On Solvent-induced Change in Intensity of Electronic Absorption and Circular Dichroism

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THE theory of solvent-dependence of electric dipole strength and of rotatory strength is usually based on the traditional Lorentz field in a continuous dielectric medium. Because of the general inadequacy of this simple correction, quantitative theoretical adjustment for solvent effect has seldom been attempted.[1] Yet, the actual influence of solvents is definitely appreciable.

There seems a danger that the inadequacy of theoretical correction technique lead to ignoring the presence of very real effects or to misinterpretation of them. The purpose of this Communication is to discuss two cases in which the empirical evaluation of such effects significantly alters conclusions derived from uncorrected data.

The electronic absorption spectrum and the circular dichroism of (+)-tris(ethylenediamine)-cobalt(III) in H_2O and D_2O have been compared recently.[2] A striking decrease in absolute magnitude of dipole strength and rotatory strength for all bands from 200 to 500 mμ was attributed to the replacement of N–H by N–D.[3]

Our determinations of the electronic absorption intensity in H_2O and D_2O (Figure 1) closely parallel those reported. A slight blue shift in D_2O is also evident from the position of the minima in the difference curve. The latter was obtained by a differential recording technique[5] which eliminates errors due to solvent absorbance and lack of recording reproducibility.

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We have carried out a similar comparison of the deuterated Co(en)$_3^{3+}$ complex ion in perdeutero-dimethyl sulphoxide to the undeuterated complex in ordinary dimethyl sulphoxide, shown in Figure 2. The change is little more than a slight blue shift with virtually no change in integrated intensity. The same result, within experimental error, is observed when the undeuterated complex replaces the deuterated complex in the perdeutero-solvent, under which conditions exchange proceeds at a very slow rate.[6]

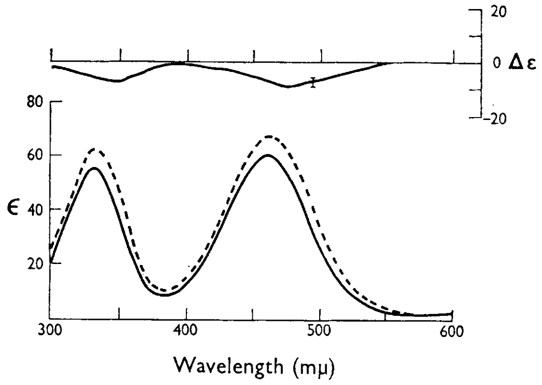

FIGURE 1. *The ordinary absorption spectrum of tris(ethylenediamine)cobalt* (III) *chloride in* D_2O (———) *compared to the spectrum in* H_2O (- - -). *The* ΔE *curve (not to be confused with the circular dichroism) obtained directly by differential recording (ref.* 5) *is essentially the difference of the spectra shown.*

One must conclude that the observed change in heavy water is predominantly a solvent effect, probably arising from the significant change in mole density. The mole densities of perdeutero- and ordinary dimethyl sulphoxide are almost equal, even though the deuteration on an atom ratio basis is nearly as great as for water. One must conclude further that the replacement of N–H and N–D in the complex produces an effect no larger than that shown in Figure 2, and in all probability is smaller Any effect observed in the ordinary absorption will also appear in the circular dichroism,[1] superposed possibly on an additional solvent dissymmetry effect unique to the circular dichroism.

The solvent effect in optical activity has been reported most often for the optical rotation at wavelengths outside the absorption region.[7] Particularly anomolous for traditional Lorentz theory is the reported *decrease* in the optical rotation of hexahelicene in paraffin hydrocarbon solvents of *increasing* refractive index.[8] The difficulties of formulating any generalized theory for the sum of many partial rotations, each with individual solvent sensitivity, has been stated earlier.[1]

The Table summarizes our observations of fractional change in hexahelicene absorption intensity on going from n-hexane to n-octane solvent. There follows an analysis for optical rotation at 550 mμ that is meant to be more illustrative of many optically active compounds than definitive for hexahelicene. Yet, the available evidence suggests it is a very good approximation to the situation in hexahelicene.[9]

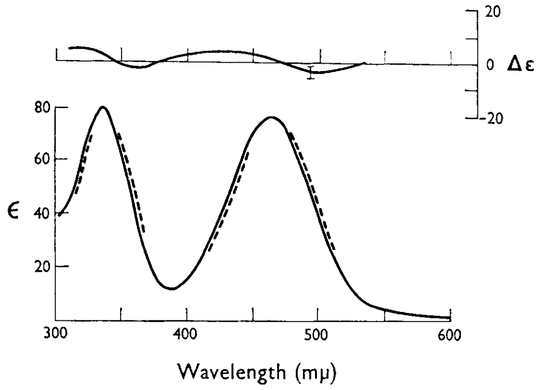

FIGURE 2. *The ordinary absorption spectrum of tris-(ethylenediamine)cobalt*(III) *chloride in* $(CD_3)_2SO$ (———) *compared to the spectrum of the deuterated complex in* $(CH_3)_2SO$ (- - -) *and the corresponding difference curve.*

TABLE

Observed change in dipole strength and calculated change in optical rotation

Transition upper state, K	$\Delta D_K/D_K{}^a$	$\Delta[\theta_K]_{550}/[\theta_K]_{550}{}^{a,b}$
^1L_b	4·46%	0·01/0·22
^1L_a	0·53%	0·03/5·46
^1B_b	−1·91%	0·00/0·17
$^1B_a(^1C_b)$	3·54%	−0·19/−5·43

a In n-octane solvent compared to n-hexane solvent.
b Reference 12.

Calculated relative partial rotations due to the various circular dichroism bands of hexahelicene[10] were assumed to undergo fractional changes parallelling that observed for dipole strength. Solvent *shifts* of band centres, suggested earlier as contributing,[8] produce changes negligible by comparison. The rotation, 0·42 in n-hexane, decreases to 0·26 in n-octane.[12] The analysis clearly demonstrates a large self-cancellation of partial rotations and a dominant solvent sensitivity (though not dominant rotational contribution) from a band deep within the ultraviolet absorption region of the molecule.

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[1] O. E. Weigang, Jr., *J. Chem. Phys.*, 1964, **41**, 1435 and references cited therein.

[2] S. F. Mason and B. J. Norman, *Chem. Comm.*, 1965, 48.

[3] The possibility of vibronic coupling with these bond vibrations has been questioned (Ref. 4). But other perturbation mechanisms could be operative to produce the observed effect.

[4] R. A. D. Wentworth, *Chem. Comm.*, 1965, 532.

[5] E. F. G. Herrington and W. Kynaston, *J. Chem. Soc.*, 1952, 3137.

[6] Controlled n.m.r. studies have confirmed the fact that the extent of exchange is immeasurable within a one hour interval. Even after 24 hours the extent of exchange is only a few percent, and a period of 2 weeks is required for exchange to be nearly 75% complete.

[7] See references cited in reference 1. Some notable exceptions are: A. Moscowitz, K. M. Wellman, and C. Djerassi, *Proc. Nat. Acad. Sci. U.S.A.*, 1963, **50**, 799; K. M. Wellman, P. H. A. Laur, W. S. Briggs, A. Moscowitz, and C. Djerassi, *J. Amer. Chem. Soc.*, 1965, **87**, 66.

[8] N. C. Kneten, N. J. Krause, T. O. Carmichael, and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, 1962, **84**, 1738.

[9] The relative rotatory strengths of ^1L_b and ^1L_a states can be measured straightforwardly;[10] that of ^1B_b is uncertain but small enough to have negligible consequence in the analysis. The rotatory strength of $^1B_a(^1C_b)$ is certain only in sign. Its anisotropy factor has arbitrarily been set equal to that for ^1L_a, consistent with observations on tetrahelicene derivatives (Ref. 11).

[10] O. E. Weigang, Jr., J. A. Turner, and P. A. Trouard, *J. Chem. Phys.*, in the press.

[11] C. M. Kemp and S. F. Mason, *Chem. Comm.*, 1965, 559.

[12] The quoted rotation values are only relative since the rotation of optically pure hexahelicene has not been measured in hydrocarbon solvents.