Correlations of Solvent Shifts in Charge-transfer Spectra with Index of Refraction

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DAVIS and SYMONS[1] have recently reported the results of their study of solvent effects on charge-transfer spectra. They found no correlation with Kosower's[2] *Z*-values and they interpreted the spectral changes in terms of solvent interactions with donor and acceptor species. It had previously been predicted that increasing solvent polarity should promote a bathochromic shift[3,4] as a consequence of increased stabilization of the polar excited state of the complex. Experimental efforts to correlate spectral changes with dielectric constant have failed.[5,6]

In our investigations[7] we have found, for aromatic hydrocarbon–tetracyanoethylene complexes, that the charge-transfer absorption bands vary monotonically with index of refraction of the solvent.

We were therefore prompted to re-evaluate previously published results on the bases of our observations. The table shows the positions of the charge-transfer absorption maxima. Solvents are tabulated in increasing order of index of refraction. It is noted, with the exception of complex G, that a satisfactory correlation exists between index of refraction and position of the charge-transfer maxima, although deviations occur for complex C in dichloromethane, dioxan, and ethanol. It is noted in the case of complex G (iodine–naphthalene) that the ground state of this complex is somewhat polar and it is significant that this complex exhibits only small solvent shifts. The deviations which occur for complex C in dichloromethane, dioxan, and ethanol cannot be rationalized at this time.

It is surprising that the relationship between index of refraction and solvent shifts for charge-transfer absorption bands, which was observed by Ham[8] during pressure studies on iodine complexes, has escaped the notice of other authors. The interpretation of this correlation follows from simple theoretical considerations.

Since the donors and ground states of the

TABLE *

Positions of the charge-transfer maxima (mμ) in various solvents

		Complex								
Solvent	n_D^{20}	A	B	C	D	E	F	G	H	I
Methanol	1·331	—	—	497	454	510	—	—	—	—
Acetonitrile	1·344	—	374	505	480	544	690	—	430	395
Ethanol	1·361	—	—	497	—	—	—	—	435	408
n-Hexane	1·375	465	—	—	—	—	—	—	—	—
n-Heptane	1·388	466	—	—	—	—	—	360	—	—
Dichloromethane	1·424	—	—	521	—	—	—	357	—	—
Dioxan	1·425	469	—	504	—	—	—	—	—	—
Cyclohexane	1·429	475	387	510	500	558	704	355	—	—
Chloroform	1·445	486	390	515	—	—	—	—	—	—
Carbon tetrachloride	1·463	484	395	516	—	—	—	360	—	—

A, 1,3,5-Trinitrobenzene–*NN*-dimethylaniline. B, 1,3,5-Trinitrobenzene–hexamethylbenzene. C, Chloranil–hexamethylbenzene. D, *m*-Dinitrobenzene–*NNN′N′*-tetramethyl-*p*-phenylenediamine. E, 2,4,6-Trinitrotoluene–*NNN′N′*-tetramethyl-*p*-phenylenediamine. F, Chlorobenzoquinone–*NNN′N′*-tetramethyl-*p*-phenylenediamine. G, Iodine–naphthalene. H, Chloro-*p*-benzoquinone–hexamethylbenzene. I, *p*-benzoquinone–hexamethylbenzene.

* Data taken from Reference 1 and references therein.

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[1] K. M. C. Davis and M. C. R. Symons, *J. Chem. Soc.*, 1965, 2079.
[2] E. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253, 3261.
[3] J. N. Murrell, *Quart. Rev.*, 1961, **15**, 191.
[4] S. F. Mason, *Quart. Rev.*, 1961, **15**, 287.
[5] G. Briegleb, "Electronen-Donator Komplexe," Springer-Verlag, Berlin, 1961, p. 38.
[6] R. Foster and D. L. Hammrick, *J. Chem. Soc.*, 1954, 2685.
[7] H. M. Rosenberg and D. Hale, in the press.
[8] J. Ham, *J. Amer. Chem. Soc.*, 1954, **76**, 388.

complexes which have been considered have small or no permanent dipoles, it may be expected that the polar excited state of the complexes should experience the major coulombic solvent interactions. In the absence of electronic excitation, the solvent molecules are randomly oriented. The interval of an electronic transition to a Franck–Condon state does not allow sufficient time for effective orientation of the permanent dipoles of the solvent. Therefore, stabilizing interactions must be attributed to the polarizability of the solvent molecules which is related to index of refraction. Bathochromic shift occurs with increasing dielectric constant of the solvent. The unconfirmed prediction[5,6] for correlation with dielectric constant results from inadequate consideration of the Franck–Condon restrictions.

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