The Association of Cobalt(II) Tetrasulphophthalocyanine

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The influence of solvent and added solute molecules on the nature of the species observed in solutions of the tetrasodium salt of cobalt(II) tetrasulphophthalocyanine has been studied by electronic absorption spectrophotometry. Water is the only solvent which promotes formation of the known dimeric species. The equilibrium between monomer (M) and dimer (D) obeys the relationship $K = [D]/[M]^2 \cdot [H_2O]^n$, where $n \simeq 12$ in both water–methanol and water–ethanol mixtures. It is suggested that the water molecules play a specific role in binding together the two monomer units through the formation of hydrogen bonds.

THERE has recently been considerable interest in the chemistry of cobalt complexes containing a conjugated equatorial ligand, particularly in organocobalt(III) complexes,[1] which may serve as models for the enzymatically important organocobalt(III) corrinoids,[2] and in the reversible uptake of oxygen by cobalt(II) complexes,[3] which may serve as models for the oxygenation of protein-bound iron(II) porphyrins. Comparatively little work has yet been reported on cobalt phthalocyanine complexes, though a few organocobalt(III) complexes are known [4] and we have observed the formation of an oxygen adduct.[5]

Although the simple cobalt(II) phthalocyanine is insoluble in most common solvents, the presence of ionised sulphonic acid groups confers solubility in water and certain other solvents. Unfortunately, salts of both metal and metal-free tetrasulphophthalocyanines behave in water like organic dyes in forming dimers through interaction between the planar conjugated ring systems.[6]

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The monomeric and dimeric forms of the cobalt tetrasulphophthalocyanine (Co^{II}tspc) have been identified, their spectra reported, and the equilibrium constant determined.[6b,c,i] Such dimerisation obviously complicates the study of the equilibria and reactions involving the axial ligands of the monomer.

Three main theories have been proposed to account for the association of charged organic dyes in aqueous solution. According to one theory,[7] association is favoured by the London dispersion forces between the extensive, polarisable, conjugated systems, but this may be hindered by coulombic repulsion between the charged dye monomers; the role of water in promoting association is then ascribed to a reduction in coulombic repulsion due to its high dielectric constant. Another theory [8,9] invokes the formation of hydrogen bonds, *i.e.* aggregation is due to hydrogen bonding either directly between the monomer units or indirectly *via* solvent molecules. The third theory [10] postulates that organic solutes in water are surrounded by structured ' icebergs ' of low entropy, and that the driving force for aggregation is the increase in entropy caused by a decrease in the number or extent of these ' icebergs.'

The aims of this paper are (1) to explore the general pattern of occurrence of the known monomers and dimers and of any other species, and (2) to establish which of the above theories of dimerisation, if any, is applicable to the case of aqueous solutions of Co^{II}tspc. The co-ordination of axial ligands and the reactions with oxygen will be considered in a later publication.[11]

EXPERIMENTAL

Cobalt(II) tetrasulphophthalocyanine was prepared by the method of Weber and Busch [12] (Found: C, 37.9; H, 1.5; N, 10.8. $C_{32}H_{16}CoNa_4N_8O_{14}S_4$ requires C, 37.84; H, 1.47; N, 11.03%). Solvents and reagents were of AnalaR grade whenever possible (*e.g.* MeOH, EtOH, $KClO_4$, and $NaNO_3$) and were used without further purification.

The variable concentration spectra (Figure 1) were measured on a Beckmann DK-2A Ratio Recording Spectrophotometer. The solutions were prepared immediately prior to use and allowed to equilibrate in a water-bath at 293 ± 1 K before the absorbance curves were recorded. Other spectra were measured on either a Pye Unicam SP 800A or an SP 8000A spectrophotometer, both of which were fitted with a repeat scan facility and a constant-temperature cell-holder. Spectral analyses were undertaken, using the method of West and Pearce,[13] by means of Algol programmes run on an Elliott 503 computer at the University of Bristol.

RESULTS

(1) *Identification of the Spectra of Monomers and Dimers.*—Previous workers have established the existence of an equilibrium between monomeric (M) and dimeric (D) forms of Co^{II}tspc in aqueous solution by determining the equilibrium constant, and have reported the spectra of the two species.[6b,c,i] We have been interested in examining whether the same simple equilibrium also exists in non-aqueous or mixed solvents and the extent to which the spectra of these species are affected by the solvent composition, in order to be able to use the observed spectra as a means for exploring the occurrence of monomers, dimers, and other possible aggregates in various solvents.

TABLE 1

Data for the identification of the dimeric form of the cobalt complex [conditions: 20% (v/v) methanol in water at 293 ± 1 K, with 5 × 10^{-3}M-$KClO_4$]

Cobalt concentration × 10^5M	Pathlength of cell (l/cm)	ε_{662}	$\frac{K_{app.} \times 10^{-5}}{l\ mol^{-1}}$	Mole fraction present as monomer
2.00	0.5	0.53	2.2 ± 0.4	0.28
1.00	1.0	0.58	2.6 ± 0.4	0.35
0.50	2.0	0.63	3.0 ± 0.4	0.44
0.25	4.0	0.72	2.7 ± 0.3	0.57

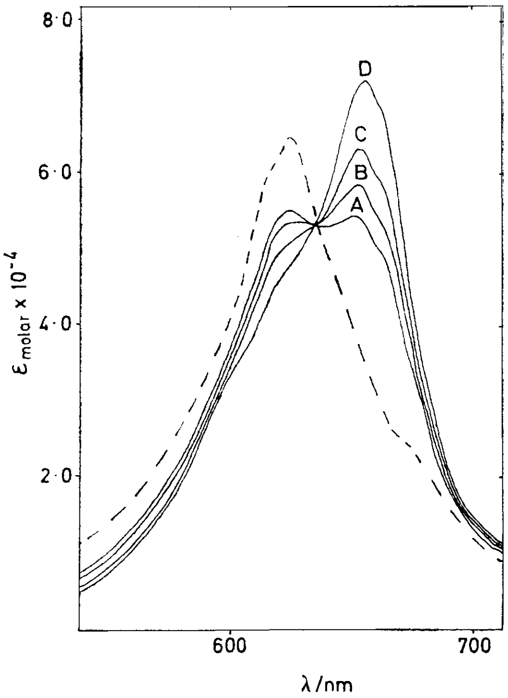

FIGURE 1 Visible absorption spectrum of Co^{II}tspc in 20% water–methanol at 293 ± 1 K. (Broken line represents calculated dimer spectrum): A = 2.0 × 10^{-5}M, B = 1.0 × 10^{-5}M, C = 5.0 × 10^{-6}M, D = 2.5 × 10^{-6}M

After qualitative studies had shown that similar equilibria appeared to exist in several aqueous–organic solvent mixtures with the proportion of D increasing with the water content [see section (4)], the existence of the simple equilibrium between M and D was confirmed in 20% v/v aqueous methanol by quantitative determination of the equilibrium constant $K_{app} = [D]/[M]^2$; for details see Table 1. The spectra showed an isobestic point at 636 nm. Taking the spectrum of the pure monomer to be that

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[7] E. Rabinowitch and L. Epstein, *J. Amer. Chem. Soc.*, 1941, **63**, 69; T. Förster, *ibid.*, 1946, **33**, 166.

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[13] W. West and S. Pearce, *J. Phys. Chem.*, 1965, **69**, 1894.

observed in 60% aqueous methanol (see below), the spectra in 20% aqueous methanol were evaluated at 13 wavelengths between 500 and 700 nm by the method of West and Pearce [13] to give the spectrum of the pure dimer (D), which shows a maximum at 627 nm (see Figure 1).[6]

Further study of the spectrum of M at higher methanol content revealed slight but definite changes depending on solvent composition:

% Methanol	60	70	80	90	100
$\lambda_{max.}$/nm	662	662	661	660	659
$\varepsilon_{max.}$ *	1.04	1.04	1.05	1.06	1.06
λ_{sh}/nm	600	600	599	598	598

* Values $\pm 0.02 \times 10^5$ l mol^{-1} cm^{-1}.

The following values were also calculated for solutions in 50% aqueous ethanol: $\lambda_{max.} = 664$ nm, $\varepsilon_{max.} = 1.21 \pm 0.04 \times 10^5$ l mol^{-1} cm^{-1}. These are very similar to the values recently reported for M in aqueous solution ($\lambda_{max.} = 663$ nm, $\varepsilon_{max.} = 1.03 \pm 0.01 \times 10^5$ l mol^{-1} cm^{-1}) [6c] and in 20% aqueous ethanol ($\lambda_{max.} = 663$ nm, $\varepsilon_{max.} = 1.2_1 \times 10^5$ l mol^{-1} cm^{-1}).[6i]

We conclude that the same equilibrium previously observed between monomers M and dimers D in aqueous solution also occurs in aqueous organic solvents and that the spectrum of M does show definite, but slight, variations in both λ and ε depending on the solvent. A similar study of the dependence of the spectrum of D is, unfortunately, hampered by its limited range of occurrence.

(2) *The Effect of Solvents on the Spectra.*—We have studied the spectra over the range 500—700 nm of solutions of Co^{II}tspc (mainly at a concentration of *ca.* 10^{-5}M) at room temperature in a variety of solvents where the donor atom is oxygen, and in mixtures of these solvents. The solvents were selected in order to test the effect of both dielectric constant and the presence and absence of hydrogen bonding.

The solid complex dissolves fairly readily at room temperature in H_2O, MeOH (no significant further reaction), Me_2SO (very slow reaction), $HCONH_2$ (slow reaction), and dimethylacetamide (DMA) (fairly rapid reaction with $\lambda_{max.}$ moving from 667 to 672 nm as the solid dissolves). These reactions probably involve the formation of Co^{III} complexes and have not been further investigated. The solid complex will not dissolve directly in dry acetone, ethanol, or higher alcohols, but solutions can be made by adding a drop of a concentrated (quarter- to half-saturated) solution in H_2O, MeOH, or Me_2SO to an excess (*ca.* 2 ml) of the required solvent. The following solvent mixtures have been studied over the whole range of composition: H_2O + MeOH, EtOH, Pr^{n}OH, Me_2SO, and Me_2CO; Me_2SO + MeOH and Me_2CO; MeOH + Pr^{n}OH.

The observed range of spectra and their variation with solvent composition can all be explained on the basis of the existence of three major types of complex linked by reversible equilibria. These are as follows.

(1) Monomers (M), already identified [see section (1)]. Their spectra show considerable structure and are characterised by an intense band in the 660—670 nm region and a second less-intense band or shoulder in the 600—610 nm region (see Figure 1). Their absorption spectra will be discussed in more detail in a later paper; it appears that the variation in band position is due mainly to changes in the number of co-ordinated axial ligands.[11]

(2) The dimer (D), already identified in water and aqueous methanolic solvents [see section (1)]. Its absorption spectrum shows a broad band with a maximum at 627 nm and lower intensity than that of M with only a small amount of additional structure (see Figure 1).

(3) New species (D′), whose spectra are characterised by a broad, low, and rather featureless band with a maximum in the 610—616 nm region (see Figure 2).

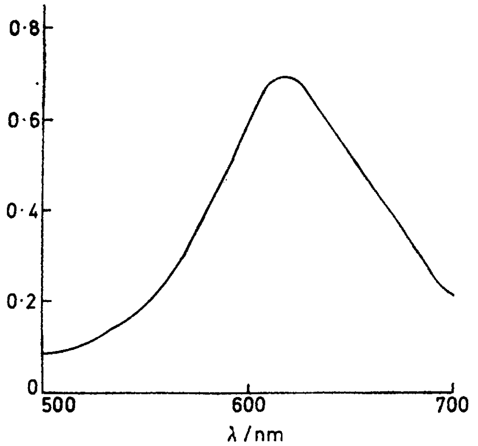

FIGURE 2 Spectrum of the D′ complex of Co^{II}tspc in Me_2CO–Me_2SO (arbitrary optical density scale)

Several spectra were also recorded in concentrated solution. Drops of saturated solutions in MeOH and Me_2SO, pressed into thin films of the appropriate thickness between the optical flats of two 1-cm quartz cells, showed spectra very similar to those in dilute solution, though the bands were not as sharp. Saturated and even half-saturated solutions in water evaporated and deposited solid too quickly to allow the spectra to be recorded, and quarter-saturated solutions had to be used; the spectra were similar to that of D in dilute solution, although the band was rather broader.

The spectra of all these solutions, both dilute and concentrated, are summarised in Table 2.

The following generalisations can be made about the occurrence of the three types of complex M, D, and D′. D Is observed only in H_2O. D′ Can be observed in both protic (*e.g.* wet EtOH) and completely aprotic (*e.g.* Me_2CO + trace of Me_2SO) solvents but, strangely enough, only in those solvents which cannot dissolve the solid complex directly. M Can also be observed in both protic (*e.g.* H_2O, MeOH, or $HCONH_2$) and aprotic (*e.g.* Me_2SO or DMA) solvents. Variation of the solvent composition shows the changes in species expected from the data in Table 2, *e.g.* the change from 100% H_2O to 100% Pr^{n}OH is accompanied by a change from a mixture of M and D through a range where only M is observed, followed by the appearance of D′ and disappearance of M over a very small composition range. It is particularly striking that there is no direct evidence for further aggregation beyond the dimeric stage. M Remains the major species even in saturated solutions in MeOH and Me_2SO, and D in nearly saturated aqueous solutions. Only the three species M, D, and D′ have been observed over the whole range of conditions studied.

The equilibrium between M and D appears to be established very rapidly under all conditions, and it can readily be studied quantitatively as a function both of cobalt concentration [see section (1)] and of solvent composition [see section (4)]. By contrast, establishment of the

TABLE 2

Spectra of Co^{II}tspc solutions in different solvents

Dielectric constant *	Solvent	Position of main band in nm (shoulders in brackets) Type of spectrum M	D	D′
		Dilute solutions (*ca.* 10^{-5}M)		
80.4	H_2O	≈660	627	
32.6	MeOH	(598) 659		
24.3	EtOH †	664		612—614
20.1	Pr^{n}OH †			614 (Me_2SO 614)
20.7	Me_2CO †			615 (Me_2SO 616)
49	Me_2SO	(604) 665		
110	$HCONH_2$	(604) 667		
37.8	DMA	⩽667		
	Saturated aqueous $NaNO_3$ †	669?		612
	Saturated aqueous urea	(608) 669		
	Saturated solution of $NaBPh_4$ in CH_3OH	659		610
		Concentrated solutions		
	CH_3OH (saturated)	(*ca.* 600) 656—660		
	Me_2SO (saturated)	(*ca.* 600) 664—665)		
	H_2O (1/4 saturated)		(*ca.* 570) 626 (*ca.* 670)	

DMA = Dimethylacetamide.

* Data taken from ref. 18 or, in the case of $HCONH_2$, from ref. 9. † Solutions prepared by adding a drop of a concentrated solution of the cobalt complex in water (or, where indicated, Me_2SO) to *ca.* 2 ml of the solvent.

equilibrium between M and D′ may be either fast (*e.g.* on diluting a solution of M in Me_2SO with Me_2CO to give D′) or slow (*e.g.* on diluting a solution of M in Me_2SO with Pr^{n}OH and *vice versa*). The presence or absence of O_2 has no apparent effect on the rate or extent of formation of D′, so the slowness cannot be ascribed, for example, to the reversible formation of the μ-peroxide. In addition, the presence of both M and D′ together can only be observed over a very small range of solvent composition and the exact position of the equilibrium seems to depend very critically on the conditions. We have, unfortunately, not yet found suitable conditions for a quantitative study of the equilibrium between M and D′.

(3) *The Effect of Solutes on the Spectra.*—The addition of electrolytes such as sodium chloride, sodium nitrate, sodium sulphate, potassium chloride, and potassium perchlorate to aqueous solutions of Co^{II}tspc initially displaces the monomer–dimer equilibrium in favour of the dimer, and good isosbestic points are observed at $<10^{-2}$M-potassium chloride, for example. Above this concentration, the main band moves to shorter wavelengths and falls in intensity. The effect of very high ionic strength was investigated by the use of sodium nitrate, chosen because of its high solubility,[14] the presence of an anion which has little tendency to co-ordinate, and the presence of the same cation as in the solid Co^{II}tspc salt. Solutions of Co^{II}tspc in saturated aqueous sodium nitrate had to be prepared by adding a drop of nearly saturated aqueous Co^{II}tspc to an excess of saturated aqueous $NaNO_3$. The resulting solution showed the presence of a complex of type D′, apparently together with a small amount of M (see Table 2). Varying the concentration of $NaNO_3$ showed that the equilibrium between D′ + M at high concentrations and D + M at low concentrations was reversible and rapidly established.

Urea was examined as an example of a non-electrolyte which is known [15] to ' break up ' the structure of water and reduce its activity through extensive hydrogen-bonding; it also has the unusual effect of increasing the dielectric constant of water.[16a] On adding increasing amounts of urea to an aqueous solution of Co^{II}tspc, the spectrum changes to that of pure M. The changes are instantaneous and unaccompanied by any slower reaction, but no isosbestic points are observed, *i.e.* the changes in spectra reflect the occurrence of two or more overlapping equilibria; this is probably due to the simultaneous occurrence of changes in the number of axial ligands as well as in the monomer–dimer equilibrium.

The effect of electrolytes on solutions of Co^{II}tspc in methanol was studied with lithium chloride, tetraphenylarsonium chloride, and sodium tetraphenylborate. The addition of either chloride caused both a rapid change (*i.e.* disturbance of an equilibrium) and a much slower change (probably irreversible oxidation to a Co^{III} complex), which resulted in a total increase in optical density over the region 500—700 nm and a shift of $\lambda_{max.}$ from 659 nm to lower energy (⩾662 nm). The addition of sodium tetraphenylborate, on the other hand, resulted in rapid and reversible changes in spectra, showing an isosbestic point at 632 nm. The optical density of the main band at 659 nm decreased, and showed a slight shift to higher energy, while the optical density increased around 610 nm, suggesting the formation of a complex of type D′; but complete formation of the new species was not observed even when the solution was saturated with the added electrolyte.

Studying the effect of added solutes has, therefore, revealed no new species in addition to M, D, and D′, but has shown that D′ may be formed in water, and possibly also in methanol, in the presence of high concentrations of added salts.

(4) *The Role of Water in the Formation of the Dimer D.*—It appears that water is unique in promoting the formation of D and in order to provide additional information on the role of water we have quantitatively studied the monomer–dimer equilibrium in dilute (*ca.* 2×10^{-5}M Co) solutions in H_2O–MeOH and H_2O–EtOH mixtures at 293 K in the absence of added salts. Under these conditions we do not expect complications due to the formation of any detectable

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[14] ' Handbook of Chemistry and Physics,' CRC Press, Cleveland, Ohio, 53rd edn., 1972, p. B-139.

[15] S. Subramanian, T. S. Sarma, D. Balasubramanian, and J. C. Ahluwalia, *J. Phys. Chem.*, 1971, **75**, 815.

[16] J. Timmermans, 'The Physico-chemical Constants of Binary Systems,' Interscience, New York, 1960, vol. 4, (*a*) pp.113—120; (*b*) pp. 152—207; (*c*) p. 154.

amounts of the third species D′, which is only observed in the presence of high concentrations of added salts [see section (3)]; this is confirmed by the occurrence of good isosbestic points (at 635, 601, 588, and 425 nm in 0—60% MeOH and at 636, 590, and 430 nm in 0—50% EtOH). Values of K_{app} for H_2O–MeOH mixtures, calculated as in section (1), are listed in Table 3. Values of $\log_{10}K_{app}$ were then plotted against the following physical and chemical properties of the mixed solvents: (1) the reciprocal of the dielectric constant (E),[16b] since the coulombic repulsion between the charged molecules should vary linearly with $1/E$, (2) the logarithm of the activity of water,[16c,17] and (3) the logarithm of the molar concentration of the water. If water plays a definite chemical role in the equilibrium, *i.e.*

TABLE 3

Variation of K_{app} in water–methanol solutions at 293 K (conditions: 1.94×10^{-5}M-Co^{II})

Concentration of water (M)	$K_{app.} \times 10^{-4}$ (l mol^{-1})
55.50	40.3
49.95	11.7
47.18	6.27
44.40	3.09
41.63	1.52
38.85	0.73
36.08	0.36
33.30	0.16
27.75	0.06

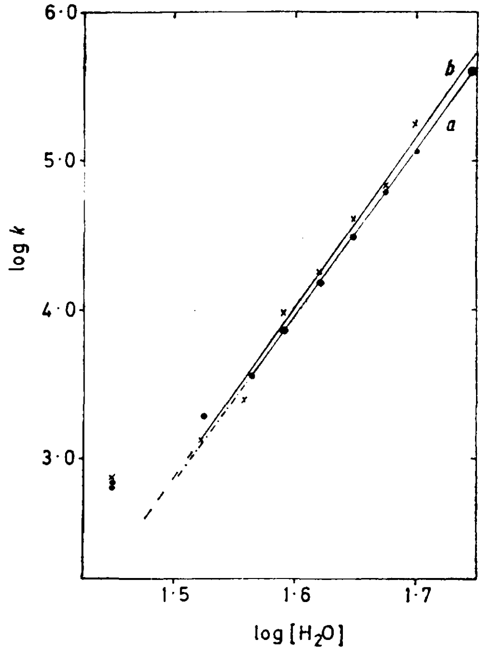

FIGURE 3 Plot of $\log_{10}K$ *vs.* $\log_{10}[H_2O]$ for (a) methanol and (b) ethanol solutions

$$2M + nH_2O \rightleftharpoons D(H_2O)_n$$

then the real and apparent equilibrium constants will be related as follows

$$K_{real} = [D]/[M]^2 \,.\, [H_2O]^n = K_{app}/[H_2O]^n$$

where the brackets can here represent either the thermodynamic activities or the observed molar concentrations of the species concerned. This can be rearranged to give

$$\log_{10}K_{app} = \log_{10}K_{real} + n\log_{10}[H_2O]$$

and there should be a linear relationship between $\log_{10}K_{app}$ and $\log_{10}[H_2O]$ with a slope equal to n. If the molecules of H_2O are present in the dimer as isolated molecules, then we would expect $[H_2O]$ to be represented by the activity of water in the mixed solvent, since the activity is related to the partial vapour pressure; if, however, the molecules act as clusters $(H_2O)_m$, then $[H_2O]$ will probably be better represented by the bulk concentration of water in the mixed solvent. Since both M and D can occur in pure water, there is no need to include molecules of alcohol in the above equilibrium. Of the four plots, only (3) gave a linear relationship (see Figure 3a): in fact, an excellent linearity is observed while K_{app} varies by over two orders of magnitude. The slope of the plot gives a value of $n = 11.4 \pm 0.8$. The analogous experiment with H_2O–EtOH mixtures produced a similar linear correlation (see Figure 3b) with a value of $n = 11.8 \pm 0.8$.

Further experiments showed that the addition of, for example, 5×10^{-2}M-$KClO_4$, led to an increase in K_{app}, the disappearance of isosbestic points, a markedly more curved plot, and a decrease in the maximum value of n. The simplest explanation is that under these conditions there is some formation of the third species D′, which is known to be promoted by the presence of electrolytes and does not require the presence of water.

DISCUSSION

The study of the visible absorption spectra (over the range 500—700 nm) of solutions of Co^{II}tspc in various solvents containing oxygen as the donor atom has revealed the existence of a large number of different complexes and equilibria. The observed range of spectra can, however, all be explained on the basis of the existence of three major types of complex, designated M, D, and D′, whose main absorption bands occur at 660—670, 627, and 610—616 nm respectively. The minor differences in spectra are probably due largely to differences in the number and nature of the axial ligands.[11]

Two of the three main types of complex (M, D) have been described before, while complexes of type D′ are reported here for the first time. The identity of the monomeric (M) and dimeric (D) species follows from the stoicheiometry of the equilibrium constant, as shown by others for solutions in water [6b] and by us in 20% aqueous methanol [section (1)]. We have not yet been able to establish the degree of aggregation of D′ by a quantitative study of its equilibrium with either M or D (but see below).

Our results show that M and D′ can be observed in both protic and aprotic solvents, while D is observed only in the presence of water. The formation of D′ is promoted by either (1) solvents of low dielectric constant or (2) the addition of electrolytes [see sections (2) and (3) and Table 2]. It is interesting that, in the absence of any added electrolyte, the dimer D is the predominant species in almost saturated aqueous solutions, while

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[17] International Critical Tables, Vol. III, McGraw-Hill, 1928, p. 290.

[18] A. J. Gordon and R. A. Ford, 'The Chemists' Companion,' Wiley–Interscience, N.Y., 1972, pp. 4—13.

saturated solutions in methanol and Me_2SO contain mainly the monomer M. The tendency to aggregate is, therefore, not very pronounced and there is no positive evidence for any further aggregation beyond the dimer stage.

The absence of any aggregates higher than the dimer in water, the existence of a simple equilibrium between M and D′ in certain solvents without the intermediate formation of D, and the similarity in spectrum between D and D′ suggest that D′ may also be a dimeric species. The role of low dielectric constant or high concentrations of electrolyte in promoting the formation of D′ can then be ascribed to their effect in increasing the formation of ion-pairs between the cations and the negatively charged sulphonate groups of the two neighbouring phthalocyanine rings. The difference in spectrum suggests a different orientation of the two rings in D and D′.

The unique effect of water in promoting the formation of D can hardly be ascribed to its high dielectric constant since D is not observed in formamide or in aqueous urea solutions (see Table 2), both of which have even higher dielectric constants. In order to obtain further information on the role of water, therefore, we have quantitatively studied the effect of varying the solvent composition, in water–methanol and water–ethanol mixtures, on the monomer–dimer equilibrium at 293 K. No correlation was found between the variation in the equilibrium constant and the variation in either the reciprocal of the dielectric constant or the activity of water. But the equilibrium constant does obey the relationship

$$2M + nH_2O \rightleftharpoons D(H_2O)_n$$

i.e.

$$K = [D]/[M]^2 . [H_2O]^n$$

where $[H_2O]$ is the concentration of water and n has the values **11.4 ± 0.8** in water–methanol and **11.8 ± 0.8** in water–ethanol systems [section (4)]. We consider that the occurrence of the same high value of $n \simeq 12$ in two different solvent systems is unlikely to be coincidental and reflects the specific role of water in binding together the two dye molecules through the formation of hydrogen bonds. This also explains the experimental observation that the addition of urea, which is known to form extensive hydrogen bonds to water molecules, increases the percentage of monomer present in aqueous solution (Table 2). The lack of correlation with the activity of water (which is determined from the partial vapour pressure and hence relates to isolated H_2O molecules) provides indirect evidence that the water in D is not present in the form of isolated molecules; and we suggest that the water may be present in the form of clusters, possibly $(H_2O)_3$, linking together the sulphonate groups and/or the aza nitrogen atoms of the two phthalocyanine rings.

As pointed out in the introduction, three theories have been proposed to account for the dimerisation of charged organic dyestuffs in water. Our results show that the dimerisation of Co^{II}tspc in aqueous solution (to form D) can be explained by a specific interaction with a discrete number of water molecules through the formation of hydrogen bonds. Neither the non-specific effect of an indefinite number of water molecules, as required by the ' iceberg ' theory, nor the role of water in increasing the dielectric constant of the medium, and hence reducing the coulombic repulsion between the monomeric units, are in accord with the experimental data.

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