DECAY AND DEPOLARIZATION OF FLUORESCENCE OF PHTALIMIDE SOLUTIONS

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The position of the maximum of the fluorescence spectrum of phtalimide solutions depends strongly on their temperature. Phtalimide molecules, when excited, change their dipole moment considerable, causing a perturbance in the state of equilibrium existing between the solvent and dye molecules in the ground state. The degree of reorientation which the molecules of the solute have reached at the instant of fluorescence emission, and thus also their energy of interaction with the surrounding solvent molecules at this instant (responsible for the fluorescence spectrum shift), are both temperature dependent. At temperatures of the solution in which the relaxation time of reorientation τ_r is of the same order as the mean duration τ of fluorescence, we observe the biggest differences in the duration of fluorescence and in the emission anisotropy in the long- and short- wave regions of the fluorescence spectrum. These differences are due to the different luminescence centers with different degrees of reorientation and mean durations of fluorescence. Because of the differences in the mean durations, the emission anisotropy $\bar{r}$ of fluorescence also becomes dependent on the wavelength of the emitted light. The strongest dependence was observed, however, at temperatures higher than those at which the largest fluorescence spectrum shift occurs. To find the reason for this effect, measurements of the mean duration and emission anisotropy of fluorescence of various phtalimide solutions were performed at different temperatures and wavelengths of emitted light. The results of these measurements show that the depolarization probability, as well as the dipole-dipole interaction, depends on the temperature of the solution (owing to the temperature dependence of the volume of the fluorescent molecule's solvatation shell).

Introduction

The fluorescence of phtalimide solutions features above all a strong dependence of the positions of the emission spectrum maxima on temperature and type of dipole solvent. This is because the interaction between the fluorescent molecule and the dye molecules is much stronger in the excited state than in the ground state (Pikulik 1960, 1962; Gladchenko 1964), In the excited state the dipole moment of the fluorescent molecule increases, thus perturbing the state of equilibrium existing between the solvent molecules and the dye molecule. The magnitude of the change in the interaction between these molecules depends

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on the extent to which a new equilibrium state is reached at the instant when emission occurs. This degree of reorientation depends on the lifetime of the dye molecule in the excited state, τ, and the relaxation time of reorientation, τ_r. For relatively high temperatures and small viscosity coefficients the reorientation relaxation time is very short, as compared with the mean lifetime of the molecule in the excited state, thanks to which there is observed a high degree of reorientation, strong interaction, and a large shift of the emission spectra towards the longer wavelengths. For low temperatures and large viscosity of solutions the case is quite the opposite; now the reorientation relaxation time is so long that during the lifetime of the molecule in the excited state there is practically no reorientation at all. For a certain range of intermediate temperatures the reorientation relaxation time, τ_r, becomes comparable with the mean lifetime of the dye molecule, *i.e.* $\tau_r \approx \tau$. Under these conditions the observed shift of the emission spectra with temperature is largest. A characteristic effect when $\tau_r \approx \tau$ is the dependence of the lifetime of the molecule in the excited state upon the wavelength of the emitted light (Veselova *et al.* 1965; Kostka *et al.* 1967). The mean duration of fluorescence, τ, is shorter in the short-wavelength part of the fluorescence spectrum, and increases in its long-wavelength part. This has been accounted for by alleging that the emission spectrum at $\tau_r \approx \tau$ issues from different luminescence centres differing in degree of reorientation of the solvent molecules and excited dye molecule. Cherkasov (1962) noted that different centres of different mean durations should emit fluorescent light of different emission anisotropies. Measurements made by Rudik (1967) and Bauer and Rudik(1968) have confirmed this supposition. In these studies the shift of the emission spectrum maximum had been investigated as a function of both temperature and wavelength of the emitted light. In the latter of these papers the fluorescence spectrum shift is compared with the emission anisotropy $\bar{r}$ of fluorescence as a function of frequency ν of the emitted light for different temperatures, the assumption being made that both effects are caused by reorientation relaxation of the molecules in the solution. When the quantity $\eta(\bar{r}_2-\bar{r}_1)/\bar{r}_1\bar{r}_2T$, taken as a measure of the change of $\bar{r}$ with change of ν (where $\bar{r}_1$ and $\bar{r}_2$ are the respective fluorescence emission anisotropies for the long- and short-wave edges of the spectrum, η is the viscosity coefficient, and T is the solution's temperature), was plotted against temperature it was noticed that the maxima of this function are not to be found in the region where the fluorescence spectrum shift depends most strongly upon temperature and the light at the edges of the fluorescence spectrum is distinctly emitted from different luminescence centers. This problem has been explained by the overlapping of two effects, viz., reorientation relaxation, and a change of the limiting emission anisotropy, r_0[1], and effective volume of the dye molecule together with its solvation shell, v, with a change of temperature. Moreover, Rudik (1967), in his study on the parallel shift of fluorescence spectra, durations and polarization coefficients as a function of temperature and emitted wavelength, arrives at the conclusion that the change in the polarization coefficient at the edges of the emission spectrum is not caused

[1] The boundary emission anisotropy, r_0, is the value of emission anisotropy which is observed when all depolarizing factors, except torsional vibrations, are eliminated. In the case when there is a depolarizing effect of Brownian rotation of the dye molecule r_0 can be calculated (Jabłoński 1961).

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by a change in the mean duration of fluorescence alone. The change in τ with a change in the fluorescent light wavelength has been accounted for by the different interactions between the fluorescent molecule and its surroundings. It may be that weaker or stronger interaction leads to different values of the depolarization probability per unit time, φ, for different centres of different mean durations. The purpose of the foregoing is to examine the quantity φ in dependence on the type of centres and temperature of the solution.

Measurements and results

Solutions of 3-aminophtalimide, 4-aminophtalimide and 3-monomethylamino-N-methylphtalimide in propyl alcohol, izobutyl alcohol and glycerine (dye concentration 10^{-4} mol per liter) were investigated at variaos temperatures between $+50$ and -130°C. The solvents were purified and dehydrated by vacuum distillation. The tested solution was refrigerated in a Dewar flask by ethyl alcohol cooled by liquid air. The temperature was measured and controlled by means of a calibrated thermocouple. The fluorescence emission anisotropy of these solutions was measured with a photoelectric polarimeter (Bauer *et. al.* 1961), fluorescence being excited by the linearly polarized light of a mercury lamp, of which the 366 nm line was filtered out. The fluorescencent light was observed through a Zeiss SPM-1 monochromator; its slit widhts were chosen so that the halfwidth of the spectrum segment would equal 4 nm. The mean durations, τ, were measured by a phase fluorometer (Fig. 1),

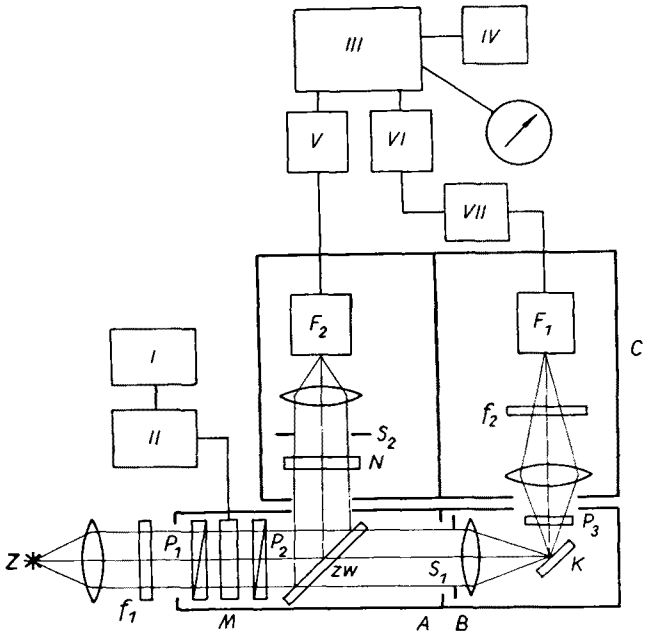

Fig. 1. Phase Fluorometer. Z — light source, f_1, f_2 — light filters, P_1MP_2 — ultrasonic light modulator, N — focussing screen, ZW — mirror (glass plate), S_1, S_2 — diaphragms, K — source of fluorescence or scattered light, P_3 — polaroid, F_1, F_2 — photomultipliers, I — generator, II — power amplifier, III — phase sensitive rectifier, IV — recorder, V, VI — H. F. amplifiers, VII — delay line

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in which the exciting light is modulated by an ultrasonic modulator ($\nu = 11.5$ megacycles per sec). This modulator consists of two crossed polaroids, p_1 and p_2, and a cube of fused quartz cemented to a plate of piezo-crystal (Bauer *et al.* 1960). High-frequency voltage (5.75 megacycles per sec) from the generator I through the power amplifier II putted on the piezo-crystal produces ultrasonic standing waves in the quartz cube. Owing to this induced birefrigence the exciting light becomes modulated sinusoidally. Some of the modulated light is received by the photomultiplier F_2, whose signal, after amplification in the amplifier V, controls the phase-sensitive rectifier III. The scattered or fluorescent light falls on the photomultiplier F_1. The signal from it goes through the delay line VII to the amplifier VI, is rectified in the phase-sensitive rectifier and is recorded by the recorder IV. The value of the voltage recorded depends on the intensity of the fluorescent (or scattered) light and on the difference between the phases of the signals coming from the two photomultipliers, F_1 and F_2. At a constant intensity of the exciting light, by altering the phase of the alternating voltage (generated in the photomultiplier F_1 by the scattered or fluorescent light) with the delay line, a mirror curve (scatterer) and a fluorescent (fluorescent solution) curve are recorded. The phase difference of the mirror and fluorescent curves is a measure of the duration, τ. The delay line enables us to shift the phase of the alternating current coming from the photomultiplier F_1 by 2π, thanks to which the recorder records a full period of the mirror and fluorescent curves. Measuring the length of the plot corresponding to a shift of 2π — L and the length of the shift between the mirror and fluorescent curves, l, we have

$$\Phi = 2\pi \frac{l}{L}.$$

The mean duration is

$$\tau = \frac{l}{\nu L}$$

The prime advantage of this fluorometer is the possibility of measuring mean durations of fluorescence within the range from 10^{-9} to 10^{-7} sec with an accuracy of up to 10^{-10} sec. The possibility of measuring relatively long durations is important, particularly in the case of phtalimide solutions.

The measurements of the mean duration were made with the use of a high-pressure mercury lamp as the light source. Fluorescence was excited by the 366 nm line of mercury filtered out with an absorption filter. The emitted light was observed through interference filters placed in the parallel beam. In this way it was possible to measure the mean durations as a function of the wavelength of the fluorescent light. The mean durations of the three components — polarized parallelly, $\tau^{\parallel}$, perpendicularly, $\tau^{\perp}$, and under an angle of 55° τ,[2] with respect to the electric vector of the linarly polarized exciting light — have been measured at different wavelengths of emitted light and temperatures ranging between 20 and —130°C for all of our solutions.

[2] Jabłoński (1936) showed that the decay of this component (coming from a single luminescence center) is exponential, and its mean duration is equal to the mean duration of fluorescence emitted in all directions.

Knowledge of the value of the mean durations of the fluorescence components and the emission anisotropy, $\bar{r}$, enables us to calculate the limiting emission anisotropy, r_0, on the basis of the formula given by Jabłoński (1961)

$$r_0 = \frac{2\bar{r}^2\tau}{\tau^{\parallel}(1+2\bar{r})-\tau} = \frac{\bar{r}^2\tau}{\tau-\tau^{\perp}(1-\bar{r})} \tag{1}$$

This formula is derived directly from the following equations:

$$\frac{\tau^{\parallel}}{\tau} = \frac{r_0+2\bar{r}^2}{r_0+2r_0\bar{r}} \quad \text{and} \quad \frac{\tau^{\perp}}{\tau} = \frac{r_0-\bar{r}^2}{r_0-r_0\bar{r}} \tag{2}$$

which state that the ratios of the mean durations of the fluorescence components, $\tau^{\parallel}/\tau$ and $\tau^{\perp}/\tau$, depend on both $\bar{r}$ and r_0. Figure 2 gives the results of measurements of the $\tau^{\parallel}/\tau$ and $\tau^{\perp}/\tau$ ratios as a function of $\bar{r}$ for 3-monomethylamino-N-methylphtalimide in izobutyl alcohol.

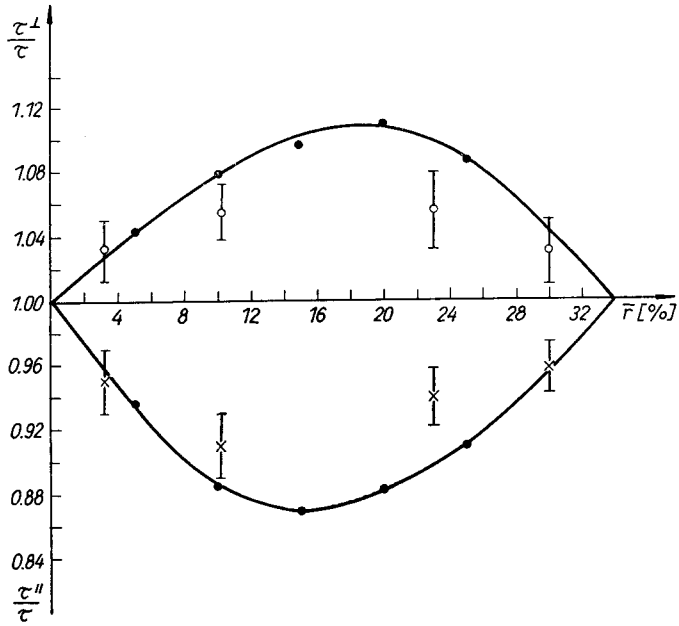

Fig. 2. Calculated and measured values of ratios of mean durations of fluorescence light components for 3-monomethylamino-N-methylphtalimide in izobutyl alcohol solution

The results of measurements for the other solutions are the same as these, qualitatively speaking. From Fig. 2 we see that *a*) the $\tau^{\perp}/\tau$ ratios reach lower values and the $\tau^{\parallel}/\tau$ ratios higher values than those calculated from Eqs (2) with the assumption of $r_0 = 0.34$ implying that the values of r_0 decrease with higher temperatures, and *b*) the smallest error achievable in determining the mean duration of fluorescence enables us to calculate the $\tau^{\parallel}/\tau$ and $\tau^{\perp}/\tau$ ratios with an accuracy of only ± 0.02. The insufficient accuracy of these ratios makes it impossible to calculate the change in the values of r_0 with a change of temperature and wavelength of fluorescent light. Work on improving the accuracy of the $\tau^{\parallel}/\tau$ and $\tau^{\perp}/\tau$ ratios is under way.

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Tables I and II present the values of the mean durations, τ, for a solution of 3-monomethylamino-N-methylphtalimide in propyl alcohol and 4-aminophtalimide in izobutyl alcohol for a number of different temperatures and three wavelengths of fluorescent light.

TABLE I

Dependence of mean duration ($\tau \times 10^9$) of fluorescence of 3-monomethylamino-N-methylphtalimide in propyl alcohol on temperature and wavelength of the emitted light

$T°$ K / nm	293	253	233	213	193	173
589	7.67	7.68	7.72	8.11	9.93	13.86
500	7.52	7.52	6.80	6.51	7.57	9.39
475	7.54	7.50	5.70	5.51	3.80	8.55

TABLE II

Dependence of mean duration ($\tau \times 10^9$) of fluorescence of 4-aminophtalimide solutions in izobutyl alcohol on temperature and wavelength of the emitted light

T °K / nm	293	253	233	213	193	173
589	9.72	10.50	11.91	13.00	15.12	14.20
500	9.81	9.20	8.42	8.70	10.50	12.65
450	9.62	8.00	6.38	4.32	5.21	9.41

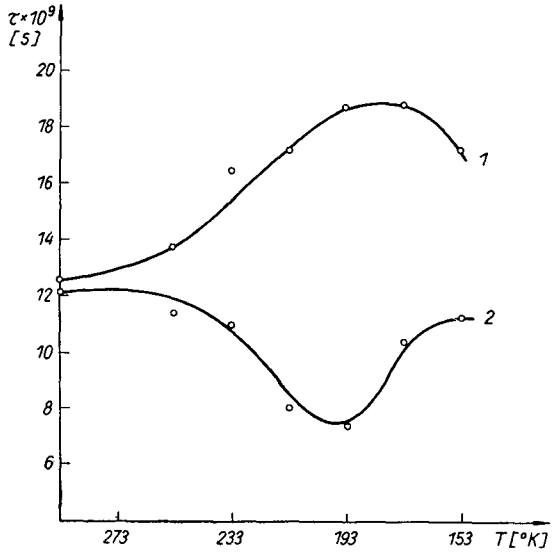

Fig. 3. Dependence of τ on the temperature of 3-aminophtalimide solution in izobutyl alcohol. Curve 1: observed emitted wavelength — 589 nm, curve 2: observed emitted wavelength — 436 nm

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The durations depend on both temperature and wavelength of emitted light, and their values confirm the results of measurements made earlier by other authors (Veselova *et. al.* 1965; Kostko *et al.* 1967), who examined the dependence of τ on emitted wavelength at various temperatures. The corresponding values of τ for 3-aminophtalimide in izobutyl alcohol are shown in Fig. 3. We see here that at lower solution temperatures the curve of the temperature dependence of the duration of fluorescence in the long-wave part of the spectrum has a characteristic maximum, whereas the corresponding curve for the short-wave part of the emission curve has a characteristic minimum. This phenomenon shows that for temperatures at which the relaxation time of reorientation, τ_r, is comparable with the mean duration of fluorescence, τ, the long- and short-wave fluorescence issues forth from different luminescence centres.

A number of papers (Sarzhevski *et. al.* 1958, 1959, 1961) on fluorescence of phtalimide solutions have dealt with the problem of the temperature dependence of the fluorescence polarization. For a solution of phtalimides in glycerine they obtained a linear dependence of $1/p$ on the ratio T/η in the temperature range from 20 to 90°C, in agreement with the Levshin–Perrin formula. In a more recent paper (Gladchenko 1964) there have been observed non-linear $\frac{1}{p}\left(\frac{T}{\eta}\right)$ dependences in alcohol solutions of phtalimides in the

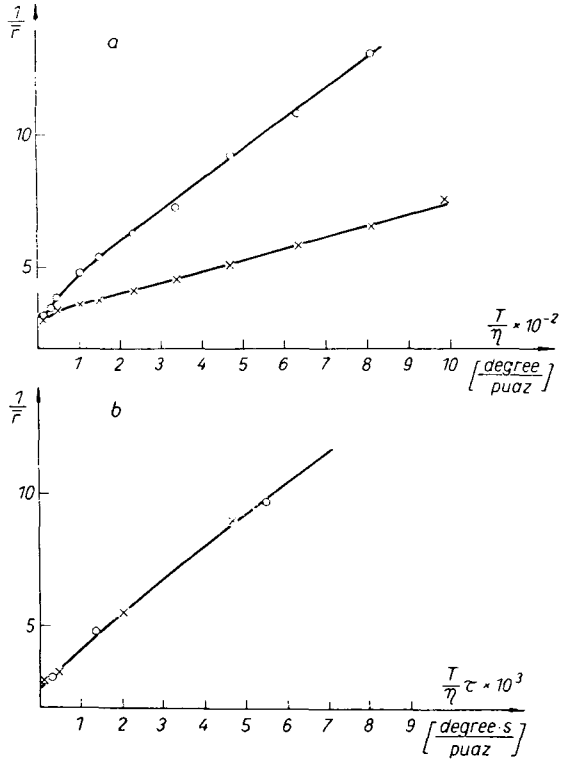

Fig. 4. Dependence of $1/\sqrt{r}$ on temperature, mean duration of fluorescence (part *b* of the figure) and the reciprocal of viscosity coefficient for 4-aminophtalimide in izobutyl alcohol solution

range of lower temperatures (down to —185°C), and this has been explained as due to changes of τ with dropping temperature. Because solutions of phtalimides in polar solvents, which become glassy at low temeratures, have the dependences $\tau = f(v)$ and $\bar{r} = f(v)$, the behaviour of the $\frac{1}{p}\left(\frac{T}{\eta}\right)$ dependence for 3-acetylamino-N-methylphtalimide in butyl alcohol solution has been studied (Rudik 1968) for various wavelengths of emitted light, λ. It proved that even after the changes of τ at lower temperatures had been taken into account the $\frac{1}{p}\left(\frac{T\tau}{\eta}\right)$ dependence is not linear. The source of this non-linearity should be sought in the temperature dependence of the emission anisotropy, r_0, and the volume of the fluorescent molecule together with its solvation shell, v.

The mean durations, τ, for various temperatures and emitted wavelengths, and the corresponding values of emission anisotropy, r, are known for 4-aminophtalimide in izobutyl alcohol solution. They are presented by the curves of $1/\bar{r}$ against T/η and $T\tau/\eta$ in Fig. 4. When the temperature dependence of τ is not taken into account, the values of $1/\bar{r}$ lie along

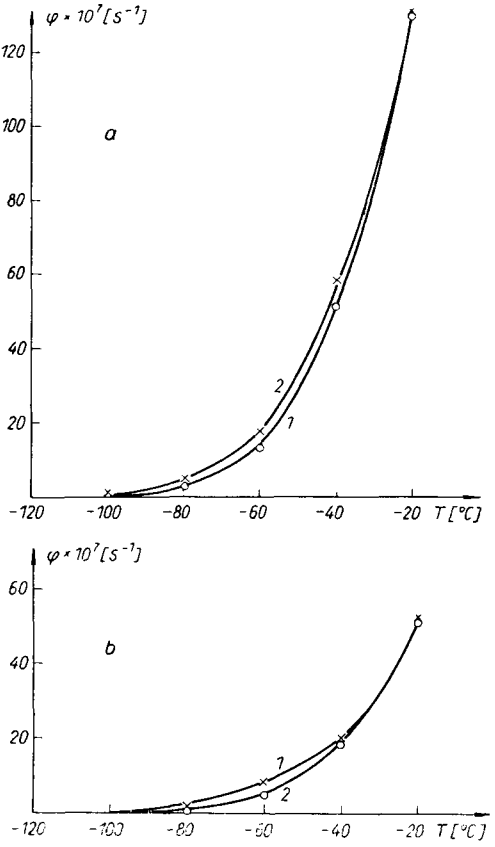

Fig. 5. Dependence of the depolarization probability φ on the temperature of the solution of phtalimides in izobutyl alcohol, a — 3-aminophtalimide (curve 1 for the wavelength 436 nm, curve 2 for the wavelength 589 nm of the emitted light), b — 4-aminophtalimide (curve 1 — 460 nm, curve 2 — 589 nm)

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two distinct curves of different slopes. On the other hand, allowance for the changes of τ causes the two curves to merge into one, practically speaking, but this curve diverges slightly from linearity. This divergence primarily shows up in the low-temperature region, in which the T/η ratio is very small and $1/\bar{r}$ is but weakly temperature dependent. Hence, it is difficult to ascertain whether the fluorescence depolarization depends on the wavelength of the emitted light. The curves in Fig. 5 show the temperature dependence of the depolarization probability per unit time, φ, for solutions of 4- and 3-aminophtalimide in izobutyl alcohol. The values of φ were determined with the use of the formula

$$\frac{1}{\bar{r}} = \frac{1}{r_0}(1+\varphi\tau), \tag{3}$$

with the assumption that $r_0 = 0.34$ and is independent of the emitted wavelength and temperature. The assumption of a constant value of the limiting emission anisotropy, r_0, yields only estimative results. Nonetheless, the relative values of φ enable us to find an explanation of the difference between the fluorescence depolarization observed in the short- and long-wave regions of the emission spectrum. In the temperature range from -40 to -80°C (Fig. 5) there is a distinct diversity in the values of fluorescence depolarization probability of the centres responsible for the short- and long-wavelength edges of the spectrum. The value of φ also differs considerably for different fluorescent molecules Thus, for example, the depolarization probability for 3-aminophtalimide dissolved in izobutyl alcohol is approximately twice as large as for 4-aminophtalimide in the same solvent and at identical temperatures. According to Perrin,

$$\varphi = \frac{kT}{v\eta}, \tag{4}$$

where k is Boltzmann's constant, T is the solution's temperature, v is the volume of the molecule, including its solvation shell, and η is the viscosity of the solution. Assuming for the time being that the macro- and micro-viscosities of the solution are identical, we come to the conclusion that the values of φ for different fluorescent molecules and for different wavelengths of the emitted light are due to different volumes, v.

Knowledge of the volume, v, of the dye molecule of a fluorescence center for different solution temperatures and different emitted wavelengths may provide an answer to the question: why, in an earlier study (Bauer and Rudik 1968), is the wavelength dependence of the fluorescence emission anisotropy of phtalimide solutions strongest for temperatures at which molecular reorientation relaxation just begins to cause a shift in the emission spectra? In Fig. 6 we have plotted the values of volume v calculated from Eq. (4) for 4- and 3-aminophtalimide in izobutyl alcohol as a function of temperature, with observations made at the 500 nm wavelength of the fluorescent light. The volumes, v, for these two solutions differ considerably and decrease when the temperature drops. In order to illustrate the fact that the temperature dependence of v also differs for different centres responsible for the short- and long-wave edges of the spectrum, we have given in Fig. 7 the results as a function of temperature for a single dye (4-aminophtalimide in izobutyl alcohol) and two wavelengths of fluorescent light (589 nm and 460 nm).

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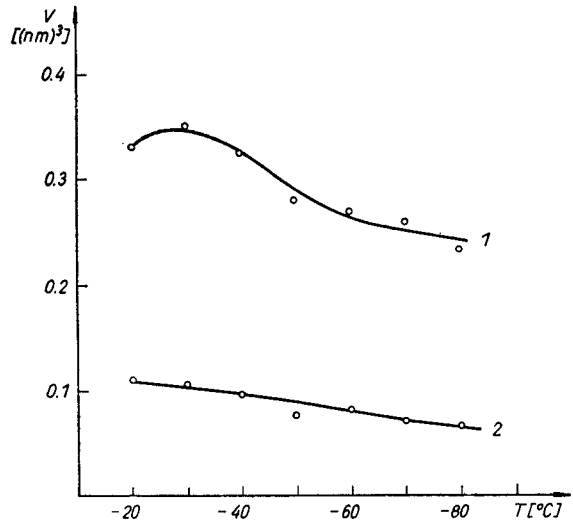

Fig. 6. Dependence of v on temperature for 4-aminophtalimide solution in izobutyl alcohol (curve 1) and 3-aminophtalimide (curve 2) in the same solvent

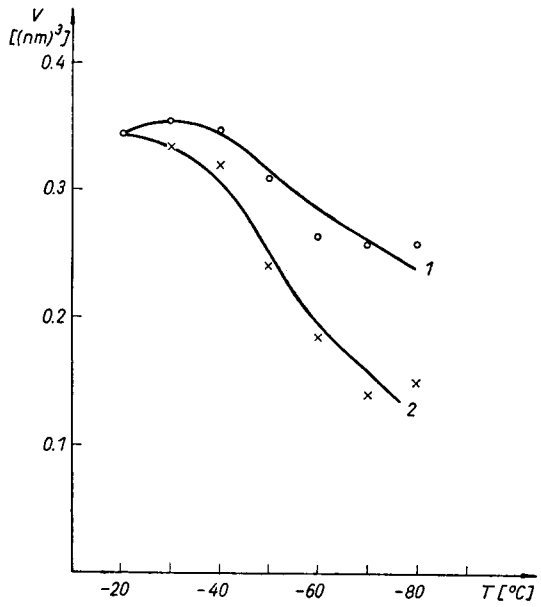

Fig. 7. Dependence of v on temperature of the solution of 4-aminophtalimide on izobutyl alcohol. Observed fluorescence wavelengths are 585 nm (curve 1) and 460 nm (curve 2)

Discussion of results

According to Samoilov (1957), solvation consists in the interaction of the fluorescent molecule on the translational and rotational motions of the solvent molecules. The volume of the solvation shell is therefore the region where this interaction extends. With this definition of the solvation shell the field of interaction of the solute molecule is probably almost spherical in shape, independently of the shape of the molecule itself. This would confirm the validity of Perrin's assumption made in the derivation of Eq. (3). In our case the decrease of v (Figs 6 and 7) with dropping temperature of the solution is probably associated with a change in the interaction of the fluorescent molecule (during its lifetime in the excited state) with the solvent molecules surrounding it. For relatively high temperatures this interaction is bigger than at low temperatures (Veselova *et al.* 1965; Cherkasov 1961). The interaction between the fluorescent molecule and its surroundings also depends on the type of the molecule and the solvent. For example, this is why the value of v for 4-aminophtalimide in izobutyl alcohol is some three times greater than the corresponding value for 3-aminophtalimide. Sarzhevski (1959, 1961) obtained very similar differences for the same solutions in his measurements of v for a fixed temperature of the solution. The dimensions of the 3- and 4-aminophtalimide molecules are identical, as they differ only by the position of the amine group. The most essential differences between the 3- and 4-aminophtalimide molecules is in the dipole moment in the ground state and in the change of this moment after excitation to the first excited state. The dipole moments for these molecules had been determined by Bakhshiev (1962) on the basis of his theory describing the effect of universal intermolecular interactions on the position of the molecular electronic spectra in bicomponent liquid solutions. In the ground state they are $\mu_g = 2.6$ D and $\mu_g = 3.5$ D, and in the excited state

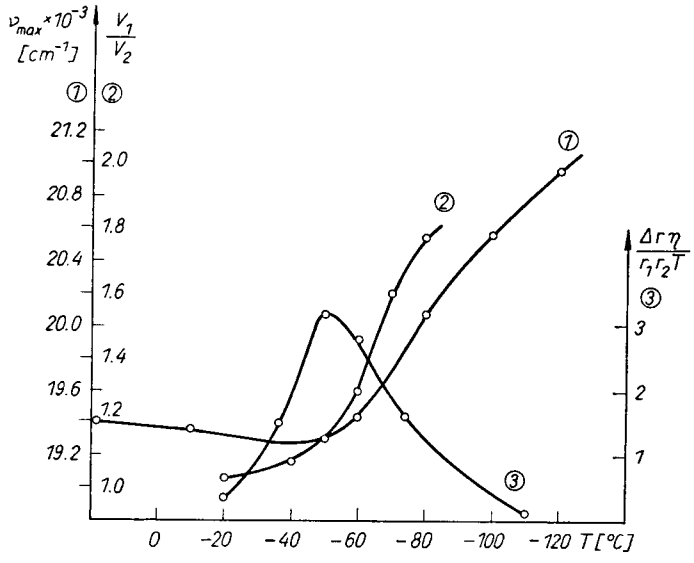

Fig. 8. Dependence of v max fluor., $\frac{(\bar{r}_2 - \bar{r}_1)\eta}{\bar{r}_1 \bar{r}_2 T}$ and v_1/v_2 on temperature of the solution of 3-monomethylamino-N-methylphtalimide

$\mu_e = 4.9$ D and $\mu_e = 6.7$ D for 3- and 4-aminophtalimide, respectively. Acceptance of the effect of dipole moment on magnitude of the interaction accounts for the different values of v for 3- and 4-aminophtalimide molecules in the same solvent and the different volumes (Fig. 7) for different centres responsible for the long- and short-wave edges of the spectrum. These centres have different degrees of reorientation, hence, they interact differently with their surroundings during their lifetimes in the excited state.The physical nature of this effect (which can formally be said to be a change in the effective volume of the fluorescent molecule together with its solvatation shell, or as the difference between micro- and macro-viscosities) lies in a change of the interaction between the fluorescent molecule and the solvent molecules.

There is still an explanation to be found for the strong dependence of fluorescence emission anisotropy on wavelength at temperatures high enough that there is almost complete reorientation relaxation, as compared with the lower temperatures at which owing to reorientation relaxation there is the strongest shift of the emission spectra. For this purpose we have presented in Fig. 8 three curves of the temperature dependence of the position of the maximum of the fluorescence spectrum, the quantity $\Delta r\eta/r$, r_2T and the ratio of volume v_1 (volume of molecule with shell for the long-wave spectrum edge) to v_2 (corresponding quantity for short-wave edge). With decreasing solution temperatures the ratio v_1/v_2 increases, hence, the ratio φ_2/φ_1 also increases. This latter increase means that there is higher depolarization of the fluorescent light of the centre responsible for the short-wave region of the emission spectrum, relative to that of long-wave fluorescence. In this way the effect of the change of emission anisotropy caused by reorientation relaxation of the solution molecules is superimposed by another effect, *viz.*, the dependence of depolarization on temperature and emitted wavelength through Brownian ratotions.

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