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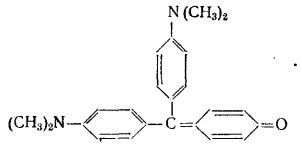
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INFLUENCE OF THE SOLVENT ON THE COLOUR OF DYES (SOLVATOCHROMISM)

A. I. Kiprianov

The colour of organic dyes always depends to a certain extent on the solvent. Acid and alkaline solvents change the colour of dyes by forming salts with them, but in most cases neutral solvents have little influence on the absorption of light by the dyestuff. There exists, however, a certain number of dyestuffs (or coloured substances) which change colour very markedly on passing from one completely neutral solvent to another. This has received the name "solvatochromism".

A classic example of solvatochromism is that exhibited by tetramethyldiaminofuchsone (I), prepared by Schlenk in 1909[1]:



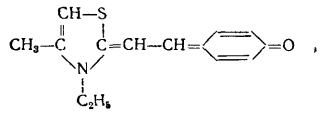
(I)

This dyestuff is yellow in benzene solution and red-violet in alcohol. Schlenk considered the change of colour as due to a change of molecular weight; the fuchsone giving a true solution in alcohol, but polymers being formed in benzene and the dyestuff dissolving as a colloid. This explanation of the solvatochromic effect in tetramethyldiaminofuchsone, as in other dyes, has since been shown to be false[2]; they dissolve, in organic solvents at least, to form monomolecular solutions.

Up to the 1940's, the solvatochromic effect was explained on the basis of the old views of the dyestuff molecule as one containing a stable system of valency bonds. Of various theories of this type by various workers[2,3,4], we shall consider only one – that of the formation of characteristically coloured complexes of the molecules with solvent molecules[2], since this type of theory is met even in later publications[5,6].

The attempt to explain solvatochromism in dyes by the formation of simple complexes with the solvent must be discarded mainly on the evidence of the study of the absorption spectra of such dyes in mixed solvents.

Kiprianov and Timoshenko[7] obtained the absorption curves of the dyestuff (II):



(II)

which shows a clear solvatochromic effect. These curves are shown in Fig. 1 (*A* in pyridine, *B* in water, and *C* in a

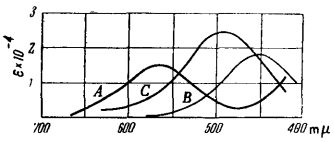


Fig. 1.

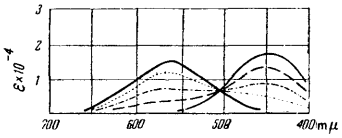
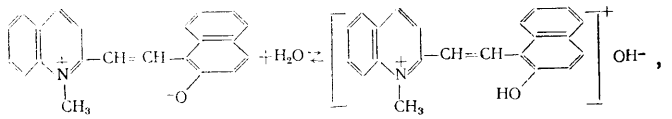


Fig. 2.

1 : 1 mixture of pyridine and water). The absorption maximum of (II) in pyridine lies at 580 mμ, and in water at 455 mμ. If the dyestuff were present in pyridine and in water as two different complexes, in the pyridine–water mixture two maxima would be observed, at the same wave-lengths as for the solution of (II) in pyridine and in water. In pyridine–water mixtures of varying composition, these curves would have a common point of intersection (the isobestic point), as shown in Fig. 2.

In actual fact, the primary maxima do not appear on the absorption curve of (II) in the 1 : 1 pyridine–water mixture (Fig. 1, *C*), but a new maximum is found at 495 mμ. Thus in the mixed solvent, (II) behaves not as an equimolar mixture of two different complexes, but as an individual substance of a new structure.

In 1940 Wizinger and Wenning[5] synthesised the dyestuff (III), which changed colour on adding water to its pyridine solution. This solvatochromic effect was explained as due to the reversible addition of a molecule of water, with the formation of the ionised hydroxide (IV):

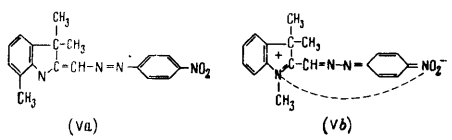


(III) (IV)

Brooker[8] showed that this explanation is incorrect. The absorption curve of the aqueous pyridine solution shows that it contains an individual substance, and not a mixture of the two compounds, the hydrated and the non-hydrated. The absorption spectrum of the cation of the hydroxide (IV) should be the same as that of the cation of the corresponding iodide, but in fact they are different.

It might be suggested that when they are formed, the complexes with solvent molecules of the dyestuffs showing the solvatochromic effect are solvates consisting of a large number of oriented solvent molecules; as the composition of the solvent changes gradually, the solvates are gradually converted into solvates of different composition. This raises the question why the formation of solvates should influence the colour of solutions of certain dyestuffs only, and not of them all. This is the more surprising since basic and acid dyes, which dissociate in solution into ions, do not exhibit the solvatochromic effect, although their ions are, of course, strongly solvated. It must be assumed that the reason for the solvatochromic effect lies not only in solvation, but also in the structural features of the molecules of those dyes for which the solvatochromic effect is observed. The structure of these dyes must be capable of gradual changes under the influence of changes in the medium, these changes providing an infinite number of intermediate forms.

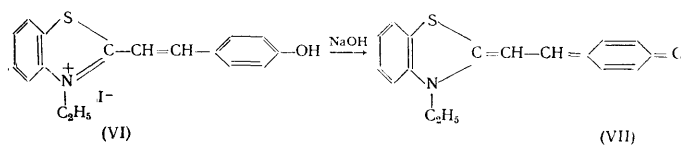
König came very close to such a viewpoint in 1924.[9] He observed a solvatochromic effect in a number of "endohalochromic" (in his terminology) azo-dyes of the type of (V):



(V*a*) (V*b*)

According to König, the structure (V*a*) is "at least equivalent" to the structure (V*b*), and between these two extreme states of the molecule, a number of intermediate states, which cannot be expressed in valency formulae, are possible.

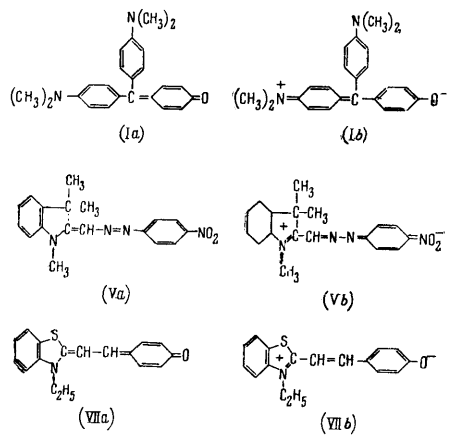
In 1940 Kiprianov and Petrun'kin[10,11] and later Kiprianov and Timoshenko[7,12,13] synthesised a series of yellow dyestuffs, the hydroxystyryl compounds of type (VI), and found that when they react with alkali, the anhydro bases (VII) are formed, these showing a clear solvatochromic effect:



(VI) (VII)

This effect is the opposite of that with tetramethyldiaminofuchsone. Whereas the absorption of the fuchsone shifts to shorter wave-lengths on passing from non-polar to polar solvents, the anhydro bases of the type (VII) react in the opposite sense to the polarity of the solvent.

The explanation of solvatochromism proposed in 1940 by Kiprianov and Petrun'kin is as follows. Attention was drawn to the fact that the solvatochromic effect is shown by dyestuffs of the so-called merocyanine * structure, that is to say, those for which two formulae may be written, one non-polar (*a*) and the other dipolar (*b*), for example:



(I*a*) (I*b*)

(V*a*) (V*b*)

(VII*a*) (VII*b*)

The actual molecular structure of each dyestuff which exhibits the solvatochromic effect is intermediate between the two formulae, and is determined by the polarising influence of the medium, the shortest absorption wave-length corresponding to that constitution of the merocyanine dyestuff at which the electrons in the conjugated chain are most evenly spread. It now becomes clear why two types of solvatochromism are observed: those merocyanine dyestuffs whose structure in the given solvent is nearer the non-polar form will absorb at a shorter wave-length on passing to a more polar solvent, since in polar solvents their molecule approaches the condition in which the electron density is most evenly distributed; those dyestuffs which have a structure approaching the dipolar form will, on the other hand, absorb at a shorter wave-length on passing to a less polar solvent.

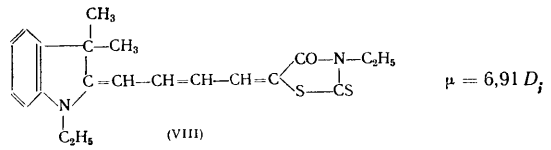
* In the original Russian the term intra-ionoid was used here and elsewhere in the review. It has been rendered as mexocyanine throughout (Ed. of Translation).

Kiprianov and Petrun'kin named the shift of absorption to shorter wave-lengths when the polarity of the solvent is decreased [as for the anhydro bases (VII)] the solvatochromism of the first type, and that when the polarity of the solvent is increased [as for the fuchsone (I)] solvatochromism of the second type. Brooker[14] later named the fuchsone type of effect normal solvatochromism, and the opposite effect reverse solvatochromism. Dimroth[15] uses the terms positive and negative solvatochromism respectively. We shall use Dimroth's terminology.

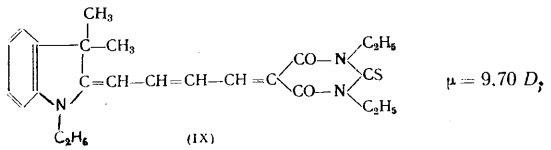
This elementary theory gives a good explanation of a number of other properties of merocyanine dyestuffs. It is known that they are adsorbed on polar adsorbents, changing their colour according to the type of solvatochromic effect they exhibit[16]. Merocyanine dyestuffs change their colour on heating the solution (thermochromism), the change again depending on the type of solvatochromic effect: with a positive effect the absorption wave-length is reduced, and with a negative effect it is increased on heating. This is due to the change in the polarising action of the solvent on increasing the temperature (loss of orientation of the solvating molecules).

The solvatochromic effect in merocyanines is observed in their fluorescence spectra as well as their absorption spectra; the change in the fluorescence spectra under the influence of the solvent has been studied mainly on simple merocyanine analogues, such as phthalimide and maleimide derivatives[17]. The relationship between the fluorescence spectra and the polarising power of the solvent is the same as for the absorption spectra.

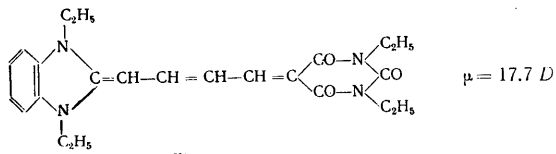
A direct confirmation of the above theories on the nature of the solvatochromic effect is given by Kushner and Smyth's determination in 1949 of the dipole moments of the merocyanine dyestuffs (VIII)–(X)[18]:



(VIII) $\mu = 6{,}91\ D$;



(IX) $\mu = 9.70\ D$;



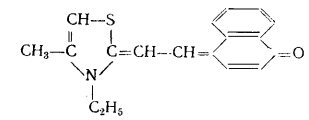
(X) $\mu = 17.7\ D$.

The calculations show that if the dyestuffs existed only in the non-polar form, their dipole moments would not exceed 2 *D*. In fact, the dipole moment of (X) (17.7 *D*) almost corresponds to that of the dipolar ion, while from its dipole moment (IX) (9.70 *D*) may be considered to be approximately half polarised. The merocyanine (VIII) shows a positive solvatochromic effect, the merocyanine (IX) suffers almost no change of colour on passing from polar to non-polar solvents, while (X) possesses a negative solvatochromic effect. The dipole moments of a number of other merocyanine dyestuffs have been determined, in relation to their solvatochromic effects, by Syrkin, Levkoev, and coworkers[19].

The above views on the nature of the solvatochromic effect in dyestuffs are now generally accepted. Almost at the same time as Kiprianov, they were proposed (without experimental confirmation) by Förster[20], and were later developed by Brooker and coworkers[8,21], Knott[22], Dimroth[15,23,24], and recently by Hünig[25,26].

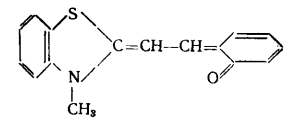
Hünig introduces the concept of the degree of solvatochromism, i.e. the amount by which the absorption maximum of various merocyanine dyestuffs is displaced on passing from one solvent to another, for example from methanol to chloroform. Brooker and coworkers[14] showed that the degree of solvatochromism of merocyanines increases as the polymethine chain increases in length.

As well as dyestuffs showing positive or negative solvatochromism, dyestuffs of intermediate type must exist, i.e. those in which maximum spreading of electron density (equalisation of the bonds) is achieved in a solvent of medium polarity; in such a case, passing from this solvent to a more polar or a less polar one would be accompanied by a decrease in the absorption wave-length. Such dyestuffs were found among the merocyanines by Levkoev, Sveshnikov, and Lifshits[27], and then among hydroxystyryl anhydro-bases by Kiprianov and Timoshenko[13]. An example of a dye with "intermediate" solvatochromism is (XI),



(XI)

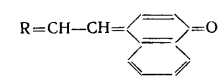
with absorption maxima at 506 mμ in water, 594 mμ in alcohol, 592 mμ in chloroform, and 574 mμ in benzene. Kiprianov and Timoshenko showed[7,13] that by making gradual alterations in the structure of the nuclei of hydroxystyryl anhydro-bases, it is possible to pass from negative solvatochromism through a compound of intermediate type to positive solvatochromism. For example, if in compound (XII)



(XII)

the *o*-benzoquinone nucleus is successively replaced by *p*-benzoquinone, 1,2-naphthoquinone, and 1,4-naphthoquinone, the relationship between the corresponding anhydro-bases and the polarity of the solvent changes in the same order as the reduction potentials of the quinones. The *o*- and *p*-benzoquinone derivatives show negative solvatochromism, the 1, 2-naphthoquinone derivative solvatochromism of intermediate type, and the 1,4-naphthoquinone derivative positive solvatochromism.

If the solvatochromism of the anhydro-bases of the general formula (XIII)

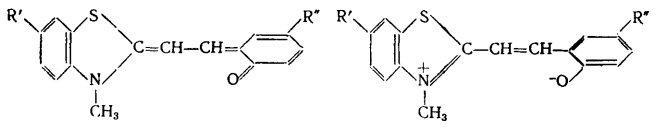


(XIII)

is compared, the molecules containing the same 1,4-naphthoquinone residue but different nitrogen-containing heterocycles R, it is found that with a very basic heterocycle (pyridine), the solvatochromism is negative, with hetero-

cycles of medium basicity (quinoline, thiazole) it is of intermediate type, and with weakly basic heterocycles (benzothiazole, indolenine), it is positive.

Finally, the nature of the solvatochromism can be altered by introducing polar substituents into the molecule of the merocyanine dyestuff[7,12,15,28,29]. If the benzothiazole nucleus of (XII) is substituted by R' or the quinone nucleus by R", we obtain dyes of structure (XIV).

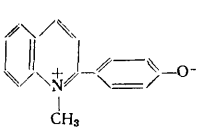


(XIV*a*) (XIV*b*)

Electropositive substituents in the benzothiazole nucleus [R' = OC_2H_5, $N(CH_3)_2$] cause the structure of the dye to approximate to the form corresponding to (XIV*b*), i.e. the form to which it is close even without the substituent; a decrease in the absorption wave-length is therefore observed in all solvents. The same substituents in the quinone nucleus [R" = OC_2H_5, $N(CH_3)_2$] cause the structure to approximate to the form (XIV*a*), and greatly deepen the colour. Electronegative substituents (e.g. NO_2) cause the opposite effects. By introducing an electronegative substituent R' and an electropositive substituent R", the negative solvatochromism of (XII) may be converted into positive.

In 1950 Kiprianov and Timoshenko[7] determined the absorption curves of several merocyanine dyes in a water–pyridine mixture. An interesting effect was observed: the intensity of absorption was greater in aqueous pyridine than in water or pure pyridine (Fig. 1). Brooker and coworkers, studying solvatochromism in mixed solvents in more detail[8], showed that the increase in the intensity of absorption, like the shift to shorter wave-lengths, is associated with the dyestuff molecule approaching the condition exactly intermediate between the non-polar and the dipolar forms; Brooker named this condition the isoenergetic point. It is particularly easily determined from the intensity maximum of the dye in mixtures of two solvents. For example, for (VII) in mixtures of pyridine with water, the isoenergetic point lies at 92.5 vol. % of pyridine (Fig. 3).

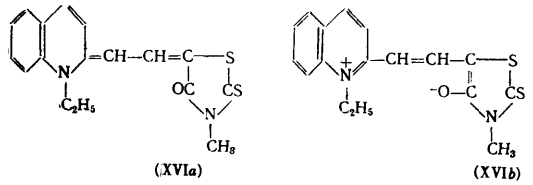
We shall now consider several typical examples of solvatochromism in dyes of various classes. After Kiprianov and Petrun'kin's work[10,11], the hydroxystyryl anhydro-bases became the most frequently studied in investigations of solvatochromism[8,12,14,22–26,30]. It is interesting that the solvatochromism of hydroxystyryl anhydro-bases had been observed in 1930 in König's laboratory[31]. No explanation of this effect was found, and the work was not published. The anhydro-bases of 2-hydroxyphenyl derivatives of heterocyclic nitrogen compounds, of type (XV),



(XV)

are similar in structure to those of hydroxystyryl compounds, and also exhibit solvatochromism[24,30].

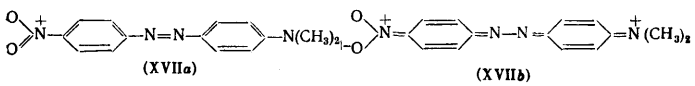
Brooker[14] and Levkoev[27,32] and their coworkers studied the solvatochromism of merocyanines, of type (XVI), in great detail.



(XVI*a*) (XVI*b*)

In most cases the merocyanines show positive solvatochromism, i.e. their structure is nearer the (*a*) form; however, if one nucleus is very positive and the other very negative, the solvatochromism may be negative (X).

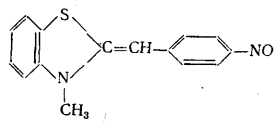
Azo-compounds change colour in solvents of differing polarity if one aromatic ring carries an electropositive substituent and the other an electronegative one. An example is the aminoazo-dye (XVII).



(XVII*a*) (XVII*b*)

The solvatochromism of these dyes is very positive, since in any solvent the structure is nearer (XVII*a*) than (XVII*b*), which contains two quinonoid nuclei.

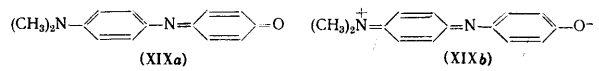
Positive solvatochromism is also found in nitroso-dyes of type (XVIII).



(XVIII)

However, if the benzothiazole nucleus carries a nitro group, the solvatochromism is negative[7]. The azo-dyes obtained from quaternary salts of heterocyclic nitrogen compounds, e.g. (V), which have been studied by König[9,31] and Kiprianov and Timoshenko[7], behave similarly.

Phenol blue (XIX) is of the tetramethyldiaminofuchsone (I) type[21,33,34].



(XIX*a*) (XIX*b*)

The positive solvatochromism of this dye, like that of tetramethyldiaminofuchsone, is due to the dipolar structure (XIX*b*) being less favourable, because of the separation of the ionic charges.

A somewhat more complex system is that of the pyrazolone-azomethines (XX), whose solvatochromism was studied by Vittum and coworkers[29]. In discussing the interaction of (XX) with solvents, at least three structures,

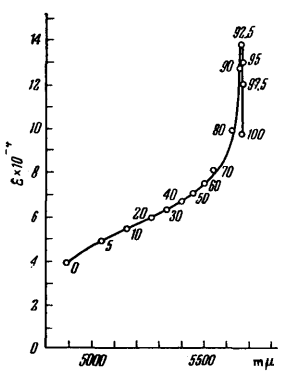
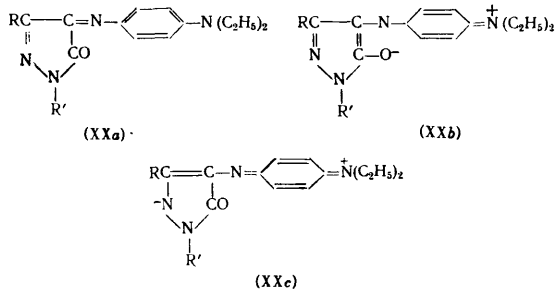


Fig. 3.

one non-polar and two dipolar, must be taken into account:

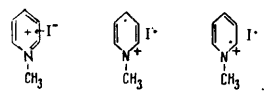


(XXa) (XXb)

(XXc)

We have thus far considered only those merocyanine dyes in which there is conjugation between the atoms carrying the positive and negative charges. The structure of such a dye can always be represented in a non-polar form. It is interesting, however, that solvatochromism is also observed with coloured dipolar compounds in which there is no conjugation between the positive and negative centres, and which consequently exist only in the betaine form. The solvatochromism of these betaines has recently been discussed by Kosower[35,36].

We may consider *N*-alkyl pyridinium salts as models of betaines in which there is no conjugation between the ionic centres. The absorption band of pyridine methioxide is displaced towards longer wave-lengths as the polarity of the solvent is decreased; this salt shows negative solvatochromism. It is assumed that in the ground state pyridine methiodide exists as the ion pair (XXI*a*). Under the action of a quantum of light, the electron of the iodide ion is transferred to the pyridine nucleus, giving (XXI*b*), or, what is equivalent, (XXI*c*):



(XXIa) (XXIb) (XXIc)

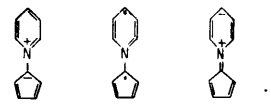
Formulae (XXI*a*) and (XXI*b*) may be represented schematically as in Figs. 4 and 5.

Thus according to Kosower, at the moment of excitation by the light quantum, the dipole moment of the molecule becomes perpendicular to the original. However, the solvent-molecule dipoles which are oriented with respect to the dipole of the unexcited molecule do not have time to rotate, in accordance with the Frank-Condon principle. The energy required to rotate the dipole of the molecule in various solvents affects the magnitude of the quantum of absorbed light.

According to Kosower and Ramsey[36], the same is true for betaines of type (XXII*a*), which are yellow in water and blue-purple in heptane; here also one electron passes from the cyclopentadiene ring to the pyridine nucleus (XXII*b*). However, for betaines of type (XXII*a*), as for all the betaines described later, the excited state may be represented not as a diradical (XXII*b*), as was done by Kosower, but as another dipolar form (XXII*c*), formed from (XXII*a*) as a result of the transfer of an electron pair from the cyclopentadiene nucleus to the pyridine nucleus.



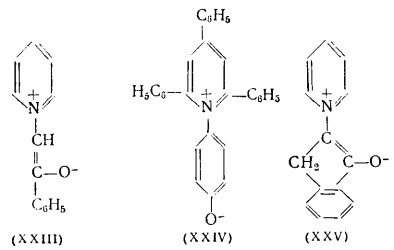
Fig. 4. Fig. 5.



(XXIIa) (XXIIb) (XXIIc)

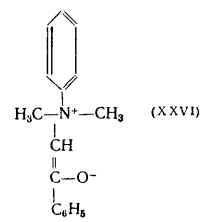
The possibility then arises of considering these betaines from the same point of view as the merocyanine dyes described above, bearing in mind that (XXII*a*) must be more polar than (XXII*c*).

Solvatochromism is observed in the pyridinium betaines described by Krönke (XXIII)[37], Dimroth (XXIV)[15,24,38], and Stafford (XXV)[39]:



(XXIII) (XXIV) (XXV)

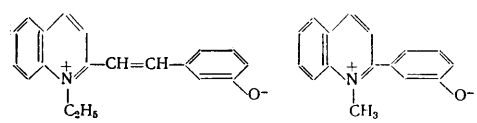
All these compounds show negative solvatochromism; they have low stability in solutions, and are easily oxidised and decolorised. The colourless compound (XXVI)



(XXVI)

apparently does not exhibit solvatochromism[39]; the transfer of electrons from the oxygen to the benzene ring is hindered by the absence of conjugation.

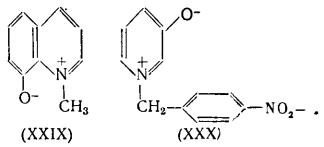
Solvatochromism and thermochromism are shown by the anhydro-bases of the *m*-hydroxystyryl compounds (XXVII)[24] and their lower vinylogues (XXVIII)[30], in which there is no conjugation between the charged atoms:



(XXVII) (XXVIII)

These betaines differ from their *o*- and *p*-isomers by their low stability and poor solubility in non-polar solvents. This type of betaine includes the anhydro-bases in which the ionic centres are in a single condensed system (XXIX)

or even in a single nucleus (XXX)[30] but are not in conjugation:



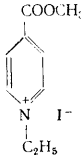
(XXIX) (XXX)

The betaine (XXIX) gives a red solution in water and a violet one in benzene; (XXX) absorbs at a shorter wave-length in chloroform than in alcohol. Apparently these betaines, for which a non-polar structure is impossible, exhibit only negative solvatochromism.

We shall now consider the part played by the dielectric constant of the solvent in solvatochromism. Solvatochromism clearly depends on the polarity of the solvent, but in earlier studies of solvatochromism[11] it was stated that no complete parallel was observed between the change of colour of a merocyanine dye and the change in dielectric constant of the solvent. Solutions of certain dyes had the same colour in chloroform and nitrobenzene, although the dielectric constants are 5.1 for chloroform and 36 for nitrobenzene; often the colour in methanol (ϵ = 32.6) is the same as in formamide (ϵ = 109.5)[25,33,40].

Kosower[35] discusses the significance of the dielectric constant in solvatochromism in detail. The dielectric constant, as is known from solvolysis studies[41], cannot be considered as a quantitative measure of the polarising power of the solvent; it reflects the behaviour of the solvent molecules in an electric field, but it does not take into account the form of the solvent molecule, the polarity of the individual bonds between the atoms, or other factors which are of great significance in the interaction with the solute. According to Kosower, a single compound for which the absorption of light changes greatly over a wide range of solvents must be chosen as standard; the displacement of the absorption maxima of this standard in these solvents will then give a scale for the polarity of the solvents.

Kosower proposes to use 1-ethyl-4-methoxycarbonylpyridinium iodide (XXXI) as standard:



(XXXI)

It is very soluble in water and in organic solvents, and the position of the absorption maximum is extremely sensitive to change in the polarising power of the solvent. As a measure of the ionising capacity of the solvent, Kosower uses Z, the energy of transfer of an electron in kcal mole^{-1}, calculated for the absorption maximum of the solution of (XXXI) in the given solvent. The calculation is made from the formula

$$Z = h\nu = 2.859 \times 10^{-3}\ \tilde{\nu}\ \text{cm}^{-1} = \frac{2859}{\lambda_{m\mu}}\ .$$

The values of Z were measured for various solvents and mixtures of solvents from chloroform (Z = 63.2) to 70% alcohol (Z = 86.4). For paraffinic hydrocarbons, in which

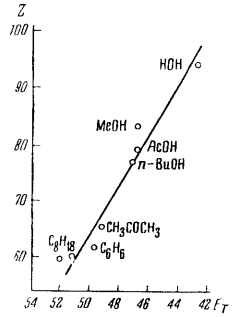


Fig. 6.

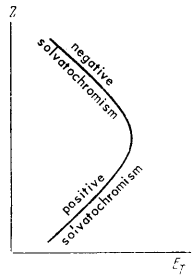


Fig. 7.

(XXXI) is insoluble, the standard used was pyridine N-oxide, which is soluble in hydrocarbons and also exhibits solvatochromism.

If Z is plotted against the energy of electron transitions ($E_T = h\nu$) at the absorption maxima of the merocyanine compound in each solvent, the points lie, according to Kosower, on a single straight line. Fig. 6 is such a curve constructed for phenol blue (XIX).

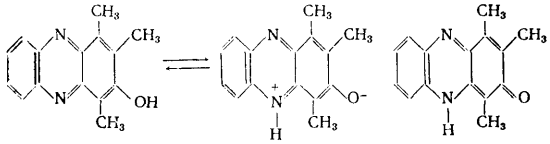
According to Kosower, this graph can be used to forecast the absorption maximum for phenol blue in any new solvent (except chloroform and pyridine) to within ± 8 mμ.

The determination of the ionising power of a solvent by using a standard solute is very useful, but Kosower is incorrect in considering that the points on the plot of Z against E_T for each merocyanine compound must lie on a straight line. In fact many such dyes, as we saw above, reach an isoenergetic point at a definite solvent ionising power, when the frequency and intensity of absorption of the solution is greatest; further increase of the ionising power of the medium changes the solvatochromism from positive to negative. For such substances, the plot of Z against E_T must be a curved line, of the general form shown in Fig. 7. Furthermore, as noted by Kosower himself, complex dyestuff molecules may exhibit large deviations from the general relationship owing to their specific interactions with the solvent molecules, depending on their size and shape.

Kosower remarks[35] that Z varies within much wider limits in hydroxylated solvents (from 71.3 in t-butanol to 94.6 in water) than in non-hydroxylated solvents (from 60.1 in isooctane to 71.3 in acetonitrile). This indicates the large part played by hydrogen bonds in solvatochromism.

The significance of hydrogen bonds in solvatochromism has been remarked upon several times. In their study of the absorption spectra of certain merocyanines, Bayliss and McRae[40] point out that they depend more on the ability of the solvent to form hydrogen bonds than on its dielectric constant. Kumler[42] makes the same comment in respect of *p*-nitroaniline. However, most workers[25,35,42] agree that hydrogen bonds play a substantial, but not the main, part in solvatochromism.

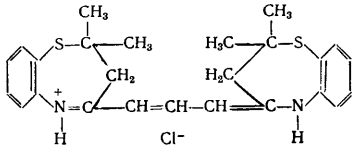
In 1947 John[43] described the solvatochromism of trimethylhydroxyphenazine (XXXII):



(XXXII) (XXXIIa) (XXXIIb)

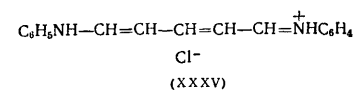
He correctly ascribed the change of colour of this compound to two factors, the tautomeric conversion of the hydroxy--form (XXXII) to the oxo-form (XXXIII*a*) or (XXXIII*b*). The hydroxy-form is yellow, while the oxo-form changes colour from red to violet, depending on the solvent. The difference in the colours is here so great that John proposed the use of this reagent for the analysis by absorption spectra of mixtures of various solvents. Later, the solvatochromism of trimethylhydroxyphenazine was studied by two other workers[44], who concluded that the change of colour is due exclusively to the formation of hydrogen bonds with the solvent, but the proofs which they give (for instance, the disappearance of solvatochromism on methylation of the hydroxy group) are not very convincing.

However, there apparently do exist cases where the main cause of the change of colour of a compound is the formation of hydrogen bonds with the solvent. Recently Mushkalo[45] described the solvatochromism of some new cyanine dyes which he prepared, containing hydrogen atoms in place of the hydrocarbon radicals on the ring nitrogen atoms, such as the dye (XXXIV):



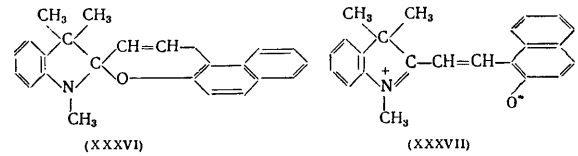
(XXXIV)

This dye, which does not have a merocyanine structure, gave absorption maxima at 550 mμ in chloroform and at 500 mμ in all oxygen-containing solvents (alcohol, acetone, formamide). The addition to a solution of (XXXIV) of small quantities of alcohol or acetone produced a sharp displacement of the absorption band towards shorter wave--lengths. Mushkalo reported analogous effects in other dyes containing the NH group as part of a ring or in side chains. However, the absorption maxima of salts of the dianils of glutaconic aldehyde, e.g. (XXXV), are the same in chloroform and alcohol.



(XXXV)

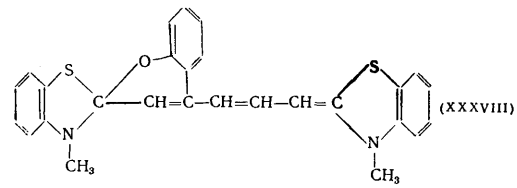
Solvatochromism and thermochromism may be associated with the opening and closing of spiro-rings. In 1940 Wizinger and Wenning[5] showed that colourless spiro-compounds of type (XXXVI)



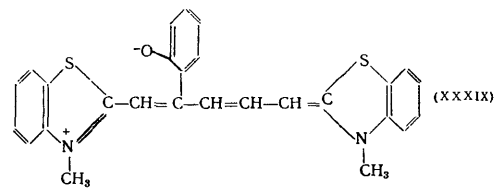
(XXXVI) (XXXVII)

are converted into (XXXVII) on heating or on solution in highly polar solvents, becoming intensely coloured. Knott[22] discusses the thermochromism and solvatochromism of spiro-compounds of type (XXXVI) in detail.

A case where the closing of the spiro-ring leads not to decolorisation but merely to a change in colour is that of the dicarbocyanine (XXXIX)[46], which in benzene gave a bright yellow solution, corresponding to the spiro-form (XXXVIII), but in alcohol is completely converted into the dark-blue form (XXXIX):



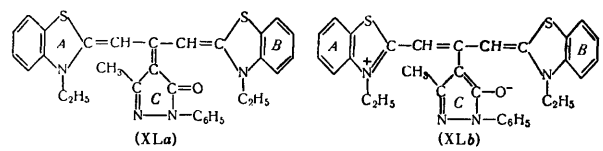
(XXXVIII)



(XXXIX)

The spectra of solutions in acetone and chloroform indicated the simultaneous presence of the yellow and blue tautomers.

The last type of solvatochromism to which we shall refer is associated with the spatial configuration of the dyestuff molecule. If there is conjugation between aromatic or heterocyclic nuclei in a dyestuff molecule, these nuclei are coplanar. If one of the nuclei leaves the plane in which the others lie and becomes perpendicular to it, this nucleus no longer takes part in the conjugation and ceases to influence the colour of the dyestuff. Brooker synthesised the trinuclear dye (XL):



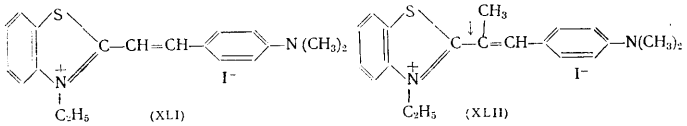
(XL*a*) (XL*b*)

A three-dimensional model of this compound shows that all three rings cannot be simultaneously coplanar. Assuming that rings *A* and *B* are coplanar and ring *C* is rotated through 90°, then ring *C* does not take part in the conjugation, and we have a typical carbocyanine with an absorption maximum at 550 mμ. This is the form in which (XL) exists in highly polar solvents (water, alcohol). On the other hand, in solvents of low polarity (lutidine), ring *A* (or *B*) leaves the plane of the other rings, and the absorption band is displaced towards shorter wave-lengths, since when rings *A* and *C* (or *B* and *C*) are coplanar, we have a typical

merocyanine with its characteristic absorption band. This type of stereosiomerism, associated with the polarising power of the solvent, was first described by Brooker[47,48], and named by him allopolar isomerism.

Allopolar isomerism is an example of how steric hindrance can change the structure and colour of a dye in solution. The influence of steric hindrance in the molecule on the absorption of light is much discussed in the literature, but no one has yet studied the influence of steric hindrance on the solvatochromism of simple merocyanine dyes. Kiprianov and Mikhailenko[49] have recently obtained some results on this question.

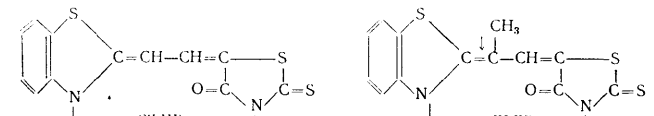
At present we know[50,51,52] that the partial destruction of the coplanarity of the rings in dyestuff molecules always leads to a reduction in the intensity of absorption, and almost always to a displacement of the absorption maximum; if a ring rotates about a single (or predominantly single) bond, the absorption maximum is displaced towards shorter wave-lengths. This is observed, for example, in the styryl dyes (XLI) and (XLII).



(XLI) (XLII)

in alcohol λ_{max} 530 mμ λ_{max} 481 mμ

Strains caused by the methyl group induce the benzothiazole ring in (XLII) to rotate by a certain angle about the single bond marked by the arrow, as a result of which the absorption band is displaced towards shorter wave-lengths. Similar steric hindrance in the merocyanine molecule (XLIV)

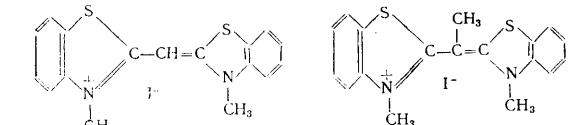


(XLIII) (XLIV)

in alcohol λ_{max} 524 mμ λ_{max} 541 mμ

causes rotation about the double bond, and the absorption maximum is displaced towards longer wave-lengths.

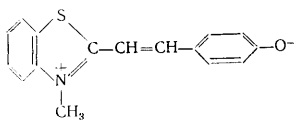
In the symmetrical monomethine cyanine (XLV), in which both bonds joining the thiazole rings are equivalent and of the order ~ 1.5, destruction of the coplanarity of the rings also causes a shift of absorption to shorter wave-lengths [longer wave-lengths ? (Ed. of Translation)].



(XLV) (XLVI)

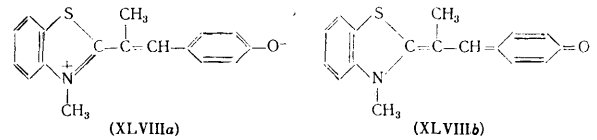
in alcohol λ_{max} 422 mμ λ_{max} 465 mμ

Knowing the above effects, it is possible to forecast to a considerable extent how the destruction of the coplanarity of the rings in simple merocyanine dyes will affect their absorption of light. If a methyl group is introduced at the β-position of the chain in the hydroxystyryl anhydro-base (XLVII)



(XLVII)

the dye (XLVIII), with a non-planar molecule, is formed,



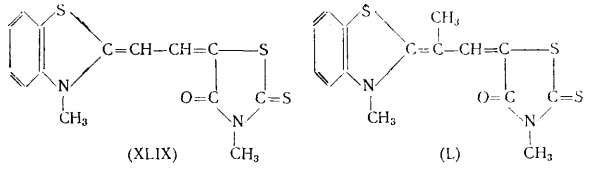
(XLVIII*a*) (XLVIII*b*)

and the following displacements of the absorption maxima, as compared with (XLVII), are observed:

in water	-65 mμ	in acetone	+ 4 mμ
in methanol	-43 mμ	in chloroform	+12 mμ.

Just these effects would be expected. The structure of (XLVIII) in water approaches the dipolar form (XLVIII*a*), and there is rotation of the ring about a single bond, causing a strong hypsochromic displacement of the absorption maximum. In methanol the order of the –C–C– bond in the molecule of (XLVIII) is higher, and the hypsochromic displacement is correspondingly less. In acetone the order of the bond is still higher, and the rotation of the ring has practically no influence on the absorption. In chloroform the bond order is ~ 1.5 (or more), and there is a marked bathochromic shift. The extinction of (XLVIII) in all solvents is much lower than that of (XLVII).

The destruction of the coplanarity of rings in the molecule of a dye exhibiting positive solvatochromism gives a different effect. If the absorption maxima of the planar (XLIX) and non-planar (L) merocyanines



(XLIX) (L)

are compared, it is seen that the destruction of the planar structure leads to a bathochromic shift of the maximum in all solvents:

in methanol	+4 mμ	in chloroform	+8 mμ
in acetone	+4 mμ	in benzene	+9 mμ.

This would be expected, since in this case there is free rotation in all the solvents about a bond of order approximately two.

The absorption maxima of (XLVII) and (XLVIII) in mixtures of pyridine and water of varying composition have also been compared. The displacements of the maxima were as follows:

in	80% pyridine	-24 mμ
	85% "	-18 mμ
	90% "	- 6 mμ
	95% "	- 1 mμ
	100% "	+ 7 mμ.

The transition from the hypsochromic effect, caused by rotation of the benzothiazole ring, to the bathochromic effect takes place at a pyridine concentration of ~ 95%. This is just the region in which, according to Brooker[8], the isoenergetic point of (XLVII) (in 92.5% pyridine) is found.

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ANALYSIS AND SEPARATION OF AROMATIC HYDROCARBONS BY GAS–LIQUID CHROMATOGRAPHY

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The rapid development of gas–liquid chromatography since 1952, when it was introduced by James and Martin, is undoubtedly due to its high analytical precision, to its speedy and reliable separations, and to the ease with which it can be applied to the automatic control of industrial processes.

The separation of a mixture in gas–liquid chromatography arises from the different rates of motion of the components along the layer of stationary phase, resulting in the formation of separate zones or bands. Thus the rate of movement of the bands and the dependence of band width on various experimental parameters form the main subject of the theory of gas chromatography[1-22]. The theories which have been put forward to explain the motion and the spreading of bands fall into three distinct groups. The first group includes the theory of theoretical plates[23-33], which discusses the chromatographic column as a plurality of elementary sections (theoretical plates), in each of which an equilibrium between the liquid and the gas is set up. No such equilibrium can exist in practice, whatever the length of column considered. The second group includes the various kinetic approaches[34-39] to the chromatographic process, based on considerations of molecular motions. These leave out of the picture all macroscopic characteristics. The third group is called the "theory of rates" or "theory of macroscopic constants"[40-46] and appears to be the most rational of the three. It describes the spreading of bands in terms of macroscopic parameters, such as diffusion coefficients, mass-transfer coefficients, etc.

Many articles and monographs have been devoted to the effects of particular factors on the efficiency of separation[47-72,235], and much attention has been given to the use of gas chromatography in the separation and analysis of various classes of organic compounds: saturated and unsaturated hydrocarbons[73-84], halogenated compounds[85-88], phenols[89-92], sulphur compounds[93-95], fatty acids and esters[96-99], amino and nitro compounds[100-105], lubricating oils[106-107], pyridine bases[108-109], products from oil refin-