

## EMISSION ANISOTROPY OF FLUORESCENCE OF ANTHRACENE SOLUTIONS. I

BY R. K. BAUER

Physics Department, N. Copernicus University, Toruń\*

*(Received April 29, 1968)*

The emission anisotropy (EA) and the mean duration of fluorescence of anthracene and d-anthracene in glycerol solutions have been measured. It was found that the limiting EA is higher than that reported in other papers. Using expressions given by Jabłoński and Perrin in their theories of fluorescence light depolarization by Brownian rotations and torsional vibrations of the luminescent molecules the limiting EA  $r_0$ , the probability of depolarization by rotation per unit time  $\varphi$ , the volume of the anthracene molecule together with its solvation shell  $v$ , as well as the frequency of its torsional vibrations and its moment of torsion were calculated. Taking into account the shortness of the mean duration and the high EA-value of the fluorescence and comparing the obtained parameters of the torsional vibrations of anthracene and d-anthracene molecules with those obtained for several different molecules by other authors, the conclusion is reached, that probably the only depolarization factor (after elimination of the Brownian rotations and the concentration depolarization) are torsional vibrations, while the admixture of the negatively polarized fluorescence produced by excitation to the electronic level  $L_b$  lying above the initial level  $L_a$  of emission of fluorescence is negligible.

*Introduction*

The value of emission anisotropy (EA)<sup>1</sup> of fluorescence of solutions is influenced by several depolarizing factors. These are torsional vibrations of luminescent molecules, their thermal rotational motion, secondary fluorescence and excitation energy transfer between luminescent molecules. Among these factors only the influence of torsional vibrations of molecules is practically independent of fluorescence decay time and, conversely, such vibrations do not influence the fluorescence decay. The influence of depolarizing factors cannot be completely eliminated, however, by decreasing the temperature and increasing the viscosity of the solution it is possible to eliminate thermal rotations of luminescent

\* Address: Katedra Fizyki, Uniwersytet M. Kopernika, Toruń, ul. Grudziądzka 5, Polska.

<sup>1</sup> The concept of emission anisotropy has been introduced by Jabłoński (1960) as  $r = \frac{I_{||} - I_{\perp}}{I_{||} + 2I_{\perp}}$ , where  $I''$  and  $I_{\perp}$  are the components of fluorescence polarized parallelly and perpendicularly to the electric vector of primary light (which is linearly polarized).

molecules, while by decreasing the concentration of the dye one can practically eliminate secondary fluorescence as well as excitation energy transfer. Only the influence of torsional vibrations cannot be eliminated in the experiment. Thus it was necessary to obtain by means of theoretical considerations a value of emission anisotropy which would occur in a solution with no depolarization factors present. It is accepted to call this value fundamental EA.

The expression for fundamental polarization in the case of linear oscillators responsible for absorption and emission and making an angle  $\beta$  with each other has been given by Perrin (1929). With the use of the EA instead of the polarization degree this expression becomes

$$r_f = 0.6 \cos^2 \beta - 0.2. \quad (1.1)$$

Jabłoński (1935) has extended the theory of EA by introducing into it, instead of linear oscillators, threedimensional oscillators in which the dipoles of the same electronic transition may have different directions in the molecule.

According to this theory

$$r_f = 0.6 \sum_i \Gamma_i' G_i - 0.2, \quad (2.1)$$

where  $\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma_3$  are the principal intensities of the absorption oscillator, normalized so that  $\Gamma_1 + \Gamma_2 + \Gamma_3 = 1$ , while  $G_1$ ,  $G_2$  and  $G_3$  are the components of the emission oscillator intensity with respect to the principal axes of the absorption oscillator (also normalized to unity). The direction of these axes (orthogonal coordinate system) are rigidly connected with the luminescent molecule, their orientations being such that the transition moment is maximum for the direction of one axis and minimum for a second axis. Assuming different values for  $\Gamma_i$  an  $G_i$  fundamental EA-values are obtained ranging from  $-0.2$  to  $0.4$ .

The purpose of this paper was to investigate the limiting EA of the fluorescence of anthracene solution by means of measurements of EA and fluorescence decay times. Several authors (Perrin 1929; Spektorov 1949; Kawski 1958) have already studied this problem and obtained pseudo-fundamental EA-values from  $0.2$  to  $0.26$ . Only Chakravarti and Ganguly (1941) have obtained the value of  $0.34$  for anthracene solution in anhydrous glycerol at  $-79^\circ \text{C}$  and Zimmerman and Joop (1960) the value of  $0.31$  for anthracene solution in ethyl alcohol ( $-180^\circ \text{C}$ ). According to Förster (1951) the small value of pseudo-fundamental EA-value is the evidence of long fluorescence decay time making impossible complete elimination of thermal rotational motion of anthracene molecules. However, it follows from the further part of the present paper that the fluorescence decay times of anthracene solution are short (of the order of  $3 \cdot 10^{-9} \text{s}$ ) and the reasons for small pseudo-fundamental EA-value should be looked for elsewhere.

Anthracene belongs to the group of aromatic hydrocarbons characterized by two close electron levels  $L_a$  and  $L_b$  (according to the nomenclature of Platt (1949)) whose transition moments are perpendicular to each other. The transition from the  $L_b$  level is quasi-forbidden and is characterized by long fluorescence decay time. In the bicyclic naphthalene the  $L_b$ -level is lower than  $L_a$ , hence the fluorescence decay time is long and its EA-value negative. In the tetra-cyclic tetracene the situation is just the opposite: the  $L_b$  level is higher than  $L_a$  and the position difference between these levels sufficiently far apart to distinguish the  $L_a$

an  $L_b$  bands by means of spectroscopic methods. When exciting tetracene molecules to the  $L_a$  level a short fluorescence decay time is observed and the EA is positive. It follows from theoretical considerations that in the case of tricyclic anthracene both levels are very near one another and they cannot be distinguished spectroscopically. Theoretical predictions yield that the  $L_b$  level is about  $1500\text{ cm}^{-1}$  higher than  $L_a$  (Klevens *et al.* 1949, Mann *et al.* 1949). Anthracene molecules, which are excited not directly to the fluorescent level  $L_a$  but to the higher  $L_b$  level from which they go over to  $L_a$  by non-radiative transition have their absorption and emission moments perpendicular. The fundamental EA of such indirectly excited fluorescence should be (according to Eq. 1.I) 0.2, whereas for excitation to the  $L_a$  level (the directions of transition moments the same) the EA should amount to 0.4. The assumption of partial excitation of anthracene molecules *via* the higher electronic level could be a reasonable explanation of the fact why the measured pseudofundamental EA-values of fluorescence of anthracene are considerably lower than 0.4. Finally there is the possibility that anthracene molecules can be regarded as threedimensional oscillators. The results of the measurements made in the present work indicate that:

1. the measurements made so far were subject to systematic errors
2. the directions of the transition moments corresponding to absorption and emission by the anthracene molecule are the same
3. fundamental EA-value is 0.4.

Thus we have here the so-called virtual linear electronic oscillator.

Direct emission from  $L_b$  level, even it would occur it would be unmeasurably weak.

## II. Factors depolarizing fluorescence light

In the simpler form of the theory of depolarization of the fluorescence of solutions through thermal rotations of dye molecules (Perrin 1926) it has been assumed first of all that these rotations are governed by laws of rotational Brownian motion of spherical particles. For isotropic solution excited by parallel beam linearly polarized light Perrin obtained expressions which have been written by Jabłoński (1959, 1960) in the following way by introducing the notion of emission anisotropy:

$$r(t) = r_0 e^{-\varphi t} \quad (1.II)$$

$$\frac{1}{\bar{r}} = \frac{1}{r_0} (1 + \varphi \tau) \quad (2.II)$$

where

$$\varphi = \frac{kT}{v\eta}, \quad (3.II)$$

( $\eta$  — is the viscosity coefficient,  $v$  — the volume of the luminescent molecule together with its solvation shell,  $h$  — the Boltzmann constant,  $T$  — absolute temperature).

Eq. (2.II) gives the dependence of the measured mean EA  $\bar{r}$  on depolarization probability  $\varphi$ , limiting EA  $r_0$  and fluorescence decay time  $\tau$ , whereas Eq. (1.II) presents the exponential EA-decay law. Assuming an exponential decay of EA as well as an exponential decay of

the whole fluorescence Jabłoński (1961) has obtained the expression for the decay and mean duration of fluorescence for various components of fluorescent light. On ground of this theory one can determine the limiting EA of fluorescence

$$r_0 = \frac{\bar{r}^2 \tau}{\tau - \tau^\perp (1 - \bar{r})}, \quad (4.II)$$

where  $\bar{r}$  is the emission anisotropy observed by steady excitation with linearly polarized light whose electric vector is perpendicular to the observation direction,  $\tau$  is the mean decay time of the total fluorescence<sup>2</sup> and  $\tau^\perp$  is the mean decay time of the component ( $I^\perp$ ) perpendicular to the electric vector of the polarized exciting light. The absolute value of limiting EA is smaller than that of fundamental EA certain due to the depolarizing action of torsional vibrations. It also differs from the pseudo-fundamental EA-value by the fact that it is not necessary to eliminate thermal rotations of luminescent molecules by extrapolating the curve of the  $1/\bar{r}$  vs.  $(T/\eta)$  — dependence to zero.

The limiting EA can be obtained from Eq. (4.II) even for solutions with small viscosity by measuring  $\bar{r}$ ,  $\tau$  and  $\tau^\perp$ . The knowledge of limiting EA permits the calculation of the probability of depolarization by thermal rotations  $\varphi$  (Eq. 1.II) and hence the calculation of the volume of the luminescent molecule together with its solvation shell (Eq. 3.II). It also permits the torsional vibration parameters to be calculated.

Torsional vibrations of molecules result in vibrations of the virtual electronic oscillator. The average period of these irregular vibrations is very short as compared with the mean fluorescence decay time. Assuming that the torsional oscillator, which is represented by the molecule in the solution, is isotropic (principal moments of inertia  $I$  and torsion coefficients are for simplicity assumed to be the same) (Jabłoński 1968) one obtains from Eq. (2.I).

$$r_0 = r_f(1 - 1.5 U)^2 \quad (5.II)$$

where  $U = \overline{\sin^2 \varepsilon}$  is the dispersion of the sine of the angle made by instantaneous directions of the transition dipole with its average direction. If the amplitudes of the torsional vibrations are so small that it is possible to decompose them into three components then  $U = \overline{\sin^2 \varepsilon} \approx \varepsilon^2 = 2\delta$ , where  $\delta$  is the dispersion of the angle of torsional vibrations along one of the two axes of the molecule (torsional vibrations about the third axis which is parallel to the direction of the absorption oscillator do not depolarize the fluorescence light). The value of  $\delta$  depends on the temperature and on the moment of torsions acting on the molecule:

$$M = \omega^2 J \quad (6.II)$$

where  $\omega$  — is the frequency of torsional vibrations,  $I$  — the moment of inertia of the molecule.

---

<sup>2</sup>  $\tau$  can be calculated or directly determined by means of a fluorometer, by observing the fluorescence component  $I^{55}$  making an angle of  $55^\circ$  with the component  $I^{11}$  (Jabłoński 1935 a).

The dispersion  $\delta$  of the angle  $\varepsilon$  can be calculated by substituting into Eq. (5.II) the value of  $r_0$ . Assuming that for small amplitudes the torsional vibrations of the three axes of inertia can be regarded as independent, Jabłoński (1950, 1960a) has given the following formula for this dispersion:

$$\delta = \overline{\varepsilon^2} = \frac{\hbar}{I\omega} \left( \frac{1}{2} + \frac{kT}{\hbar\omega} \right) \quad (7.II)$$

which, together with Eq. (5.II), permits the calculation of the frequencies of torsional vibrations about one axis. The moment of inertia can be calculated on ground of the known structure of the molecule. In this way one can estimate from experimental data the main parameters of the torsional vibrations such as the amplitude, frequency and the torsion moment. Torsional vibrations occur approximately about the three axes of the flat molecule of anthracene. The symmetry of the transition moment responsible for the first electronic band in anthracene is of the type  $A_{ig} - B_{2u}$  (Klevens *et al.* 1949). Torsional vibrations about the V-axis (of a rectangular coordinate system) do not result in depolarization of fluorescent light observed perpendicularly to the direction of the electric vector of plane-polarized exciting light. A depolarization like this occurs, however, as the result of torsional vibrations about the remaining axes  $U$  and  $W$ . The moments of inertia of the molecule with respect to the axes  $U$  and  $W$  are different and as the result of it one obtains different frequencies of torsional vibrations ( $\omega_U$  and  $\omega_W$ ) and different moments of torsion ( $M_U$  and  $M_W$ ). Because of different moments of inertia the calculated values of  $\omega_{U,W}$  and  $M_{U,W}$  are only some estimates, which, however, should be regarded as upper and lower limits, the real values lying in between.

The conclusions drawn from depolarization studies are valid only if the concentration depolarization is negligible. The theory of concentration depolarization has been given by Förster (1951) Ore (1959) and other authors. A more general theory of depolarization of photoluminescence of rigid solutions *via* energy migration has been elaborated by Jabłoński (1955). The dependence of EA on dye concentration is given by Jabłoński (1958):

$$\frac{r'_0}{\bar{r}} = \frac{\nu^2}{2(\nu - 1 + e^{-\nu})} \quad (8.II)$$

where  $\nu = \nu n$  ( $\nu$  is the active sphere volume,  $n$  — the number of molecules per one  $\text{cm}^3$  of the solution). The value of  $r'_0$  in Eq. (8.II) is the EA which is obtained by extrapolation of the  $1/\bar{r}(\nu)$  curve to zero concentration. If  $\nu$  is much smaller than unity, Eq. (8.II) can be written in a much simpler form:

$$\frac{r'_0}{\bar{r}} = 1 + \frac{1}{3} \nu \quad (9.II)$$

### III. Experimental

Anthracene ( $\text{C}_{14}\text{H}_{10}$ ) and d-anthracene ( $\text{C}_{14}\text{D}_{10}$ ) purified by zone melting was solved in anhydrous methyl alcohol in such amounts to obtain after mixing with anhydrous glycerol (1 part methyl alcohol per 9 parts of glycerol) five solutions with the following dye concen-

trations:  $3 \times 10^{-4}$ ,  $10^{-4}$ ,  $3 \times 10^{-5}$ ,  $10^{-5}$  and  $3 \times 10^{-6}$  mole/litre. The viscosity coefficient  $\eta$  was measured by means of a Hoespler viscosimeter for a number of temperatures from  $80^\circ\text{C}$  to  $-40^\circ\text{C}$  with the accuracy up to 1%. Since the dependence of  $\log \eta$  on reciprocal temperature is linear it was possible to determine the viscosity coefficients by extrapolation also for  $-60^\circ\text{C}$  and  $-80^\circ\text{C}$ . The measurements of the absorption and emission spectra were made at two temperatures:  $20^\circ\text{C}$  and  $-60^\circ\text{C}$  (Fig. 1 and 2) and the wavelengths of purely electronic

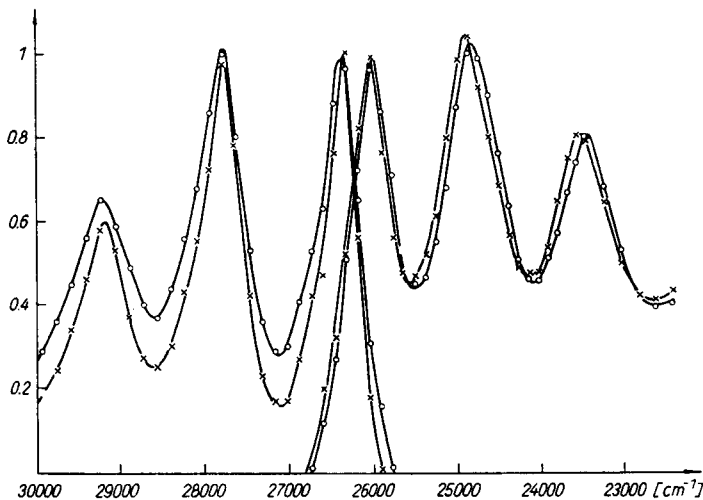


Fig. 1. Absorption and emission spectra of anthracene solutions in glycerol. The temperatures of the solutions are  $20^\circ\text{C}$  (o) and  $-60^\circ\text{C}$  (x). The concentration of the dye is  $10^{-5}$  m/l. The pure electronic transition wavelength is 381.4 nm

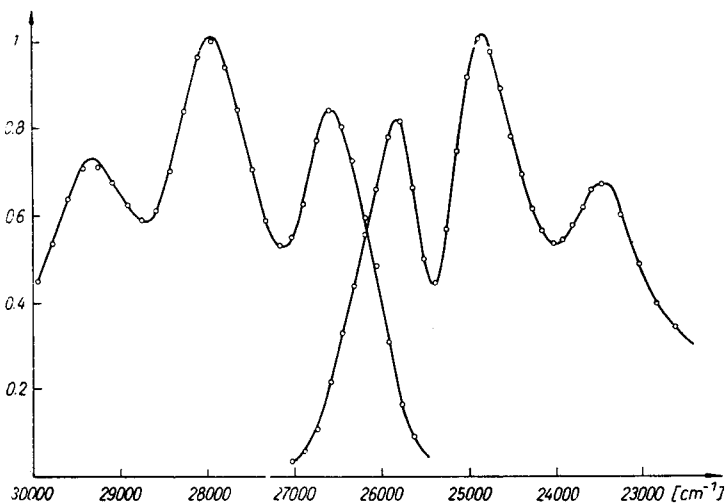


Fig. 2. Absorption and emission spectra of d-anthracene solutions in glycerol. The temperature of the solution is  $20^\circ\text{C}$ . The concentration is  $10^{-5}$  m/l. The pure electronic transition wavelength is 382.2 nm

transition hence established were 381.4 nm for anthracene and 382.2 nm for d-anthracene. The measurements of emission spectra were made by means of a set-up consisting of a Zeiss SPM-1 monochromator, a photomultiplier and galvanometer. Fluorescence was excited with the 366 nm mercury line obtained from a high pressure HBO-50 mercury lamp. Absorption measurements were made with the same apparatus with the use of a hydrogen lamp as light source. The fluorescent solution was contained in a Dewar vessel cooled with ethyl alcohol and liquid air. Because of the possibility of anthracene dimerization under the influence of U. V. illumination into the so-called dianthracene (Chandross 1966), low intensities of exciting light were applied and the sample was illuminated only for few seconds necessary for galvanometer reading. A similar procedure was used in measurements of EA and decay times. EA was measured by means of a photoelectric polarimeter (Bauer *et al.* 1961) by exciting the fluorescence with a XBO-150 xenon lamp through a double Hilger-Müller monochromator. To eliminate depolarizing action of "initial shock" the EA measurements were carried out by exciting the anthracene solution with different wavelengths successively in the whole absorption spectrum. From the "polarization" spectrum measured in such a manner only those EA have been used in the present work which were measured when exciting the fluorescence with wavelength corresponding to 0-0 transition. The essential feature of the "initial shock" phenomenon is that by exciting the fluorescence with light having shorter wavelength than that corresponding to purely electronic transition the molecule and its nearest neighbourhood obtains a certain surplus of energy giving rise to a temperature increase of such a luminescent centre. During the life time of the molecule in excited state the temperature increase reduces only partly so that at the emission instant the temperature of the luminescent centre is higher than that of the solution. This surplus of temperature of the luminescent centre gives rise to increased depolarizing action of torsional vibrations and thermal rotations and hence to observation of EA decrease when exciting with wavelengths shorter than of purely electronic transition. The problem of "initial shock" has been worked out theoretically by Jabłoński (1964), (Bauer *et al.* 1968). Measurements of depolarizing action of "initial shock" have been carried out by Lisicki (1963). The fluorescence of a low concentration solution of anthracene ( $3 \times 10^{-6}$  mole/litre) shows a few percent EA decrease when changing the wavelength from 381.4 nm to 322 nm. On the other hand for anthracene concentration of  $3 \times 10^{-4}$  mole/litre the emission anisotropy falls to about one half of its former value, if instead of exciting with the wavelength of purely electronic transition excitation in the region of the short-wave edge of the absorption spectrum (322 nm) is used (Fig. 3). The phenomenon can no more be explained in terms of depolarizing action of "initial shock". It will be the subject of a further paper concerning the study of EA of aromatic hydrocarbons. It is probable that for high concentrations there is a possibility of energy migration from higher oscillation levels. The occurrence of a strong dependence of EA on exciting wavelength for concentrations greater than  $3 \times 10^{-6}$  mole/litre could be the reason why the authors quoted above have obtained EA value about 0.25 when exciting the fluorescence of anthracene solutions with the 366 nm Hg-line for concentrations of  $5 \times 10^{-5}$  mole/litre. When exciting the fluorescence of anthracene solutions by means of the 381.4 nm (for such slit widths for which the half-width of the spectrum interval would be equal to 4 nm) and the fluorescence

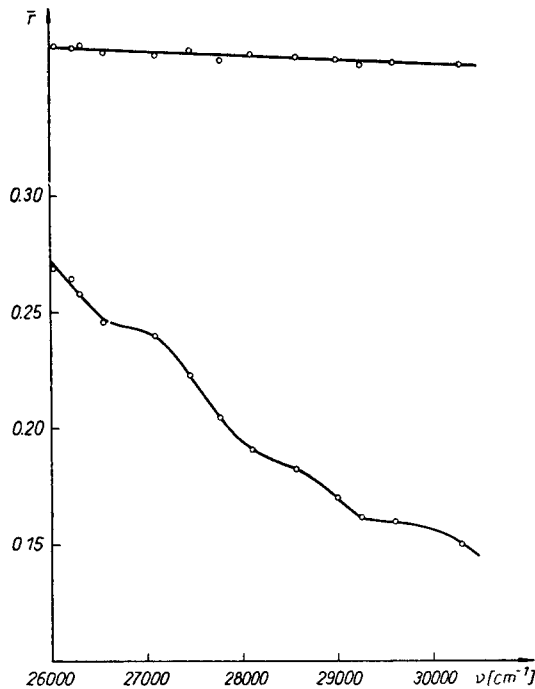


Fig. 3. EA of the fluorescence of anthracene in glycerol solutions *versus* the wavelength of the exciting light. The temperature of the solution is  $-60^{\circ}\text{C}$ . The upper curve is for the concentration  $3 \times 10^{-6}$  m/l, whereas the lower curve is for a dye concentration of  $3 \times 10^{-4}$  m/l

TABLE I

The dependence of the EA of the fluorescence of anthracene solutions in glycerol on the concentration and the temperature. Exciting wavelength 381.4 nm

Temperature \ Concentration	+20°C	0°C	-20°C	-40°C	-60°C	-80°C
$3 \times 10^{-4}$ m/l	0.122	0.208	0.241	0.256	0.264	0.267
$10^{-4}$ m/l	0.169	0.274	0.297	0.312	0.323	0.328
$3 \times 10^{-5}$ m/l	0.199	0.307	0.328	0.340	0.350	0.354
$10^{-5}$ m/l	0.208	0.314	0.335	0.346	0.359	0.364

TABLE II

The dependence of the EA of the fluorescence of d-anthracene solutions in glycerol on the concentration and the temperature. Exciting wavelength 382.2 nm

Temperature \ Concentration	+20°C	0°C	-20°C	-40°C	-60°C	-80°C
$3 \times 10^{-4}$ m/l	0.117	0.208	0.251	0.261	0.267	0.270
$10^{-4}$ m/l	0.166	0.275	0.308	0.317	0.325	0.328
$3 \times 10^{-5}$ m/l	0.191	0.306	0.333	0.343	0.352	0.358
$10^{-5}$ m/l	0.201	0.313	0.339	0.352	0.359	0.363
$3 \times 10^{-6}$ m/l	0.207	0.322	0.342	0.354	0.364	0.366



of d-anthracene with the wavelength of 382.2 nm (these are the wavelengths of purely electronic transition) the values of EA have been measured for different dye concentrations and different temperatures of the solutions (see Tables I and II). These values were plotted *versus* the reciprocal EA on the concentration of anthracene and d-anthracene (Figs 4 and 5).

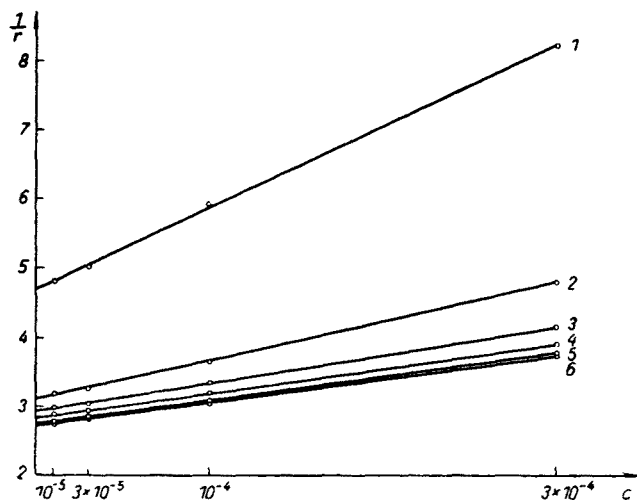


Fig. 4. The reciprocal of the EA of the fluorescence of anthracene in glycerol *versus* the dye concentration. 1 — 20°C, 2 — 0°C, 3 — -20°C, 4 — -40°C, 5 — -60°C, 6 — -80°C

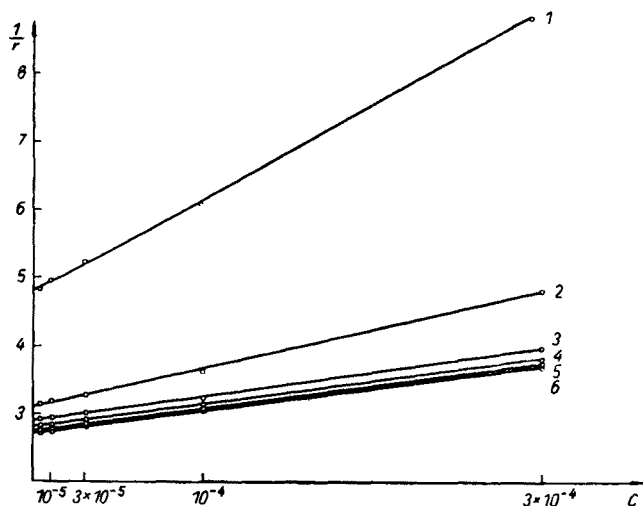


Fig. 5. The reciprocal of the EA of the fluorescence of d-anthracene in glycerol *versus* the dye concentration. 1 — 20°C, 2 — 0°C, 3 — -20°C, 4 — -40°C, 5 — -60°C, 6 — -80°C

The curves thus obtained have been extrapolated to zero concentration and the values of emission anisotropy obtained in this way were the basis for further calculations (see Tables III and IV). Using Eq. (10.II) the radius of the active sphere for energy migration was calculated.

TABLE III

Results of measurements and calculated values concerning the fluorescence of anthracene in glycerol solutions

Temperature in °K	293	273	253	233	213	193
Viscosity coeff. $\eta$ in g/cm s	2.43	23.97	216.8	1497	21650	556200
EA $\bar{r}$	0.212	0.321	0.340	0.353	0.363	0.365
Mean decay time $\tau_{\perp}$ in ns	3.39	3.41	3.55	3.70	3.86	3.90
Mean decay time $\tau$ in ns	3.08	3.22	3.45	3.64	3.83	3.88
Depolarization probability $\varphi \times 10^{-8}$	2.9	0.4	0.17	0.13	—	—
Volume $v$ in $\text{cm}^3 \times 10^{24}$	57.3	39.3	9.5	1.7	—	—
Limiting EA $r_0$	0.34	0.36	0.36	0.37	—	—
Angular deflection $\delta$	0.027	0.017	0.017	0.13	—	—
Angular frequency $\omega_U$ in $\text{Hz} \cdot 10^{-12}$	6.5	8.0	7.8	8.7	—	—
Moments of torsions $M_U$ in $\text{gcm}^2/\text{s}^2 \cdot 10^{12}$	1.6	2.4	2.3	2.9	—	—
Angular frequency $\omega_W$ in $\text{Hz} \cdot 10^{-12}$	3.0	3.9	3.6	3.9	—	—
Moments of torsions $M_W$ in $\text{gcm}^2/\text{s}^2 \cdot 10^{12}$	1.4	2.4	2.1	2.4	—	—

TABLE IV

Results of measurements and calculated values concerning the fluorescence of d-anthracene in glycerol solutions

Temperature in °K	293	273	253	233	213	193
Viscosity coeff $\eta$ in g/cm s	2.43	23.97	216.8	1497	21650	556200
EA $\bar{r}$	0.208	0.323	0.344	0.355	0.369	0.372
Mean decay time $\tau_{\perp}$ in ns	4.03	4.10	4.16	4.23	4.21	4.20
Mean decay time $\tau$ in ns	3.60	3.83	4.00	4.09	4.17	4.22
Depolarization probability $\varphi \times 10^{-8}$	2.2	0.45	0.23	0.16	0.07	—
Volume $v$ in $\text{cm}^3 \times 10^{24}$	43.5	35.0	7.0	1.4	0.9	—
Limiting EA $r_0$	0.372	0.377	0.376	0.379	0.380	—
Angular deflection $\delta$	0.012	0.01	0.01	0.009	0.008	—
Angular frequency $\omega_U$ in $\text{Hz} \cdot 10^{-12}$	9.2	10.1	9.5	9.7	9.8	—
Moments of torsions $M_U$ in $\text{gcm}^2/\text{s}^2 \cdot 10^{12}$	3.8	4.6	4.1	4.2	4.3	—
Angular frequency $\omega_W$ in $\text{Hz} \cdot 10^{-12}$	4.3	4.7	4.6	4.7	4.9	—
Moments of torsions $M_W$ in $\text{gcm}^2/\text{s}^2 \cdot 10^{12}$	3.3	4.0	3.8	4.0	4.3	—

Within the experimental error this radius is the same for anthracene and d-anthracene and is independent on the temperature (in the temperature interval from  $-80^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$  for which one can assume that the solutions are practically rigid). The value of this radius is 11.5 nm.

Although in the further part of the paper the values of limiting EA are calculated by means of Eq. (4.II) the author has also calculated the pseudo-fundamental emission anisotropy. In order to do this the results of EA measurements obtained by extrapolation to zero concentration have been plotted in the form of the dependence of reciprocal EA  $1/r$  on the ratio of the solution temperature to its viscosity ( $T/\eta$ ) (Fig. 6). Because of the large

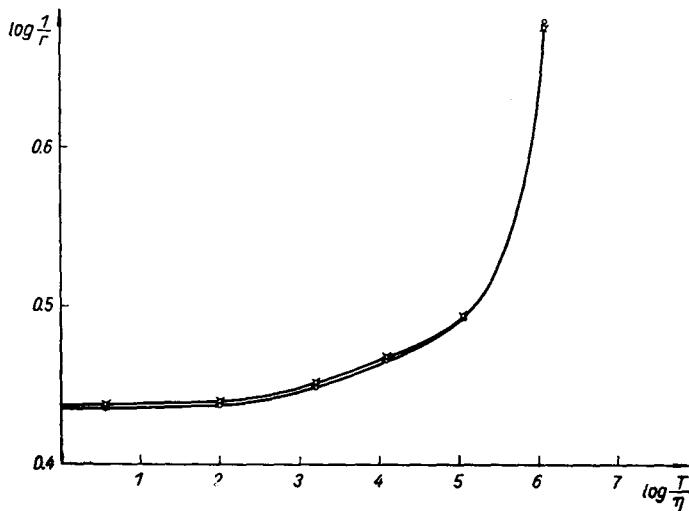


Fig. 6. The reciprocal of the EA of the fluorescence of anthracene (upper curve) and d-anthracene (lower curve) solutions versus temperature and reciprocal values of the viscosity coefficient. The EA values were obtained by extrapolation of the curves given in Figs 4 and 5 to concentrations equal zero

range of viscosity the scale used is double-logarithmic. In agreement with the results given below for temperatures below  $0^{\circ}\text{C}$  the dependence of EA on temperature becomes weak and is no more due to depolarization by thermal rotations but only to torsional vibrations. The pseudo-fundamental EA for anthracene is 0.366 and for d-anthracene 0.374.

In addition to EA-measurements mean decay times of fluorescence components  $\tau$  and  $\tau^{\perp}$  were measured to obtain the limiting emission anisotropy by means of Eq. (4.II). The measurements were made by means of a phase fluorometer (Bauer *et al.* 1959). Fluorescence was excited by means of a HBO-200 mercury lamp using a filter which transmitted the 366 nm mercury line only (it follows from the unpublished results of Grudziński that the mean life time of fluorescence is independent of exciting light wavelength). The fluorescence was observed through a crossed filter and a polaroid. The results of measurements of mean decay times of the components  $I^{55}$  and  $I^{\perp}$  of the fluorescence of anthracene and d-anthracene are given in Tables III and IV.

The knowledge of EA obtained by extrapolation of the dye concentration to zero as well as the knowledge of mean decay times of the fluorescence components permits the limiting EA-values  $r_0$  to be calculated and hence the probability of depolarization by thermal rotations  $\varphi$  and the volume of the dye molecule together with its solvation shell. These values are listed in Tables III and IV. As the temperature decreases and the viscosity increases the probability of depolarization by thermal rotations rapidly decreases. In spite of this the limiting EA values further slightly decreases indicating a dependence of the amplitude of torsional vibrations on temperature. The amplitude, frequency and moment of torsion of torsional vibrations were calculated using Eqs (5.II), (6.II) and (7.II). The results are given in Tables III and IV.

#### IV. Results

The mean decay times ( $\tau$ ) of fluorescence of anthracene and d-anthracene solutions change from 3.1 nsec to 4.2 nsec depending on the temperature. Since the measurements of mean decay times were made with a phase fluorometer with the frequency of exciting light modulation of 12 MHz, there was the possibility that there exists a fluorescence component with long decay time which cannot be measured with this fluorometer. To observe

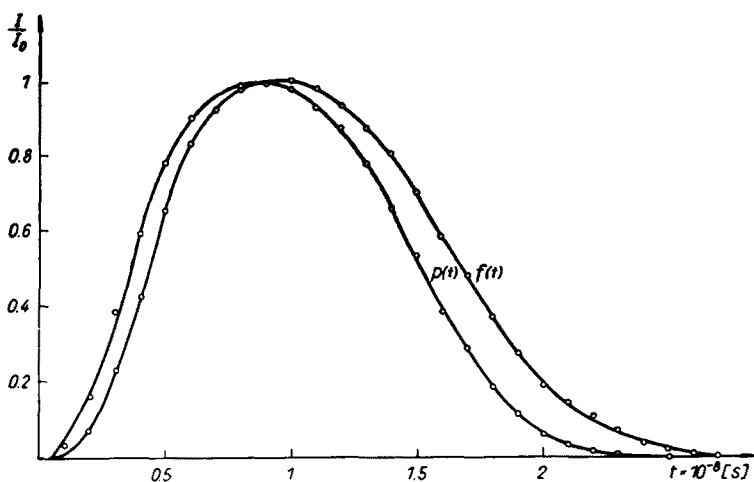


Fig. 7. Pulse shape of the exciting light of a hydrogen discharge tube  $p(t)$  and the fluorescence of an anthracene solution  $f(t)$  excited by it

this suspected component, the anthracene solution was excited by a short light pulse from a hydrogen flash lamp and the fluorescence was measured by means of a photomultiplier connected to an oscilloscope (Birks 1962,) both of high time resolution.

Fig. 7 shows the shape of the exciting light pulse and that of the fluorescence. The decay time cannot be determined from the shape of the decay curve because of the comparatively long exciting pulse, however, one can definitely exclude the existence of a fluorescence component of long decay time. The lack of such component and pseudo-fundamental EA

values close to 0.4 seem to indicate that fluorescence of anthracene solutions is due only to transitions from the allowed electronic level  $L_a$ . The intensity of delayed fluorescence from the  $L_b$ -level if any cannot be greater than 1% of the  $L_a$ -level fluorescence. The pseudo-fundamental EA is smaller than the fundamental EA-value (0.366 for anthracene and 0.374 for d-anthracene). Thus there exists a possibility that in addition to torsional vibrations the depolarization is partly due to the admixture of negatively polarized fluorescence from the  $L_a$  level excited indirectly through the  $L_b$  level. It is difficult to decide on the basis of the experimental results so far available what is the ratio of the intensities of negatively and positively polarized fluorescence components of anthracene solutions. Therefore it is assumed that even if there would exist such a possibility it would be negligible small. This presumption is confirmed by the comparison of the results of calculations of torsional vibration parameters obtained under this assumption with the results obtained by other authors who had studied molecules with undoubtedly single initial fluorescence level where the fundamental EA is equal to 0.4.

Eqs (1.II)—(7.II) have been derived under the assumption (among others), of spherical shape of the molecule together with its solvation shell. To explain deviations of experimental results from his simpler theory of depolarization by thermal rotations Perrin (1936) assumed ellipsoidal shape of the molecule (and its shell). Calculations based on this assumptions have shown that as long as the ratio of the axes of the ellipsoid is less than about 10 the assumption that the molecules with their shells are spherical is a sufficient approximation.

In a previous paper (Bauer 1968) the author has compared the values of the uranine molecule volume  $v$  determined by means of joint measurements of EA and mean decay times of fluorescence components of uranine in glycerol + 10% ethyl alcohol with the corresponding values determined by means of diffusion rate measurements. An agreement was obtained within the limits of experimental error. Also those measurements have shown that the assumption of a spherical shape of the dye molecule with its solvation shell is full justified. It has been therefore assumed that the same applies in glycerol solutions with 10% of methyl alcohol for both the anthracene and d-anthracene molecules. The limiting EA of fluorescence of anthracene and d-anthracene solutions deviates only slightly from the pseudo-fundamental EA-value and grows with decreasing solution temperature. Thus the results obtained earlier by Grzywacz (1958), Bauer (1963) and Heldt (1966) are again confirmed. These results implied that there is a dependence of the limiting EA value on the temperature and the viscosity of the solution (a dependence which is the main source of disagreement between the simpler form of Perrin's theory and experiment, especially for small viscosities of solutions). Decreasing the temperature of the solution gives rise to a decrease in the probability of depolarization by thermal rotation  $\varphi$ . The dye molecules perform torsional vibrations about instantaneous equilibrium orientation which is changed jumplike. The mean duration of a given orientation  $\tau'$  is in general much longer than the period of torsional vibrations  $\tau'_0$ . According to Frenkel (1946)  $\tau' = \tau'_0 \exp(E/kT)$ , where  $E$  is the activation energy for reorientation. The volume of the anthracene molecule together with its solvation shell calculated by means of Eq. (3.II) is not constant and decreases with decreasing temperature of the solution. Reorientation of the instantaneous axis of torsional vibrations of the molecule can occur to-

gether with its solvation shell or without it (Samoylov 1957). The ratio of the mean number of reorientations (in unit time) of the molecule together with its solvation shell ( $n_2$ ) to the mean number of reorientations of the molecule alone ( $n_1$ ) is

$$\frac{n_2}{n_1} = \alpha \exp (\Delta E/kT), \quad (1.IV)$$

where  $\Delta E$  is the difference in activation energy of reorientations of the molecules of the solvent and dye, and  $\alpha$  is a constant.

This ratio decreases with decreasing temperature when  $\Delta E$  is negative. According to Samoylov a negative value of  $\Delta E$  means negative solvation (the microviscosity coefficient is smaller than the macroviscosity coefficient). Such negative solvation was reported in an earlier paper (Bauer 1968). A possible cause of the dependence of  $v$  on the temperature of the solution (in particular for low temperatures and very viscous solutions) may be an increase in the number of reorientations of the molecule without the solvation shell and the resulting decrease in the effective volume of the dye molecule together with its solvation shell.

Further results obtained in this work concern the depolarization of fluorescence by torsional vibrations. The limiting EA value depends on the amplitude of torsional vibrations (Eq. 5. II) whose measure is the dispersion of the angle made by instantaneous directions of the transition dipole with its mean direction. The amplitude depends on the moment of inertia of the dye molecule and the frequencies of torsional vibrations (Eq. 7.II). The latter depend on the square root of the ratio of the moment of torsions to the moment of inertia. The increase in the moment of inertia of the dye molecule weakens the depolarization by torsional vibrations. The moments of inertia of the anthracene molecule with respect to the axes  $U$  and  $W$  (which are perpendicular to the directions of the transition moments responsible for emission and absorption) are  $I_U = 381.2 \times 10^{-40} \text{ gcm}^2$ , and  $I_W = 1598 \times 10^{-40} \text{ gcm}^2$  for anthracene and  $I_U = 449.5 \times 10^{-40}$  and  $I_W = 1788 \times 10^{-40} \text{ gcm}^2$  for d-anthracene. On the basis of the results available it is not possible to calculate the frequencies of torsional vibrations of flat molecules. Thus the first approximation is the calculation of these frequencies for hypothetical spherical molecules with moments of inertia  $I_U$  and  $I_W$ . It is assumed in this procedure that the moments of inertia of these spherical molecules are equal to the respective moments of inertia of the anthracene or d-anthracene molecule with respect to their  $U$ - and  $W$ -axes. The frequencies calculated in this way, denoted by  $\omega_U$  and  $\omega_W$ , as well as the torsion coefficients  $M_U$  and  $M_W$  are only rough estimates. In spite of that it follows from the results given in the Table III and IV for anthracene and d-anthracene that they are significantly different, the depolarizing action of torsional vibrations being smaller in the case of d-anthracene. The mean square  $\sin^2 \varepsilon = 2\delta$  is smaller for d-anthracene molecules ( $\sqrt{\varepsilon^2}$  are equal to  $6^\circ$  at  $20^\circ\text{C}$  and  $5^\circ$  at  $-60^\circ\text{C}$ ) compared with that for anthracene molecules ( $\sqrt{\varepsilon^2} \cong 9^\circ$  for  $20^\circ\text{C}$  and  $\cong 6^\circ$  for  $-40^\circ\text{C}$ ).

The differences between the  $\delta$ -values of the anthracene and d-anthracene molecules are smaller than it would follow from the consideration of the change in the moments of inertia only, as there is a simultaneous change in the frequencies  $\omega_U$  and  $\omega_W$  and in the moments

of torsions  $M_U$  and  $M_W$ . The influence of the temperature of the solution on the frequency of torsional vibrations and moments of torsions  $M$  is less distinct in the temperature interval  $-80^\circ$ – $20^\circ\text{C}$  than for the higher temperature interval ( $20^\circ\text{C}$ – $100^\circ\text{C}$ ) which has been investigated by Heldt (1966), however, as the temperature decreases the values of  $M$  still increase. According to Rousset (1945) the frequencies of torsional vibrations of anthracene molecules in a crystal are:  $\omega_U = 12.8 \times 10^{12} \text{ s}^{-1}$  and  $\omega_W = 9 \times 10^{12} \text{ s}^{-1}$ , *i. e.* greater than the corresponding values in glycerol solutions. As it should be expected the moments of torsions acting on anthracene molecule are smaller in solution than in a crystal. The comparison of the estimated parameters of torsional vibrations of anthracene and d-anthracene molecules in glycerol solution with the results of Heldt (1966) obtained for acryflavine molecules in the same solution indicates that the depolarization by torsional vibrations (at  $20^\circ\text{C}$ ) of anthracene and d-anthracene molecules is comparable with that of acryflavine molecules in spite of much smaller moments of inertia of these molecules.

Summarizing the results of measurements of the decay times and the limiting EA as well as of torsional parameters estimates it can be concluded that after the elimination of thermal rotations, concentration depolarization and depolarization by "initial shock", the only factor leading to depolarization of fluorescence in anthracene and d-anthracene solutions is torsional vibration.

### V. Conclusions

The results of measurements of EA of fluorescence of anthracene solutions known so far (ranging from 0.2 to 0.26) indicate that strong depolarization of fluorescent light occurs in this process. This depolarization was explained by various authors either by long fluorescence decay times making difficult complete elimination of Brownian rotations, or by the existence of two electronic levels near each other and perpendicular directions of transition moments connected with the absorption from the ground state. If such electronic levels exist then negatively polarized fluorescence should be observed by excitation of the lower level indirectly through the higher one. The present measurements have shown that: 1. the mean decay time of fluorescence of anthracene solutions is very short, 2. the limiting EA of this fluorescence is 0.38. This indicates that the measurements made hitherto were subject to systematic errors. The maximum value of pseudo-fundamental EA (0.374) is mostly due to fluorescence emission from the directly excited lower level (fundamental EA equal to 0.4) and perhaps partly from indirectly excited lower electronic level (fundamental EA equal to  $-0.2$ ). However it is more probable that the depolarization of fluorescence of the directly excited level occurs solely under the influence of torsional vibrations. This however cannot be definitely decided on the basis of the results of the present paper. However, on the assumption that torsional vibrations are the only depolarizing factor their parameters such as the amplitude, the frequency and the moment of torsion, have been calculated. According to the predictions the amplitude of torsional vibrations of d-anthracene molecules is smaller than that of anthracene molecules whose moments of inertia are smaller than the moments of inertia of the d-anthracene molecule. Moreover, the moment of torsion of a molecule in solution is smaller, as expected, than in a crystal.

The parameters of torsional vibrations of anthracene and d-anthracene molecules are comparable with parameters of torsional vibrations of other luminescent molecules whose fundamental EA of fluorescence equals 0.4 and the moments of inertia are much higher than those of anthracene and d-anthracene. This enables the conclusion to be drawn that the fluorescence emission of anthracene and d-anthracene solutions occurs practically solely from the directly excited electronic level  $L_a$ .

The author is much indebted to Professor A. Jabłoński for help, valuable advice and his kind interest in this work. He is also indebted to Dr H. Grudziński for kind help in measurements of the fluorescence decay times.

## REFERENCES

- Birks, J. B., *Proc. Phys. Soc.*, **80**, 355 (1962).  
 Bauer, R., Rozwadowski, M., *Optik*, **18**, 37 (1961).  
 Bauer, R., Rozwadowski, M., *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys.*, **7**, 365 (1959).  
 Bauer R., *Z. Naturforsch.*, **18a**, 6 (1963).  
 Bauer, R., *Acta Phys. Polon.*, **33**, 121 (1968).  
 Bauer, R., Grudziński, H., Jabłoński, A., Lisicki, E., *Acta Phys. Polon.*, **33**, 301 (1968).  
 Charkravarti, D. C., Ganguly, S. C., *Trans. Faraday Soc.*, **37**, 562 (1941).  
 Chandross, E. A., *J. Chem. Phys.*, **45**, 3546 (1966).  
 Förster, Th., *Fluoreszenz Organischer Verbindungen*, Stuttgart 1951.  
 Frenkel, J., *Kinetic Theory of Liquids*, Oxford 1946.  
 Grzywacz, J., *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys.*, **6**, 705 (1958).  
 Heldt, J., *Acta Phys. Polon.*, **30**, 3 (1966).  
 Jabłoński, A., *Z. Phys.*, **96**, 236 (1935).  
 Jabłoński, A., *Z. Phys.*, **95**, 53 (1935a).  
 Jabłoński, A., *Acta Phys., Polon.* **10**, 259 (1950).  
 Jabłoński, A., *Acta Phys. Polon.*, **14**, 295 (1955).  
 Jabłoński, A., *Acta Phys. Polon.*, **17**, 471 (1958).  
 Jabłoński, A., *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys.*, **7**, 655 (1959).  
 Jabłoński, A., *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys.*, **8**, 259 (1960).  
 Jabłoński, A., *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys.*, **9**, 655 (1961).  
 Jabłoński, A., *Z. Naturforsch.*, **16a**, 1 (1961).  
 Jabłoński, A., *Acta Phys. Polon.*, **26**, 427 (1964).  
 Jabłoński, *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys.*, **16**, 601 (1968).  
 Kawski, A., *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys.*, **6**, 533 (1958).  
 Klevens, H. B., Platt, J. R., *J. Chem. Phys.*, **17**, 470 (1949).  
 Lisicki, E., *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys.*, **11**, 655 (1963).  
 Mann, D. E., Platt, J. R., *J. Chem. Phys.*, **17**, 481 (1949).  
 Ore, A., *J. Chem. Phys.*, **31**, 442 (1959).  
 Perrin, F., *J. Phys.*, **7**, 390 (1926).  
 Perrin, F., *Ann. Phys. (France)*, **12**, 169 (1929).  
 Perrin, F., *J. Phys. Radium*, **7**, 1 (1936).  
 Platt, J. R., *J. Chem. Phys.*, **17**, 484 (1949).  
 Rousset, A., *Ann. Phys. (France)*, **20**, 53 (1945).  
 Spektorov, A. L., *Dokl. Akad. Nauk SSSR*, **65**, 485 (1949).  
 Samoylov, O., *Structure of Solutions of Electrolytes in Water and Hydration of Ions*, Akad. Nauk. SSSR 1957.  
 Zimmermann, H., Joop, N., *Z. Elektrochem.*, **64**, 1215 (1960).