PHYSICS

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1957

SovietRxiv

Abstract

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PHYSICS

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ON THE QUESTION OF DETERMINING THE VOLUMES OF MOLECULES IN SOLUTIONS BY THE METHOD OF POLARIZED LUMINESCENCE

(Presented by Academician A. N. Terenin, 28 XI 1956)

S. I. Vavilov (^{1}) pointed out the possibility of studying questions connected with the nature of the liquid state by means of the luminescence of solutions. One such method is the investigation of the limiting polarization of fluorescence. The fluorescence of solutions is polarized only under anisotropic excitation. The degree of polarization p is determined by the lifetime of the excited state of the molecule τ and by the angle through which the molecule turns during this time interval as a result of Brownian rotation, which, in turn, depends on the temperature T and the viscosity η of the medium and on the effective volume of the molecule V. Quantitatively this dependence is expressed by the well-known Levshin–Perrin formula:

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3}\right)\frac{RT}{V\eta}\tau. \tag{1}$$

Here p_0 is the limiting polarization of fluorescence, corresponding to the case $T/\eta \to 0$ (i.e., to the absence of Brownian rotation). This quantity is obtained by extrapolating the linear dependence of $1/p$ on T/η.

Formula (1) is a consequence of applying hydrodynamics and the theory of Brownian rotation to an individual molecule, with the molecule being considered as a hard sphere; η is the coefficient of macroscopic viscosity of the medium. If the motion of an individual molecule is under discussion, then one must use the molecular viscosity, or microviscosity. It cannot be stated in advance what the relation is between macroscopic and molecular viscosity. An important result of polarization measurements by a number of authors was the establishment that these quantities are of the same order. At the same time, as S. I. Vavilov writes, deviations from the hydrodynamic formulas may provide valuable material on the microstructure of liquids.

Formula (1) contains the effective volume of the molecule V. If, on the basis of the experimental data mentioned, one regards η as the macroviscosity and

Fig. 1. Limiting polarization of fluorescence of 9,10-diphenyldiaminoanthracene: 1 —in glycerin; 2 —in castor oil; 3 —in vaseline oil

Figure 1: Fig. 1. Limiting polarization of fluorescence of 9,10-diphenyldiaminoanthracene: 1 —in glycerin; 2 —in castor oil; 3 —in vaseline oil

uses the results of viscometric measurements, then these volumes can be determined. On the other hand, one can estimate the volumes of molecules from their structural formulas and known bond lengths and compare them with the values obtained from experiment.

It is also possible to carry out measurements of the polarization of fluorescence of the same fluorescing substance in different solvents. This makes it possible to draw conclusions about the presence and nature of solvation shells, by which is meant a monomolecular layer of solvent surrounding the molecule of the dissolved substance and more or less firmly bound to it. The study of solvation shells is of interest for physical chemistry. In particular, as V. L. Levshin (2) notes, they may play an essential role also in questions of the luminescence of solutions, along with

with phenomena of molecular association and other physicochemical factors.

Measurement of the polarization of fluorescence in the present work was carried out with a Kavraiskii polariscope (3) with a compensating stack. This polariscope has a number of advantages in comparison with Savart' s polariscope and has already been used for studying the polarization of luminescence (4).

The measurements were carried out in a comparatively small temperature interval, 20—60° (at higher temperatures the phenomena are sometimes complicated by temperature quenching). In this interval the linearity of $1/p\,(T/\eta)$ was well obeyed. The viscosity of the solvents at different temperatures was measured by the usual viscometric method—by the rate of flow through a capillary. Constancy of the required temperatures was maintained by an ultrathermostat. The fluorescence lifetime τ was measured on a phase fluorometer*.

Fig. 1. Limiting polarization of fluorescence of 9,10-diphenyldiaminoanthracene: 1 —in glycerin; 2 —in castor oil; 3 —in vaseline oil

As solvents (which must be sufficiently viscous), in the given temperature interval it proved possible to use only glycerin, castor oil, and vaseline oil. The intrinsic luminescence of twice-purified glycerin is negligible; the stronger luminescence of the oils could be separated rather reliably by filters from the yellow-green luminescence of the substances under investigation. The concentration of the solutions was 10^{-4}—10^{-5} g/cm^3. Three groups of fluorescing organic substances were investigated: phthalimides, acridine derivatives, and arylamino derivatives of anthracene—a total of 9 substances.

Graphs of the dependence of $1/p$ on T/η for one of the substances are shown as an example in Figs. 1 and 2. The data obtained are summarized in Table 1. The effective volumes V were calculated from formula (1), and from them the molecular radii r were found (assuming a spherical model of the molecule).

If the mean molecular radii r' are calculated from the known bond lengths and the structural formula, the following approximate estimate is obtained:

Substances	Phthalimides	Acridines	Anthracenes
r', Å	2	3	5

In the same way one can estimate the sizes of the solvent molecules. The glycerin molecule may also be roughly considered spherical; its diameter is $d \simeq 3$ Å. The molecule of the triglyceride of ricinoleic acid, which makes up 86% of castor oil, is very elongated in one direction, and it is more correct to regard it as an ellipsoid of revolution, for which the minor axis is equal to the diameter of the glycerin molecule, while the major axis is 8 times longer.

Considering the results presented in Table 1, one may note an increase in the effective volumes of molecules of different classes with increasing complexity of structure, which can be traced in glycerin solutions (80–190 Å^3 for phthalimides, 280–570 Å^3 for acridines, and 2040–3700 Å^3 for anthracenes).

If one compares the experimental values of r with the calculated r'

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* The authors express their deep gratitude to M. D. Galanin for providing the opportunity to carry out measurements on the fluorometer.

Table 1

Summary table of results

Fluorescing substances	Solvents	p, %	$\tau \cdot 10^9$, sec.	v, Å^3	r, Å
3-aminophthalimide	Glycerin	40	11.5	190	3.6
3-aminophthalimide	Castor oil	41	10.5	350	4.4
3-dimethylamino-6-aminophthalimide	Glycerin	40	1.1	80	2.6

Fluorescing substances	Solvents	p, %	$\tau \cdot 10^9$, sec.	v, Å^3	r, Å
3-dimethylamino-6-aminophthalimide	Castor oil	33	3.2	170	3.5
Acridine orange	Glycerin	38	2.5	550	5.1
Acridine orange	Castor oil	36.5	3.9	990	6.2
2-aminoacridine	Glycerin	37	5.7	570	5.2
2-aminoacridine	Castor oil	38	4.6	230	3.8
3-aminoacridine	Glycerin	38	6.6	310	4.2
3-aminoacridine	Castor oil	37	5	200	3.6
3,6-diaminoacridine	Glycerin	43.5	3.9	280	4.1
3,6-diaminoacridine	Castor oil	40	6	765	5.7
9,10-diphenyldiaminoanthracene	Glycerin	35	6.7	3700	9.6
9,10-diphenyldiaminoanthracene	Castor oil	41	2.7	165	3.4
9,10-diphenyldiaminoanthracene	Vaseline oil	39	4.4	790	5.8
9,10-dimetachlorophenyldiaminoanthracene	Glycerin	38	8.3	2040	7.9
9,10-dimetachlorophenyldiaminoanthracene	Castor oil	42	4.2	420	4.6
9,10-dimetachlorophenyldiaminoanthracene	Vaseline oil	32	4.6	1000	6.2
9,10-diorthomethoxyphenyldiaminoanthracene	Castor oil	33	7.6	1080	6.3
9,10-diorthomethoxyphenyldiaminoanthracene	Vaseline oil	39	5.5	960	6.1

and d, using the model of a monomolecular solvate shell ($r = r' + d$), then for glycerol solutions we see agreement in order of magnitude for acridines and anthracenes; for phthalimides, however, experiment gives a smaller value than follows from the calculation. For castor oil this model does not correspond to reality at all, since r in this case is of the same order, and in a number of cases considerably smaller, than in glycerol, whereas in accordance with the indicated model it should be considerably larger. Vaseline oil, in which only anthracenes dissolve, judging from the results obtained, has a small solvating effect.

Thus, the experimental results obtained cannot be interpreted unambiguously from the standpoint of ideas about solvate shells. However, there is another possibility for interpreting the results—from the standpoint of the difference between macroscopic and molecular viscosities. Earlier experiments with a single solvent testified only to agreement in their orders of magnitude. The comparison carried out for different solvents possibly indicates that it is improper to use, in formula (1), values of the macroscopic viscosity. The physical nature of the phenomenon (which may formally be described both as a change in effective volume and as a difference between macroscopic and molecular viscosities) consists in the interaction of the molecular fields of the solvent and the solute.

In this connection it is of interest to compare the magnitudes of the effective volumes with the values of the dipole moments of the molecules of the solute and the solvent. Analysis of the experimental data shows that there is no parallelism between these quantities. For example, the dipole moment of the triglyceride of ricinoleic acid is apparently greater than that of glycerol, if one proceeds from the additivity of bonds in these molecules and the known dipole moments of individual bonds ([5,6]), while the solvating action of castor oil is substantially less than that of glycerol.

Among the acridines, 2-aminoacridine and 3-aminoacridine have larger moments than 3,6-diaminoacridine and acridine orange, and the former correspond to a smaller solvating action of castor oil than the latter. At the same time, among the phthalimides, the smaller solvating action of this same solvent corresponds to 3-dimethylamino-6-aminophthalimide, whose dipole moment is smaller than that of 3-aminophthalimide.

It should also be noted that the limiting degree of polarization of the fluorescence of one and the same substance in different solvents is found to be different, although these differences are small. This can be explained only by the influence of the solvent on the electronic cloud of the molecule, which leads to some change in the oscillator of the radiation.

In order that the indicated phenomena might be studied in greater detail by the proposed method, it would be desirable to use a homologous series of solvents, for example various alcohols at low temperature.

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Received
23 XI 1956

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Note: Figure translations are in progress. See original paper for figures.