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Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Abstract

Full Text

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ON THE PROPORTIONAL SENSITIVITY OF THE ABSORPTION SPECTRA OF MEROCYANINES TO THE ACTION OF SOLVENTS

(Presented by Academician B. A. Kazanskii, 17 VIII 1961)

In recent years, an increasing number of works have appeared in which the authors seek to analyze the action of a solvent on a spectrum, taking into account not only the direction but also the magnitude of the solvatochromic shift ([1–9]). We shall consider the application of one of the methods of quantitative comparison of experimental data, which consists in the following. In studying the solvatochromism of any two substances, for example Ia and Ib, the values of $\nu_{\max}$ of substance Ia in various solvents are plotted along the abscissa, and the values of $\nu_{\max}$ of substance Ib in the same solvents are plotted along the ordinate* (see Fig. 1). We shall mark by a point the intersection of the abscissa and ordinate belonging to one and the same solvent. Then, in rectangular coordinates, we obtain a series of points, each of which characterizes a definite solvent. These points may be scattered over the entire plane; they may lie on a smooth curve; they may lie on a straight line. The last case, according to the terminology we propose, means that substances Ia and Ib possess proportional sensitivity to the action of solvents.

Fig. 1. Proportional sensitivity to solvents of 2-(*n*-dimethylaminobenzylidene)-3-keto-2,3-dihydrothionaphthene Ia and 2-(*n*-dimethylaminobenzylidene)-5-nitro-3-keto-2,3-dihydrothionaphthene Ib (*A*); substances Ia and 2-(*n*-dimethylaminobenzylidene)-6-nitro-3-keto-2,3-dihydrothionaphthene Iv (*B*).

Fig. 2. Proportional sensitivity to solvents of substance Ia and 2-(*n*-dimethylaminophenylimino)-5-nitro-3-keto-2,3-dihydrothionaphthene IIb (*B*); substances Ia and 2-(dimethylaminophenylimino)-6-nitro-3-keto-2,3-dihydrothionaphthene IIv (Γ).

Cases of proportional sensitivity have already been described in the literature and served as material for the creation of a "universal"scale (or series) of solvents

([3,5]). The position of a solvent in the scale is determined by the magnitude

* ν_{max} denotes the wave number of the maximum of the absorption band.

Table 1

ν_{max} (cm^{-1}) of the long-wavelength absorption band of substances Ia–IIb in various solvents

No.	Solvent	Ia	Ib	Iv	IIa	IIb	IIv
1	*n*-Hexane	21690	20750	20160	21060	20040	18730
2	*n*-Octane	21600	20580	20000	20970	19800	18480
3	Cyclohexane	21500	20490	19920	20880	19730	18350
4	Ether	21370	20410	19350	20580	19490	18520
5	Carbon tetrachloride	21140	20240	19420	20410	19270	18050
6	Dioxane	21100	20280	19080	20330	19380	18320
7	*p*-Xylene	21060	20240	19080	20290	19310	18120
8	Benzene	20920	20080	18900	20000		
9	Ethyl acetate	21100	20200	19050	20200	19200	18210
10	Acetone	20880	20000	18840	19880	18940	18020
11	Acetonitrile	20830	19960	18770	19840	18800	17860
12	Chlorobenzene	20620	19760	18520	19690	18660	17610
13	Dimethylformamide	20620	19690	18450	19570	18620	17640
14	Dimethylaniline	20490	19690	18480	19530	18690	17640
15	Ethyl alcohol	20490			19230		
16	Methyl alcohol	20450	19690	18350	19310	18410	17540
17	Pyridine	20330	19530	18280	19460	18410	17450
18	Isoamyl alcohol	20370	19840	18380	19420	18350	17450
19	Propyl alcohol	20330			19380		
20	Nitrobenzene	20330	19310	18050	19230	18120	17120
21	Quinoline	20200	19350	18050	19200	18180	17150

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

No.	Solvent	Ia	Ib	Iv	IIa	IIb	IIv
22	Formamid	19920	19040	17670	18700	17760	16850
23	Aniline	19800	19080	17640	18620	17890	16710
24	Water	19570			18770		

the shift ν_{max} of the standard substance caused by it. The magnitude of the shift, as is known, is in turn determined by several properties of the solvent, each of which makes its own contribution to the displacement of ν_{max}.* Separately, these properties are not taken into account when constructing a "universal" scale: they appear implicitly and in aggregate form, and with those "specific weights" that are characteristic of the displacement of ν_{max} of the standard substance. For dissolved substances that differ strongly from the standard, other properties of the solvent may prove more important, and the scale will be inapplicable.

Chemical structures shown:

(I) with substituents:

(a) $R_1 = H;\ R_2 = H;$

(b) $R_1 = NO_2;\ R_2 = H;$

(c) $R_1 = H;\ R_2 = NO_2$

(II)
(III)
(IV)
(V)
(VI)

We measured the absorption spectra of substances having the general formulas I (a, b, c) and II (a, b, c) in various solvents (see Table 1). If one compares

* See (7); it is possible that some of the properties have not yet been sufficiently identified and studied.

plotting the ν_{max} of any one of these substances against the quantity S* or against the quantity Z**, no clear rectilinear dependence is found. If, however, one of our merocyanines is taken as the standard substance (we took substance Ia) and its ν_{max} in various solvents is plotted on the abscissa, while the corresponding ν_{max} values of another merocyanine (Ib, Iv, IIa, IIb, or IIv) are plotted on the ordinate, a satisfactory rectilinear dependence is obtained (see Figs. 1-3).

Fig. 3. Proportional sensitivity to solvents of substances Ia and 2-(*p*-dimethylaminophenylimino)-3-keto-2,3-dihydrothionaphthene (A); substances Ia and the base of 3-ethylbenzthiazole-(2)-3-keto-2,3-dihydrothionaphthene-(2)-dimethinecyanine (III) (B); substances Ia and the base of 3-ethylbenzthiazole-(2)-2-methylindole-(3)-dimethinecyanine (IV) (C).

Fig. 4. Proportional sensitivity to solvents of substances V and VI. On the abscissa are plotted the values for substance V.

Using literature data on the solvatochromism of merocyanines III and IV ([10]), we showed that a linear dependence is also observed between the ν_{max} values of these substances and the ν_{max} of substance Ia (Fig. 3). Probably many, if not all, merocyanines that exhibit positive solvatochromism are proportionally sensitive among themselves. Conversely, merocyanines with negative solvatochromism (for example V and VI ([11])) do not belong to this group and do not exhibit a sensitivity proportional to Ia. On the other hand, V and VI are "proportionally sensitive" to one another (Fig. 4)***.

Thus, the absence of a rectilinear relationship between the ν_{max} of our substances and the quantity S (or Z) is not a consequence of any experimental errors, just as the presence of proportional sensitivity to the action of solvents in merocyanines I and II is not a consequence of mutual compensation of these errors.

The creation of "universal" solvent scales is a necessary and useful stage in the study of solvatochromism; however, it narrows the field of application of the method of proportional sensitivity and gives an incorrect picture of the prospects for the development of this method. It is not sufficient to compare the observed shift of ν_{max} of the substance under study only with the conditional number S or Z, i.e., with the masked shift of ν_{max} of the standard substance. If expected
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* S is a number characterizing the position of a solvent on Zelinsky' s scale (standard substance: amino-*N*-methylphthalimide) ([3]).

** Z is a number characterizing the position of a solvent on Kosower' s scale (standard substance: carbomethoxypyridinium iodide) ([5]).

*** Published data on the spectra of azamerocyanines ([12]) are sufficient only to conclude that investigation of the sensitivity of these substances to a broader series of solvents could give very interesting results.

if the given linear dependence is not observed, it is necessary to investigate whether the substance under study has proportional sensitivity with respect to substances related to it. As can be seen, by using as a criterion the presence (or absence) of proportional sensitivity in various substances, one can distinguish groups of substances that respond in the same way to solvents. It is possible that, when comparing substances belonging to one such group, it will be possible to deepen our understanding of the electronic structure of the systems responsible for light absorption, and of the mechanism of their interaction with solvents of different types. The tangent of the slope angle of the straight line apparently

characterizes the relative polarizability of the molecules of the substances being compared, which is also not without interest. Cases are possible in which the points for one or two solvents deviate sharply from the existing straight line of proportional sensitivity. Such cases deserve special attention, since they may shed light on the mechanism of interaction of the "deviating" solvent with the dissolved substances being compared.

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