. However, apparently, the non-luminescent associated molecules that are formed are largely responsible for the development of intensive extinction of luminescence since the changes of τ are small (Fig. 12*b*).

The association of molecules is also probably of chief importance in the case of other two-ring compounds (Fig. 1), since τ for them is completely independent of concentration in investigated range. The majority of acridine compounds have luminescent power in the crystalline state as well as in

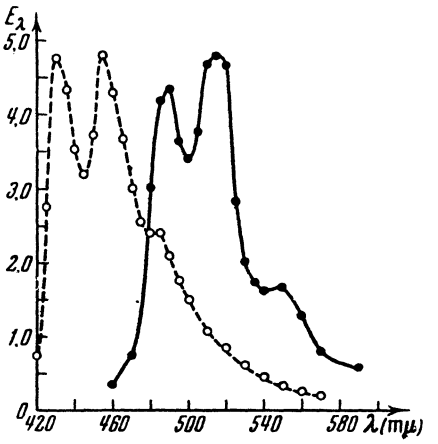

Fig. 13. The comparison of luminescence spectra of ethyl solution of 9-aminoacridine with that of its crystalline state.
● = spectrum of crystals, ○ = spectrum of the solution ($c = 2 \times 10^{-5}$ gm/cm³).

their solutions. Only in case of few materials (2 - aminoacridine, dibromethylate ; 9, 9′- biacridyl) does the transition from a solution to a crystal lead to the disappearance of luminescence.

In this work the luminescence spectra of crystals of many acridine compounds were studied. In Fig. 13 the luminescence spectra of a diluted solution of 9 - aminoacridine and its crystals are shown as an example. The common rule which holds for the majority of acridine compounds, and also for the great majority of other luminescent compounds in crystalline state (see, for instance, reference 10) is the bathochromic shift of luminescence spectra of the crystal with respect to luminescence spectra of the solutions (Fig. 13). The only exception is 1 - aminoacridine, where the reversed phenomenon is observed.

CONCLUSIONS

1. An increase in concentration of the solutions of the acridine compounds (Fig. 1) results in the development of molecular association. It is possible to assume that a joining of many molecules takes place in the shape of a "chain" during the association. This explains the small changes in the shape of the absorption spectra. The 9, 9′- biacridyl molecule can apparently be regarded as an analogue of an associated acridine molecule.

2. Processes of inductive migration of the excitation energy are also important for explanation of the effects of concentration in the solutions of acridine compounds.

3. The associated molecules that are formed through an increase of concentration either lose their luminescence power or have their own emission different from the emission of molecules in monomeric state.

4. The increase of volume of the 9 - aminoacridine molecules in a concentrated solution is a direct proof of their association.

5. For most acridine compounds the transition from the solution to a crystal causes the shift of luminescence spectrum in the long wave direction. This is also a characteristic property of the majority of known luminescent crystals of other compounds.

In conclusion I express deep appreciation to Prof. P. A. Bazhulin for his attention in guidance of this work, to Prof. A. M. Grigorovskii for kindly providing me with chemical supplies and for his consultations, M. D. Galanin for giving me the opportunity to use his fluorometer, N. D. Zhevandrov for great help during measurements of polarization and his advice during discussion of this work.

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