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## Abstract

## Full Text

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# Measurement of Spectra in Mixed Solvents Based on Alkanes as a Method for Studying the Interaction of a Substance with a Solvent

*(Presented by Academician B. A. Kazanskii, March 21, 1961)*

### Chemistry

Studies (1–6) and others have led to the conclusion that solvatochromic* shifts of spectra are caused by two types of interaction of the dissolved substance with the solvent: universal interaction (collective) and specific (individual) interaction (66). There has been no experimental method that would make it possible to evaluate which of these effects is predominant in a particular case.

The absence of an isosbestic point for spectra in pyridine, water, and their mixtures (7–9) led to the conclusion that, in solution, under the influence of the medium, gradual changes in mesostructure occur, "and these changes may give an infinite number of intermediate forms" (8). The use of pyridine-water mixtures is not very suitable for resolving the question of the nature of the interaction of each of these solvents with the dissolved substance: 1) both solvents—pyridine and water—can exhibit not only universal but also specific interaction; 2) the picture may be complicated by the formation in solution of a hydrate $[C_5H_5N\ldots HOH] \rightleftarrows [C_5H_5N]^+OH^-$ (11).

Spectra with fine vibrational structure, closest to the absorption spectrum of vapors, are obtained when the substance is dissolved in hexane. Alkanes are, in a certain sense, a standard solvent exhibiting only universal interaction with the dissolved substance, and in the simplest form. On this basis, we propose, for the study of solvatochromic changes in spectra, a spectroscopic method in mixed solvents based on alkanes. By diluting dye solutions in various solvents with *n*-hexane, one can trace how the solvatochromic effect is "born" in each individual case. So far, three types of spectral changes have been found.

We applied the proposed method to the study of the solvatochromism of 2-(*n*-dimethylaminobenzylidene)-3-keto-2,3-dihydrothionaphthene (Ia), whose mesostructure is determined by an electronic shift toward structure (Ib): (Ia) ~ (Ib)**.

(Ia) (Ib)

**First type of spectral change: gradual displacement of the curve.** In

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

quinoline-hexane mixtures, as the composition of the mixed solvent changes, the form of the spectral curve substantially changes only to the left of the maximum. With an increase in the content (molecular percent) of hexane in the mixture, the curve shifts toward shorter wavelengths, and a secondary maximum gradually appears on it (Fig. 1). The same type of spectral change was observed for benzene-hexane, chlorobenzene-hexane mixtures and, apparently, for other solvents that enter into interactions with (I) predominantly of the universal type.

**Fig. 1.** Absorption spectra of solutions (I) in quinoline-hexane mixtures of different composition: **1**—100% quinoline, **2**—62.7 mol.% quinoline, **3**—36.8 mol.% quinoline, **4**—28.2 mol.% quinoline, **6**—5.7 mol.% quinoline

**Fig. 2.** Absorption spectra of solutions (I) in alcohol-hexane mixtures of different composition: **a**—100% alcohol, **1**—84 mol.% alcohol, **2**—59.7 mol.% alcohol, **3**—36 mol.% alcohol, **4**—19.9 mol.% alcohol, **5**—10.6 mol.% alcohol, **6**—100% *n*-hexane

**The second type of spectral change: the appearance of a new absorption band.** The absorption maximum of substance (I) in alcohol (99.5%) (Fig. 2, *a*) is a new maximum, and not a shifted first or second maximum observed in hexane (Fig. 2, *b*). Starting from a certain composition of the alcohol-hexane solvent (84 mol.% alcohol and lower), all spectral curves (Fig. 2, 1—6) intersect at a single isosbestic point. The type of spectral change described here is also observed for solutions of (I) in mixtures of hexane with methanol or with acetic acid, i.e., solvents capable of entering into strong specific interaction with (I).

Usually the existence of an isosbestic point is considered indirect evidence for the presence in solution of an equilibrium between two substances or two forms

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* The meaning of the term *solvatochromism* should be somewhat broadened, understanding by it the change in the form of the spectral curve, and in the position and intensities of maxima, as a result of the influence of solvents, without restricting it to the visible part of the spectrum (just as is now accepted for the term *chromophore*).

** The symbol $\sim$ indicates a lowering of the energy of the molecule as a result of conjugation (mesomerism) in comparison with energy values calculated on the basis of possible limiting ( “extreme” ) structural formulas (13).

of one and the same substance. We have previously shown that (I) is capable of existing in two isomeric forms, $A$ and $B$ ($^{12}$). However, the reason for the presence of the isosbestic point in Fig. 2 cannot be equilibrium between forms $A$ and $B$ of substance (I): 1) the isosbestic point of the latter equilibrium, which appears upon irradiation of the solution, is very indistinct in alcohol, lies at 512 mμ, and shifts depending on the composition of the mixed solvent; 2) we carried out all the experimental work on solvatochromism in the dark, with the pure form $A$, whereas the transformation of form $A$ into form $B$, according to our observations, occurs only in the light.

**Comparison of calculated* and found optical densities of solutions**

| Curve No.** | Mol.% alcohol in mixture | $C_s$* | $C_n$* | $D$*** 410 mμ, calc. | $D$*** 410 mμ, found | $D$ 420 mμ, calc. | $D$ 420 mμ, found | $D$ 430 mμ, calc. | $D$ 430 mμ, found | $D$ 440 mμ, calc. | $D$ 440 mμ, found | $D$ 450 mμ, calc. | $D$ 450 mμ, found | $D$ 460 mμ, calc. | $D$ 460 mμ, found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 84 | 1 | 0 | – | 0.13 | – | 0.16 | – | 0.23 | – | 0.35 | – | 0.48 | – | 0.61 |
| 2 | 59.7 | 0.92 | 0.08 | 0.14 | 0.13 | 0.17 | 0.17 | 0.27 | 0.27 | 0.37 | 0.38 | 0.50 | 0.50 | 0.64 | 0.64 |
| 3 | 36 | 0.785 | 0.215 | 0.16 | 0.14 | 0.20 | 0.21 | 0.32 | 0.32 | 0.40 | 0.43 | 0.52 | 0.55 | 0.69 | 0.69 |
| 4 | 19.9 | 0.631 | 0.369 | 0.17 | 0.17 | 0.23 | 0.25 | 0.37 | 0.39 | 0.44 | 0.48 | 0.55 | 0.60 | 0.74 | 0.75 |
| 5 | 10.6 | 0.463 | 0.537 | 0.19 | 0.18 | 0.25 | 0.28 | 0.43 | 0.45 | 0.48 | 0.52 | 0.59 | 0.64 | 0.80 | 0.80 |
| 6 | 0 | 0 | 1 | – | 0.24 | – | 0.34 | – | 0.59 | – | 0.59 | – | 0.68 | – | 0.97 |

* For the initial assumptions and the course of the calculation, see the text of the article; $C_s$—concentration of the solvate in the sol[ution]

** Curve numbers, see Fig. 2.

*** Found from the corresponding curve and calculated by (d).

Thus, we had grounds to suppose that the isosbestic point in Fig. 2 at 468 m$\mu$ corresponds to an equilibrium between the alcohol-dye solvate of a definite composition (for example, II) (henceforth we shall call it simply the "solvate") and the nonsolvated dye.

[Structural formulas]

(II) (III)

Assuming that curve 1 (Fig. 2) is the spectrum of the solvate, and also that the spectrum of the nonsolvated dye molecules in the mixed solvent is the same as in pure hexane (Fig. 2,6), we attempted to find, by calculation, the intermediate curves 2-5 (Fig. 2). For each of these curves (for definiteness, below we shall

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refer to curve 4 and the corresponding solution 4), the following equalities are valid:

$$C_s = (D_{490}/D^0_{490})\, C_{\text{tot}}; \tag*{( )}$$

$$C_n = C_{\text{tot}} - C_s \quad \text{or} \quad C_n = C_{\text{tot}} - D_{490}/D^0_{4(90)}\, C_{\text{tot}} \tag*{( )}$$

$$D_{\text{tot}} = \varepsilon_n C_n l + \varepsilon_s C_s l, \tag*{( )}$$

$$\varepsilon_n = D^0_n/(C_{\text{tot}} l); \qquad \varepsilon_s = D^0_s/(C_{\text{tot}} l), \tag*{( )}$$

where $D_{490}$ is the optical density according to curve 4 at 490 m$\mu$; $D^0_{490}$ is the optical density at 490 m$\mu$ according to curve 1; $C_{\text{tot}}$ is the total (overall) concentration of dye in the solution; $C_n$ is the concentration of nonsolvated dye in solution $4_{\text{B}}$, $C_s$ is the concentration of solvate in solution 4, $D_{\text{tot}}$ is the optical density according to curve 4; $\varepsilon_n$ and $\varepsilon_s$ are the molecular extinction coefficients, respectively, of the nonsolvated dye and of the solvate; $l$ is the thickness of the solution layer; $D^0_n$ is the optical density according to curve 6; $D^0_s$ is the optical density according to curve 1.

Equality (a) is valid because the dye dissolved in pure hexane does not absorb light at 490 m$\mu$. Equalities (b) hold because

**Table 1**

substance I in a mixed alcohol-hexane solvent of various compositions

| $D_{\text{tot}}$ 470 mμ calc. | $D_{\text{tot}}$ 470 mμ found | $D_{\text{tot}}$ 480 mμ calc. | $D_{\text{tot}}$ 480 mμ found | $D_{\text{tot}}$ 490 mμ calc. | $D_{\text{tot}}$ 490 mμ found | $D_{\text{tot}}$ 500 mμ calc. | $D_{\text{tot}}$ 500 mμ found | $D_{\text{tot}}$ 510 mμ calc. | $D_{\text{tot}}$ 510 mμ found | $D_{\text{tot}}$ 520 mμ calc. | $D_{\text{tot}}$ 520 mμ found | $D_{\text{tot}}$ 530 mμ calc. | $D_{\text{tot}}$ 530 mμ found | $D_{\text{tot}}$ 540 mμ calc. | $D_{\text{tot}}$ 540 mμ found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| – | 0.72 | – | 0.76 | – | 0.76 | – | 0.69 | – | 0.53 | – | 0.34 | – | 0.18 | – | 0.09 |
| 0.71 | 0.72 | 0.70 | 0.72 | – | 0.69 | 0.64 | 0.59 | 0.49 | 0.41 | 0.31 | 0.23 | 0.17 | 0.10 | 0.08 | 0.05 |
| 0.69 | 0.71 | 0.61 | 0.65 | – | 0.58 | 0.54 | 0.44 | 0.41 | 0.26 | 0.26 | 0.13 | 0.14 | 0.06 | 0.07 | 0.02 |
| 0.65 | 0.70 | 0.50 | 0.56 | – | 0.46 | 0.43 | 0.30 | 0.33 | 0.16 | 0.21 | 0.07 | 0.12 | 0.02 | [[unclear]] | [[unclear]] |
| 0.62 | 0.66 | 0.39 | [[unclear: value ending in 6]] | – | 0.33 | 0.32 | 0.19 | 0.24 | 0.09 | 0.16 | 0.04 | – | – | – | – |
| – | 0.539 | – | 0.071 | – | 0 | – | 0 | – | 0 | – | 0 | – | 0 | – | 0 |

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$C_s$ –concentration of solvate in solution, calculated according to (a); $C_n$ – concentration of dye not solvated by alcohol (calculated according to (b)).

for all solutions whose spectra are compared in Fig. 2, the total dye concentration was constant. Equality (c) follows from the assumption that there are only two types of absorbing particles in the solution: the nonsolvated dye molecule and the solvate of definite composition. Equalities (d) follow from our initial assumption.

Equality (c), after the necessary transformations, takes the form:

$$D_{\text{obs}} = D^0_{\text{n}}\,(1-(D_{490}/D^0_{490})) + D^0_{\text{s}}(D_{490}/D^0_{490}); \qquad \text{(d)}$$

The values of $D_{\text{obs}}$, calculated from equality (d) and found directly from curve 4, agree satisfactorily in the wavelength range 410-480 m$\mu$ (see Table 1). At wavelengths greater than 490 m$\mu$ the calculated and found values differ strongly. Thus, the assumption that in a solution of substance (I) there is an equilibrium of an individual solvate (dye–alcohol) of definite composition and nonsolvated dye does not exhaust the full complexity of the situation that actually takes place.

**Fig. 3.** Absorption spectra of solutions of (II) in benzene–hexane mixtures of different composition: 1–100% benzene, 2–77.4 mole % benzene, 3–59.5 mole % benzene, 4–38.6 mole % benzene, 5–14.1 mole % benzene, 6–100% hexane.

**The third type of spectral change:** $\lambda_{\text{max}}$ does not shift; the secondary maximum becomes the most intense. This type of spectral change was observed by us for 2-benzylidene-3-keto-2,3-dihydrothionaphthene (III).

If one approaches the matter formally and compares the $\lambda$' s of the most intense maxima, then the solvatochromic shift of the maximum on going from hexane to benzene is 14 m$\mu$ (compare 6, 1, Fig. 3). However, when the absorption spectra were measured in mixed benzene–hexane (Fig. 3) or alcohol–hexane solvents, it became clear that the more intense maximum becomes secondary, while the secondary one increases and becomes the most intense. The true solvatochromic effect consists not in a shift of $\lambda_{\text{max}}$, but in a characteristic change of the spectral curve.

The method of spectroscopy in mixed solvents based on alkanes makes it possible, more finely than other known methods, to differentiate and classify the action of the solvent on the spectrum of the dissolved substance. It may be hoped that in a number of cases the method will be useful for detecting specific interaction of the solvent with the dissolved substance.

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

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