Spectroscopic Studies of Solute–Solvent Interactions

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1 Introduction

In the past two decades, there have been numerous studies of solute–solvent interactions by spectroscopic and other methods. Some of the important types of interaction considered in such studies are as follows: van der Waals attractive forces attributed to dispersion interactions; dipole–induced-dipole and dipole–dipole interactions; and specific short-range interactions. Several theoretical models have been proposed to interpret solvent-induced changes of various spectral parameters of solute molecules due to non-specific interactions. The spectral parameters generally studied are electronic and i.r. band frequencies and intensities, n.m.r. chemical shifts and spin–spin coupling constants, and so on. Most of the studies make use of the continuum model or Onsager's reaction field[1,2] to obtain expressions for changes in the spectra of solute molecules in polar and non-polar solvents in terms of solvent parameters. Use of spectroscopic methods to study specific interactions between solute and solvent molecules is well-documented in the literature. In this review, we have attempted to give a concise account of the highlights of the different treatments employed to investigate non-specific solute–solvent interactions through changes in spectra, and to illustrate the common and unifying features in the various treatments. We have included a discussion of solvent effects on the electronic spectra of electron donor–acceptor complexes in view of the interesting spectral shifts they exhibit depending on the nature of interaction in the ground states of complexes. Analogy between solvent and pressure effects in spectra is indicated and analysis of equilibria in systems involving specific interactions briefly discussed. This review is not intended to be an exhaustive article covering all experimental details and correlations of data, and we have limited ourselves to the bare discussion of the quantitative treatments of solvent effects on spectra. We would like to apologize for any oversight or errors in judgement.

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[1] L. Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486.

[2] C. J. F. Bottcher, 'Theory of Electric Polarization', Elsevier, Amsterdam, 1952.

2 Free Energy of Interaction in Liquids

The potential energy of a system of interacting particles can be obtained in two ways. One approach is to sum over pair-wise interactions of all molecules as described by London[3] for computing the lattice energy of a variety of non-polar substances. An alternative method is to consider interactions between a specific molecule and its surroundings, considering the latter as a uniform infinite dielectric.[4–9] In the latter model, the work done in transferring a molecule from empty space into a cavity inside the dielectric is calculated. The field produced by the molecule polarizes the dielectric which in turn sets up a field at the centre of the cavity. The interaction energy is then obtained from the coupling between the dipole moment and the local field.

For polar substances, the free energy of interaction is given by equations (1) and (2). Here, μ_0 is the dipole moment, D the dielectric permittivity of the

$$F_\mu = -\tfrac{1}{2}\mu_0{}^2 g_0/(1 - \alpha g_0) \tag{1}$$

$$g_0 = \frac{(D-1)}{(2D+1)}\frac{2}{a^3} \tag{2}$$

medium, a the radius of the molecule, and α its static electronic polarizability. If α is replaced by $(n^2 - 1)/(n^2 + 2)a^3$, where n is the refractive index of the substance, equation (1) becomes equation (3). Since the free energy of interaction

$$F_\mu = -\tfrac{1}{3}\mu_0{}^2 \frac{(n^2 - 1)}{\alpha}\frac{(D-1)}{(2D+n^2)} \tag{3}$$

depends upon the square of the dipole moment, the dispersion contribution to the free energy should also be included because the mean square value of the (time-varying) dipole moment is not zero even for non-polar molecules. The dispersion contribution is given by equation (4), where $g = (2n^2 - 1)/(2n^2 + 1)a^3$

$$F = -\tfrac{1}{8}\langle m^2\rangle g \tag{4}$$

and $\langle m^2\rangle$ is the average square of the oscillating dipole moment of the free molecule. The partial molar dispersion energy of a solute in a solvent in the limit of infinite dilute solution is given by equation (5), where subscripts 1 and 2

$$F = -\tfrac{1}{4}\langle m_2{}^2\rangle g \frac{\nu_1}{\nu_1 + \nu_2} \tag{5}$$

refer to solvent and solute, respectively, and ν is the mean absorption frequency.

For non-spherical molecules, an ellipsoidal approximation[10] is made and g is

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[3] F. London, *Z. Physik*, 1930, **63**, 245.
[4] A. R. Martin, *Trans. Faraday Soc.*, 1937, **33**, 191.
[5] R. P. Bell, *Trans. Faraday Soc.*, 1935, **31**, 1557.
[6] J. G. Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351.
[7] W. B. Bonnor, *Trans. Faraday Soc.*, 1951, **47**, 1143.
[8] B. Linder, *J. Chem. Phys.*, 1960, **33**, 668.
[9] B. B. Howard, B. Linder, and M. T. Emerson, *J. Chem. Phys.*, 1962, **36**, 485.
[10] I. G. Ross and R. A. Sack, *Proc. Phys. Soc.*, 1950, **B63**, 893.

given by equations such as (6) and (7). Here, s is the potential produced in a

$$g_a = \frac{3(D-1)\,A_a\,(1-A_a)}{[D-(D-1)A_a]abc} \tag{6}$$

$$A_a = \frac{abc}{2}\int_0^\infty \frac{\mathrm{d}s}{\{(s+a^2)^3\,(s+b^2)\,(s+c^2)\}^{\frac{1}{2}}} \tag{7}$$

uniform dielectric field, a, b, and c are the semi-axes of the ellipsoid considered, and A_a is one of three shape factors given by Osborn and Stoner.[11]

3 Electronic Spectra

Absorption and Emission Band Shifts.—Mataga and Kubota,[12] Nicol,[13] and Rao[14] have reviewed some aspects of solvent effects on electronic spectra. One of the early treatments of the effect of solvents on the electronic absorption spectra of polar and non-polar molecules in solutions is that due to Bayliss and McRae,[15] who showed that electronic transitions of non-polar molecules dissolved in polar and non-polar solvents suffer a red shift, the magnitude of the shift depending on the solvent refractive index. For polar solutes in non-polar solvents, a red shift is predicted if the solute dipole moment increases during the transition. If the solute dipole moment decreases during the transition, a blue or red shift is observed depending on whether dispersion effects are respectively less or more than the effects due to the change in dipole moment and refractive index of the solvent. For polar solutes in polar solvents, a blue shift is predicted if the solute dipole moment decreases during the transition and a red shift is predicted if the dipole moment increases. Generally, n–π^* transitions suffer blue shifts whereas π–π^* transitions suffer red shifts in polar solvents because of the preferred stabilization of the non-bonding orbital in the former and the anti-bonding orbital in the latter case.[14] The magnitude of the shift depends on the change in dipole moment of the solute during transition, the refractive index of the solvent, the dipole moment of the solute molecule, the sizes of the solute and solvent molecules, and London dispersion forces.

Longuet-Higgins and Pople,[16] on the basis of a perturbation approach, derived equation (8) for band shifts of non-polar solutes in non-polar solvents; α_A and α_B

$$\Delta\nu = \tfrac{1}{8}\alpha_B Z R^{-6}\,(\tfrac{1}{4}E\alpha_A + M^2) \tag{8}$$

are the molecular polarizabilities of the solute and solvent molecules respectively, M and E are the dipole moment and the energy of the transition respectively,

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[11] J. A. Osborn, *Phys. Rev.*, 1945, 67, 351; E. C. Stoner, *Phil. Mag.*, 1945, 36 803.

[12] N. Mataga and K. T. Kubota, 'Molecular Interactions and Electronic Spectra', Marcel Dekker, New York, 1970.

[13] M. F. Nichol, *Appl. Spectroscopy Rev.*, 1974, **8**, 183.

[14] C. N. R. Rao, 'Ultraviolet and Visible Spectroscopy', Butterworths, London, 3rd Edn., 1975.

[15] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, 1954, **58**, 1002, 1006.

[16] H. C. Longuet-Higgins and J. A. Pople, *J. Chem. Phys.*, 1957, **27**, 192.

and Z is the number of solvent molecules surrounding each solute molecule at a mean distance of R.

Employing second-order perturbation theory, McRae[17] proposed that the band shift in solutions is given by equation (9), where $\langle \Delta W \rangle$, the difference

$$\Delta\nu = \langle \Delta W \rangle / h \tag{9}$$

between the mean stabilization energies, is calculated by making use of the dipole moments of the solute molecule in the ground and excited states, the polarizability of the solute molecule, and the refractive index of the solvent medium. In its specific form, $\Delta\nu$ is given by equation (10), where n is the refractive

$$\Delta\nu = \text{dispersion term} + B\frac{n^2 - 1}{2n^2 + 1} + C\left(\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}\right) + \text{Stark effect term} \tag{10}$$

index, D the dielectric permittivity of the solvent, and B and C involve the molecular volume of the solute molecule and its dipole moment in the electronic ground and excited states.

In equation (10), the first term due to dispersion effects accounts for the effect of non-polar solvents on non-polar solutes. The second term represents the contribution from the interaction of the solute permanent dipoles with the solute-induced solvent dipoles. The third term represents the interaction between permanent solute and solvent dipoles, and one can evaluate the excited-state dipole moment of the solute from the constant C. The ability of the different terms in equation (10) to explain solvent shifts in different types of solvent system has been examined for both π–π^* and n–π^* transitions of organic molecules, including dyes.[17–19] n–π^* Transition energies of C=O and C=S groups in different solvents are found to vary linearly with the stretching frequencies in the same solvents, indicating the importance of ground-state stabilization by solvents.[18,19]

The London dispersion term in equation (10) (causing red shifts with respect to gas phase) also involves the function $(n^2 - 1)/(2n^2 + 1)$. A plot of spectral shifts of non-polar solutes like aromatic hydrocarbons against $(n^2 - 1)/(2n^2 + 1)$ is found to be linear. The linearity is strictly expected for non-polar solvents (aliphatic hydrocarbons and so on). It is not surprising, therefore, that different linear plots are found for different families of solvents, particularly when some of them, like ketones, are quite polar.[13,20] It is noteworthy that solvent shifts of polar solutes in non-polar solvents are also accounted for by the $(n^2 - 1)/(2n^2 + 1)$ term, although the observed solvent shift would be due to the combined effect of the first two terms in equation (10). One could, in principle, rationalize spectral shift data in different types of solvent by incorporating a dielectric permittivity or Stark effect term. This has been done by Nicol,[13] who found

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[17] E. G. McRae, *J. Phys. Chem.*, 1957, **61**, 562; *Spectrochim. Acta*, 1958, **12**, 192.
[18] A. Balasubramanian and C. N. R. Rao, *Spectrochim. Acta*, 1962, **18**, 1337.
[19] M. Ito, K. Inuzuka, and S. Imanishi, *J. Amer. Chem. Soc.*, 1960, **82**, 1317.
[20] O. E. Weigang and D. D. Wild, *J. Chem. Phys.*, 1962, **37**, 1180.

linear plots of shifts in the absorption maxima of aromatic hydrocarbons in a variety of solvents by employing equation (11).

$$\Delta\nu = A\left(\frac{n^2-1}{2n^2+1}\right) + B\left(\frac{(D-n^2)(2D+n^2)}{D(n^2+2)^2}\right) + C\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right) \qquad (11)$$

Equation (11) is similar to equation (10), and shows that the dispersion effect or the refractive index term of the solvent alone cannot account for spectral shifts in polar solvents.

Equation (10) can be simplified to study the effect of the dielectric permittivity term (third term) alone by measuring band shifts in two polar solvents of nearly the same refractive index but different dielectric permittivity.[18,19] From such a study, one can obtain estimates of the excited-state dipole moments of solute molecules. Diethyl ether ($n = 1.356$ and $D = 4.3$) and acetonitrile ($n = 1.344$ and $D = 37.5$) seem to make a good pair of such solvents. Basu[21] has given a detailed quantum mechanical treatment of frequency shifts in solutions by considering Onsager's reaction field model. Basu evaluates the stabilization energy of electronic states due to solute–solvent interaction in terms of second-order perturbation theory. The main framework of this treatment is not very different from that in earlier treatments.

A general explanation of solvent effects on emission spectra has been given by Lippert.[22] The fluorescent molecule has a higher dipole moment in the excited state. If there is large dipole interaction in solution, the emitted photon will have much less energy than the absorbed photon, *i.e.* there will be a large Stokes shift. Thus, emission spectra in polar solvents are found to occur at longer wavelengths than in non-polar solvents. Lippert calculated dipole moments of excited states of molecules from their spectral shifts using equation (12), where

$$(\nu_A - \nu_F) = \frac{2\Delta f}{hca^3}(\mu_e - \mu_g)^2 + \text{constant} \qquad (12)$$

ν_A and ν_F are the 0–0 band maxima (in cm^{-1}) of the absorption and emission bands, μ_e and μ_g are the dipole moments of the excited and ground states of the fluorescing molecule, and Δf is the reorientation polarization factor defined by equation (13). A plot of $(\nu_A - \nu_F)$ values against Δf of solvents yields a linear

$$\Delta f = \frac{(D-1)}{(2D+1)} - \frac{(n^2-1)}{(2n^2+1)} \qquad (13)$$

relation whose slope gives μ_e if μ_g is known. Similar treatments for the determination of μ_e have been described by other authors.[23,24] Dipole moments in

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[21] S. Basu, in 'Advances in Quantum Chemistry', ed. P. O. Lowdin, Vol. I, Academic Press, New York, 1964.

[22] E. Lippert, *Z. Electrochem.*, 1957, **61**, 962.

[23] L. M. Kutsyna and L. A. Ogurtsova, *Bull. Acad. Sci. U.S.S.R., Ser. phys.*, 1963, **27**, 733.

[24] N. G. Bakhshiev, *Optics and Spectroscopy*, 1962, **13**, 104.

excited states have been obtained by the measurement of fluorescence polarization induced by electric fields.[25–28] It is to be noted that historically, it was Sambursky and Wolfson[29] who first correlated $(\nu_A - \nu_F)$ with a solvent parameter. They found that a plot of $(\nu_A - \nu_F)$ of anthracene against $[2(n^2 + 2)^2(2D + 1)(D - 1)]/9(2D + n^2)^2$ of solvents was linear. Veljković[30] extended this study and showed that the energy of the fluorescence maximum, as well as $(\nu_A - \nu_F)$ of anthracene, was proportional to the polarizability of the solvent. These correlations were by no means universal and showed deviations when solvents were polar.

Liptay[31–35] has carried out extensive theoretical and experimental studies on the effect of solvents on the absorption and emission spectra of molecules. Besides deriving expressions for solvent effects on the electronic absorption and emission spectra, he obtained good values of dipole moments in excited states, and compared such values determined by the field dependence of optical absorption and fluorescence and by the solvent dependence of absorption and fluorescence. Liptay's expression for solvent shift of absorption maxima is given by equation (14), where F is the reaction field induced by the solute in an Onsager

$$\Delta\nu = -2a^{-3}f'D' - (\mu_e - \mu_g)F/hc \qquad (14)$$

cavity, f' is the refractive index function $(n^2 - 1)/(2n^2 + 1)$, and D' represents dispersive interactions. Equation (14) gives consistent results for a large number of polar solute molecules. Since $f' > 0$ and $D' > 0$, the first term in equation (14) always gives a red shift; this is nothing but the polarization red shift of non-polar solutes in non-polar solvents. Solvation of a polar solute with $\mu_e < \mu_g$ would result in a blue shift.

Before closing our discussion of quantitative treatments of solvent effects on electronic spectra of molecules, a comment on the work of Weigang and Wild[20] referred to earlier would be in order. In treating solvent effects on the spectra of non-polar solutes, these workers related the spectral shifts to the average density of specific classes of bonds. Relative shift strengths estimated by them could be correlated with bond dipole moments and polarizabilities and could account for the effect of polar solvents on spectra. Although microscopic in nature, the

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[25] J. Czekalla, *Z. Electrochem.*, 1960, **64**, 1221.

[26] J. Czekalla and K. O. Meyer, *Z. phys. Chem.*, 1961, **27**, 185.

[27] J. Czekalla and G. Wick, *Z. Electrochem.*, 1961, **65**, 727.

[28] J. Czekalla, W. Liptay, and K. O. Meyer, *Ber. Bunsengesellschaft phys. Chem.*, 1963, 67, 465.

[29] S. Sambursky and G. Wolfson, *Phys. Rev.*, 1942, 62, 357.

[30] S. R. Veljković, *Trans. Faraday Soc.*, 1957, **53**, 1181.

[31] W. Liptay, 'Modern Quantum Chemistry', Pt II and Pt III, Academic Press, New York, 1965.

[32] W. Liptay, *Z. Naturforsch.*, 1965, **20a**, 1441; 1966, **21a**, 1605.

[33] W. Liptay, W. Eberlein, H. Weidenberg, and O. Elflein, *Ber. Bunsengesellschaft phys. Chem.*, 1967, **71**, 548.

[34] W. Liptay, H. Weisenberger, F. Tiemann, W. Eberlein, and G. Konopka, *Z. Naturforsch.*, 1968, **23a**, 377; W. Liptay, B. Dumbacher, and H. Weisenberger, *ibid.*, p. 1601; W. Liptay, H.-J. Schlosser, and B. Dumbacher, *ibid.*, p. 1613; see also W. Liptay, *Angew. Chem.*, 1969, **8**, 177, 195.

[35] W. Liptay, in 'Excited States', ed. E. Lim, Academic Press, New York, 1973, Vol. I.

general utility of such a treatment is limited. A treatment was proposed by Abe *et al.*[36] in which they related spectral shifts to 'lattice parameters' of solvents in terms of molar volumes, but this approach again is rather imprecise and is not of much relevance.[13,37]

Kosower[38] has given a solvent polarity scale based on the effects of solvents on the intramolecular charge-transfer band of pyridinium iodide. This scale is defined in terms of Z values of solvents given by the energies in kcal mol^{-1} of the absorption maxima of 4-methoxycarbonyl-1-ethylpyridinium iodide. The solvents listed in this scale vary from non-polar to highly polar and hydrogen-bonding solvents. The changes in charge-transfer absorption spectra are so large and their measurement so readily made that Z values have been preferred by physical organic chemists over the Y values[39] obtained from solvolysis kinetics of t-butyl chloride. CTTS (charge-transfer-to-solvent) spectra of I^- and other systems have been correlated with Z values.[40,41] While such empirical parameters may be useful for correlations, they do not provide the exact mechanism of solvent effects, considering the wide variation in the nature of solvents included in obtaining the scale.

Absorption Band Intensities.—On the basis of the classical oscillator theory of light interaction, Chako[42] long ago gave a relation for the increase in intensity of electronic absorption bands of organic molecules in solution phase relative to the vapour phase in terms of solvent refractive index. It has since been shown[43–47] that in explaining solvent effects on electronic band intensities, polarization of the solute molecule by the solvents and the corresponding change in transition moment should also be considered. Considering the solute transition dipole at the centre of a spherical cavity, Schuyer[45] included the Onsager reaction field factor and proposed a relation for $f_{\text{soln}}/f_{\text{vap}}$ in terms of the solvent refractive index.

Liptay[32] considered changes in the dipole moments of the ground and excited states of solute molecules and proposed that the perturbed intensity was proportional to R^2. The reaction field R is given by equation (15), where g_{n} and g_{D}

$$R = g_{\text{D}}(1 - g_{\text{D}}\alpha)^{-1}\mu_{\text{g}} + \tfrac{1}{2}g_{\text{n}}(1 - g_{\text{n}}\alpha)^{-1}(\mu_{\text{e}} - \mu_{\text{g}}) \qquad (15)$$

are the reaction field factors and α is the polarizability of the solute molecule

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[36] T. Abe, Y. Amake, T. Nishioka, and H. Azumi, *Bull. Chem. Soc. Japan*, 1966, **39**, 845.

[37] M. Nicol. J. Swain, Y. Y. Shun, R. Merin, and R. H. H. Chen, *J. Chem. Phys.*, 1968, **48**, 3587.

[38] E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253, 3261.

[39] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

[40] P. C. Dwivedi and C. N. R. Rao, *Spectrochim. Acta*, 1970, **26A**, 1535.

[41] M. J. Blandamer and M. F. Fox, *Chem. Rev.*, 1970, **70**, 59.

[42] N. Q. Chako, *J. Chem. Phys.*, 1934, **2**, 644.

[43] O. E. Weigang, jun., *J. Chem. Phys.*, 1960, **33**, 892; 1964, **41**, 1435.

[44] N. S. Bayliss, *J. Chem. Phys.*, 1950, **18**, 292.

[45] J. Schuyer, *Rec. Trav. chim.*, 1953, **72**, 933.

[46] G. W. Robinson, *J. Chem. Phys.*, 1967, **46**, 572.

[47] N. S. Bayliss and G. Wills-Johnson, *Spectrochim. Acta*, 1968, **24A**, 551, 563.

(assumed to be the same for the ground and excited states). Weigang[43] has derived the more general equation (16), considering various transition moments,

$$\frac{f_{\text{soln}}}{f_{\text{vap}}} = \frac{(n^2 + 2)^2}{9n}\left[1 + A\,\frac{n^2 - 1}{2n^2 + 1} - C\left(\frac{D - 1}{D + 2} - \frac{n_0{}^2 - 1}{n_0{}^2 + 2}\right)\right]^2 \qquad (16)$$

where n_0 is the solvent refractive index extrapolated to zero frequency and n the refractive index at the mean frequency at which measurements are made. A and C contain μ_{0i}, the transition moment of the solute transition being perturbed, as well as μ_{0j} and μ_{ij}, the moments of other solute transitions to the ground and higher states. Bayliss and Wills-Johnson[47] have treated variations in intensities in the solution phase on the basis of generalized dispersion interactions between solvents and solutes expressed in terms of a fluctuating electric field in the cavity. Linder's treatment[8] of long-range dispersion interactions was employed to explain the perturbation of band intensities of saturated ketones and nitroparaffins in solution.

Relation between Solvent Shifts and Pressure Effects.—Band shifts in the electronic spectra of molecules induced by solvents are similar to those produced by the application of pressure. Such a relationship was pointed out by Robertson and co-workers,[48,49] who found increasing red shifts of the π–π^* bands of aromatic hydrocarbons with increasing pressure (*i.e.* density of the solvent medium) in accordance with the theory of solvent effects. Agreement with McRae's theory[17] could be obtained by accounting for the density dependence of n and D of the solvent. The major effect of pressure was on the distribution of the solvent molecules around the solute. The rate of change of frequency with density could be correlated with the oscillator strength, following the suggestion of Longuet-Higgins and Pople.[16] Offen[50] has also studied spectral shifts due to pressure in aromatic hydrocarbons and has found the shifts to be proportional to the square of the density of the solute. It appears that compression of the solute should also be considered besides the variation of n and D. Furthermore, pressure-induced shifts vary for different transitions of the same molecule. While $\Delta\nu/\Delta p$ varies for different absorption bands of phenanthrene, it appears to be the same for the fluorescence and the phosphorescence bands.[13,51]

Spectra of Electron Donor–Acceptor (EDA) Complexes.—Solvent effects on the spectra and equilibria of electron donor–acceptor (EDA) complexes have been studied by several workers.[52–55] These systems are discussed here because of the

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[48] W. W. Robertson, O. E. Weigang, jun., and F. A. Matsen, *J. Mol. Spectroscopy*, 1957, **1**, 1.

[49] W. W. Robertson and A. D. King, jun., *J. Chem. Phys.*, 1961, **34**, 1511.

[50] H. W. Offen, *J. Chem. Phys.*, 1965, **42**, 430; see also *J. Chem. Phys.*, 1969, **46**, 4509.

[51] M. Nicol, W. D. Ellenson, and R. Geffner, in 'Organic Scintillators and Liquid Scintillation Counting', ed. D. L. Horrocks and C. T. Reng, Academic Press, London, 1971.

[52] R. S. Mulliken and W. B. Person, 'Molecular Complexes', Wiley-Interscience, New York, 1969.

[53] C. N. R. Rao, S. N. Bhat, and P. C. Dwivedi, *Appl. Spectroscopy Rev.*, 1971, **5**, 1.

[54] H. W. Offen, in 'Molecular Complexes', ed. R. Foster, Elek Science, London, 1973, Vol. I.

[55] M. Tamres, in 'Molecular Complexes', ed. R. Foster, Elek Science, London, 1973, Vol. I.

interesting variations of solvent-induced spectral shifts exhibited by them depending on the strength of interaction between the D and A units in the ground state. Equation (14) when applied to weak π–π^* complexes with $\mu_e \gg \mu_g$ predicts the observed solvent red shift. The first term in this equation contributes *ca.* 1000 cm^{-1} (or less) to the red shift of a transition with an oscillator strength of *ca.* 0.1. Solvent effects in weak complexes are much greater (*ca.* 2500 cm^{-1}), which may partly be due to the second term in this equation and also possibly to the solvent Stark effect which becomes important when the dielectric permittivity is sufficiently high. Voigt[56] observed a linear dependence of ν_{CT} on $f' = (n^2 - 1)/(2n^2 + 1)$ in non-polar solvents. The observation that a smaller slope is obtained for perfluorocarbon solvents compared with hydrocarbon solvents reflects the importance of the term D' in equation (14). If the first term is mainly responsible for the solvent effect, extrapolation to $f' = 0$ $(n = 1)$ should give ν_0. This is nearly the case in benzene–TCNE where the difference between predicted and observed ν_0 is 1000 cm^{-1}.

In highly polar solvents, some of the π–π complexes show blue shifts.[26,57,58] Highly polar solvents may significantly modify the complex through environmental co-operative action. It would appear that a general solvent shift theory may be inapplicable and other concepts such as the solvation of the no-bond and dative structures may be necessary to explain net blue shifts with increasing dielectric permittivity.[58] The CT process could indeed be in competitive equilibrium with strongly bound solvation shells surrounding the solute components of the complex.[59] Recently, however, Rao and Dwivedi[60] have employed the ether–MeCN binary solvent system[18,19] and have obtained the right signs of the solvent shifts of the CT bands. It is possible that use of the mixed solvent system is superior to using assorted polar solvents since it provides the shift mainly due to increments in solvent dielectric permittivity. It is interesting that Rao and Dwivedi obtained solvent red shifts in the case of weak complexes (π–π type) which have a small contribution from the dative structure in the ground state, and blue shifts in the case of strong complexes (n–σ type) with major contribution from the dative structure. Further, the values of μ_e estimated by this method are similar to the values obtained from the electric field dependence of CT maxima. For weak complexes, $\mu_e > \mu_g$ and for strong complexes, $\mu_e < \mu_g$, as we would expect.

Solvent effects on the fluorescence spectra of EDA complexes are described by equation (12), and μ_e of complexes can be readily estimated from Lippert plots. Electron-donor molecules like *NN*-diethylaniline (DEA) when mixed with aromatic molecules give rise to a broad, structureless emission band to the red of the fluorescence band of the aromatic hydrocarbon.[61,62] This anomalous fluores-

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[56] E. M. Voigt, *J. Phys. Chem.*, 1966, **70**, 598.
[57] K. M. C. Davis and M. C. R. Symons, *J. Chem. Soc.*, 1965, 2079.
[58] H. W. Offen and M. S. F. A. Abidi, *J. Chem. Phys.*, 1966, **44**, 4642.
[59] S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.*, 1965, 2048.
[60] C. N. R. Rao and P. C. Dwivedi, *J. Chem. Phys.*, 1973, **59**, 1555.
[61] H. Leonhardt and A. Weller, *Ber. Bunsengesellschaft phys. Chem.*, 1963, **67**, 791.
[62] A. Weller, *Pure Appl. Chem.*, 1968, **16**, 115.

cence is ascribed to the formation of an exciplex: $^1A^* + D \rightarrow {}^1(A^-D^+)$. By using appropriate components, emission can be found from exciplexes formed by excited donor molecules (D^*) as well. The position of the exciplex emission band depends on the ionization potential of the donor and electron affinity of the acceptor.[63] Polar solvents produce a red shift and decrease the intensity of the exciplex band.[64] By examining the variation of the emission maximum with solvent polarity, the dipole moment of an exciplex can be estimated. In the case of DEA–anthracene system,[65] the dipole moment of the exciplex is estimated to be 12.5 ± 2 D. This value corresponds to a CT complex in which the charged components are separated by a distance of 3—3.5 Å, but the dipole moment is somewhat lowered by induction effects.

Other than the dielectric theory, solvent effects on the spectra of EDA complexes have been discussed in terms of geometrical modifications in the donor–acceptor pair when present in a condensed medium (bond compression model).[54] The modification of the absorber by the solvent cage is a bond compression which implies a decrease in the distance between D and A and possibly changes in their mutual orientation.[66] Such bond compression may be treated as being due to the mechanical pressure of the medium.[48–50,67] Although this model may not provide a complete picture of solvent effects, we arrive at conclusions similar to those of Kroll,[68] who treated the effect of the dielectric on the potential energy surfaces along the distance co-ordinate. The suggestion that the geometry of an EDA complex is different in the vapour and in solution phases is supported by the large solvent effects. As suggested by Offen,[54] bond compression could be treated by the dielectric theory by taking into account the difference in polarizability of the ground and CT states. Apart from the above treatments, it has also been shown[53,57,69] that an essentially non-ionic complex AD may ionize in a solvent of high ionizing power giving $A^-_{\mathrm{solv}} + D^+_{\mathrm{solv}}$. The values of equilibrium constants for EDA complex formation are known to vary with solvent and this aspect has been dealt with elsewhere in the literature.[53,70]

Hydrogen-bonding solvents cause marked blue shifts of n–π^* transitions of chromophores.[14,18] Any interpretation of these shifts should consider stabilization of the excited state by hydrogen-bonding, as pointed out by Pimentel.[71] Such stabilization of excited states is best measured by studying solvent effects on fluorescence spectra. Extensive MO calculations have been reported in the literature on a variety of hydrogen-bonded systems,[72,73] but studies on hydrogen-

[63] H. Knibbe and A. Weller, *Z. phys. Chem.*, 1967, **55**, 95, 99.
[64] H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, 1967, **47**, 1183.
[65] H. Knibbe, Doctoral Thesis, Univ. of Amsterdam, 1969; see also K. G. Rao, V. V. Bhujle, and C. N. R. Rao, *Spectrochim. Acta*, 1975, **31**A, 885.
[66] J. Prochorow and A. Tramer, *J. Chem. Phys.*, 1966, **44**, 4545; *ibid.*, 1967, **47**, 775.
[67] P. J. Trotter, *J. Amer. Chem. Soc.*, 1966, **88**, 5721.
[68] M. Kroll, *J. Amer. Chem. Soc.*, 1968, **90**, 1097.
[69] R. L. Ward, *J. Chem. Phys.*, 1963, **39**, 852.
[70] R. Foster, 'Organic Charge-Transfer Complexes', Academic Press, New York, 1969
[71] G. C. Pimentel, *J. Amer. Chem. Soc.*, 1957, **79**, 3323.
[72] P. A. Kollman and H. C. Allen, *Chem. Rev.*, 1972, **72**, 283.
[73] A. S. N. Murthy and C. N. R. Rao, *J. Mol. Structure*, 1970, **6**, 1253.

bonding in electronically excited states of molecules are limited. There is some spectroscopic evidence[18,74] to indicate that hydrogen bonds are weaker in the excited state than in the ground state. On the basis of extended Hückel calculations, Hoffmann and co-workers[75] showed that hydrogen-bond energy in the pyridine–water system is lower by 0.8 kcal in the excited state. Rao and Murthy,[76] on the basis of CNDO calculations, have shown that hydrogen bonds formed by carbonyl compounds with H_2O and MeOH are slightly weaker in the excited state than in the ground state. Similar conclusions about excited-state stabilization by hydrogen-bonding have been reported by other workers.[77–79]

4 Infrared Spectra

Solvent-induced i.r. frequency shifts were briefly reviewed some time ago by Hallam[80] and Rao.[81] Kirkwood, Bauer, and Magat[82,83] gave the well-known relationship between the band shift of a diatomic oscillator and the dielectric permittivity of the solvent on the basis of Onsager's reaction field theory [equation (17)], where $C = 10^{28}(\mu_1^2 + 2\mu_0\mu_2)/(2\pi\nu_0 c)^2 Ia^3$. Here, a is the radius

$$\frac{\Delta\nu}{\nu} = C\frac{D-1}{2D+1} \tag{17}$$

of the solute molecule, c the velocity of light, I the moment of inertia, and μ_0, μ_1, and μ_2 are the dipole moment and its first and second derivatives, respectively, with respect to internuclear distance. For HCl molecule, West and Edwards[84] modified this expression considering the non-equality of the molecular and cavity radii, and suggested that a^3 in the above relation should be replaced by expression (18), where b is the cavity radius. The relation does not hold good for solutions

$$b^3\left[\left(1+\frac{a^2}{b^2}\right)+\left(1-\frac{a^2}{b^2}\right)^3\right]^{-1} \tag{18}$$

in polar solvents.

Pullin[85] derived an expression for i.r. frequency shifts by taking into consideration changes in equilibrium bond lengths in solution and the electronic and atomic polarization of the solute molecule. He also assumed that the solute is not necessarily at the centre of a spherical cavity. Solvent shifts in HCl and acetone

[74] V. G. Krishna and L. Goodman, *J. Amer. Chem. Soc.*, 1961, **83**, 2042.

[75] W. Adam, A. Grimison, R. Hoffmann, and C. Z. de Ortiz, *J. Amer. Chem. Soc.*, 1968, **90**, 1509.

[76] C. N. R. Rao and A. S. N. Murthy, *Theor. Chim. Acta*, 1971, **22**, 392.

[77] W. H. DeJeu, *Chem. Phys. Letters*, 1970, **7**, 153.

[78] J. E. Del Bene, *Chem. Phys. Letters*, 1973, **23**, 287.

[79] S. Iwata and K. Morokuma, *Chem. Phys. Letters*, 1973, **19**, 94.

[80] H. E. Hallam, *Spectrovision (Unicam)*, 1961, 11; see also 'Infrared Spectroscopy and Molecular Structure', ed. M. Davies, Elsevier, Amsterdam, 1963, p. 405.

[81] C. N. R. Rao, 'Chemical Applications of Infrared Spectroscopy', Academic Press, London, 1963.

[82] J. G. Kirkwood, *J. Chem. Phys.*, 1939, **7**, 911.

[83] E. Bauer and M. Magat, *J. Phys. Radium*, 1938, 9, 319.

[84] W. West and R. T. Edwards, *J. Chem. Phys.*, 1937, **5**, 14.

[85] A. D. E. Pullin, *Spectrochim. Acta*, 1959, **13**, 125; *ibid.*, 1960, **16**, 12.

thus calculated were much lower than the observed values. It was suggested that the radius of the solvent rather than the solute molecule determines the cavity radius.

Buckingham[86] proposed a theoretical model to explain solvent effects on the i.r. band frequencies and intensities. The model Hamiltonian consisted of H_0, the harmonic oscillator part, H_a, the anharmonicity part, and U, the potential energy contribution from the solute–solvent interactions. Considering the free energy of interaction of the solvent as derived by Onsager's reaction field theory for spherical and ellipsoidal cavities, Buckingham derived equation (19). where

$$\begin{aligned}(\Delta\omega)_{m,n} &= [(W_{sn} - W_n) - (W_{sm} - W_m)]/hc \\ &= (n - m)\frac{B_e}{hc\omega_e}\left[U'' - 3\frac{A}{\omega_e}U'\right] \\ &= C + C_D\frac{D-1}{2D+1} + C_n\frac{n^2-1}{2n^2+1} \text{ (polar solvents)} \\ &= C + \tfrac{1}{2}(C_D + C_n)\frac{D-1}{2D+1} \text{ (non-polar solvents)} \qquad (19)\end{aligned}$$

$\Delta\omega$ is the frequency shift for the $m \rightarrow n$ transition, W_{sn} and W_{sm} are the energies of mth and nth vibrational levels of the oscillator in solution, and W_m, W_n, those in the vapour state. U' and U'' are the first and second derivatives of the interaction energy U with respect to normal co-ordinates, A/ω_e is the anharmonic constant, B_e is the rotational constant, $\Delta\omega$ and ω_e represent the observed frequency shift and the fundamental frequency for $0 \rightarrow 1$ transition, and C, C_D, and C_n are constants for the solute under consideration. Buckingham's treatment is certainly a great improvement over the KBM treatment and provides a good correlation of solvent shifts in i.r. spectra in the absence of specific interactions.

Polo and Wilson[87] derived equation (20) for the change in i.r. band intensities from vapour phase (A_g) to solution phase (A_s); n is the refractive index of the

$$A_s/A_g = (n^2 + 2)^2/9n \qquad (20)$$

solvent. They obtained the same expression by considering Debye's as well as Onsager's theory of dielectric polarization. The expression was found to be valid for n-hexane in non-polar solvents. Hirota[88] considered detailed electrostatic effects on intensities and gave the relationship (21). The expression was

$$\frac{A_s}{A_g} = \left[\frac{(n^2 + 2)(2D + 1)}{3(2D + n^2)}\right]^2 \qquad (21)$$

found to be applicable to C=O vibrations of a few compounds in carbon tetrachloride and chloroform. These treatments predict an increase in intensity in going from vapour to solution phase, which is not always true. Brown[89] has

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[86] A. D. Buckingham, *Proc. Roy. Soc.*, 1958, **A248**, 169.
[87] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, 1955, **23**, 2376.
[88] E. Hirota, *Bull. Chem. Soc. Japan*, 1953, **26**, 397.
[89] T. L. Brown, *Spectrochim. Acta*, 1957, **10**, 149.

explained this anomaly by considering the electric moment of the solute molecule in non-polar solvents as a function of the vapour-state electric moment, the dielectric permittivities of the solute and the solvent, the shape of the solute molecule, and the location of the dipole. The ratio of intensities for two different media having refractive indices n_1 and n_2 was found to be equation (22), the

$$\frac{A_2}{A_1} = \frac{n_1}{n_2}\left[\frac{1 + C - C/n_2^2}{1 + C - C/n_1^2}\right]^2 \tag{22}$$

sign and magnitude of the constant C depending on the geometry of the solute molecule.

Buckingham[86] has derived equation (23) for the intensity ratio A_s/A_g considering the refractive index of the solvent, its dielectric permittivity, the first derivative of the dipole moment of the solute molecule with respect to the normal

$$[A_s/A_g]^{\frac{1}{2}}\,\frac{2n^2 + 1}{3n\sqrt{n}} = 1 + 0.6\left(\frac{n^2 - 1}{2n^2 + 1}\right) + \left(\frac{2\mu_e\alpha'}{\mu' a^3} \times \frac{D - 1}{2D + 1}\right) \tag{23}$$

co-ordinate, and that of polarizability along the molecular axis; α' and μ' are the polarizability and dipole moment derivatives.

Bellamy and co-workers[90] plotted the $\Delta\nu/\nu$ values of one solute against the $\Delta\nu/\nu$ values of another solute in different solvents. Linear plots obtained in these cases were explained on the basis of specific solute–solvent interactions. Several authors have attempted to apply KBM and Buckingham expressions for relating solvent effects on i.r. frequencies of a variety of solute molecules. The general conclusion is that these expressions are useful where specific solute–solvent interactions are absent or when the interactions are uniformly similar. Thus, the KBM equation is found to hold good for the ν_{OH} in binary solvent mixtures.[91] The increase in ν_{OH} of alcohol solutes with the increasing concentration of the polar solvents has been explained on the basis of Buckingham's relationship.[92–94] Mann and Horrocks[95] have calculated the values of the first and the second derivatives of the solute–solvent interaction energy with respect to internal co-ordinates for HCN and DCN in various solvents using Buckingham's equation for solvent-induced frequency shifts, and found that the second derivative term makes significant contributions to the observed shifts.

5 Magnetic Resonance Spectra

Effects of solvents on n.m.r. chemical shifts and spin–spin couplings have been

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[90] L. J. Bellamy, H. E. Hallam, and R. L. Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120; L. J. Bellamy and R. L. Williams, *Proc. Roy. Soc.*, 1960, **A254**, 119; **A255**, 22; L. J. Bellamy and P. E. Rogasch, *Spectrochim. Acta*, 1960, **16**, 30.

[91] A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 371.

[92] H. Horak and J. Pliva, *Spectrochim. Acta*, 1965, **21A**, 911.

[93] H. Horak, J. Moravec, and J. Pliva, *Spectrochim. Acta*, 1965, **21A**, 919.

[94] H. Horak, J. Polakova, M. Jakoubkova, J. Moravec, and J. Pliva, *Coll. Czech. Chem. Comm.*, 1966, **31**, 622.

[95] R. H. Mann and W. Horrocks, jun., *J. Chem Phys.*, 1966, **45**, 1278.

reviewed by Laszlo[96] and Homer.[97] Solvent effects on n.m.r. chemical shifts are more difficult to understand than those in i.r. or electronic spectra since a number of factors contribute to nuclear screening in fluids. Several theories have been put forward to explain each of these factors. The general expression for the effects of solvents on nuclear screening, as proposed by Buckingham,[98] is equation (24);

$$\sigma_{\text{solvent}} = \sigma_B + \sigma_W + \sigma_A + \sigma_E + \sigma_S \qquad (24)$$

here, σ_B is the contribution due to the bulk magnetization of the sample, σ_W due to dispersion forces, σ_A due to magnetically anisotropic solvent molecules, σ_E due to the effect of polar solutes on the reaction field of solvent molecules as well as of the electric field due to permanent dipoles *etc.*, and σ_S due to specific interactions between solute and solvent molecules. Of these terms, we can account for σ_B fairly satisfactorily.[97,99] If we ignore or eliminate contributions from σ_S in the first instance (although specific interactions would generally be present in solution phase), we should, in principle, be able to obtain data of σ_W, σ_A, and σ_E. Data on σ_W can be obtained easily in the case of isotropic solvents, but in the case of asymmetric molecules (even if non-polar) it is not possible to get unique data on σ_W alone. In the case of polar solutes and solvents, we obtain information on the combined effects of σ_W, σ_A, and σ_E. Several models have been proposed for describing these three quantities of interest. When component molecules have similar shape and $\sigma_S = 0$, the screening of a nucleus varies linearly with the mole fraction of one of the components,[100] but the concentration dependence is more complex when the component molecules have dissimilar shapes.[101]

Three main models are employed in the evaluation of σ_W, σ_A, and σ_E. They are the gas-phase model, the cage model, and the continuum model.[97] In the gas phase, chemical shifts vary linearly with density[102] and gas-phase theories can be extended to the liquid phase by employing appropriate virial expansions. In the cage model, one considers only the first solvation shell. The continuum model employs the reaction field and is the one we are used to in the case of i.r. and electronic spectral shifts. In the present discussion, we are primarily interested in examining the formulations suggested for the evaluation of σ_W and σ_E.

Howard *et al.*[9] first employed the continuum model and derived equation (25),

$$\sigma_W = -\tfrac{3}{4}Bhg\frac{\nu_1\nu_2}{\nu_1 + \nu_2} \qquad (25)$$

where ν_1 and ν_2 are the mean absorption frequencies of the solute and solvent, respectively, and B is a constant. [Note that equation (25) is similar to equation

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[96] P. Laszlo, in 'Progress in Nuclear Magnetic Resonance Spectroscopy', ed. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon Press, Oxford, 1967, Vol. 2.

[97] J. Homer, *Appl. Spectroscopy Rev.*, 1975, 9, 1.

[98] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.

[99] W. C. Dickinson, *Phys. Rev.*, 1951, **81**, 717.

[100] M. J. Stephen, *Mol. Phys.*, 1958, **1**, 223.

[101] A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, 1957, **26**, 1647, 1651.

[102] See, for example, W. T. Raynes, A. D. Buckingham, and H. J. Bernstein, *J. Chem. Phys.*, 1962, **36**, 3481.

(5)]. The solvent parameter, g, is given by $(2n^2 - 1)/a^3(2n^2 + 1)$. If the coupling between electrostatic and dispersion forces is ignored, equation (25) becomes applicable to both polar and non-polar solutes. The values of σ_W vary to some extent depending on the choice of the method employed to evaluate ν_1 and ν_2 values.[103] While equation (25) has been employed by some workers to evaluate σ_W, expression (26), due to de Montgolfier,[104] seems to be more appropriate.

$$\sigma_W = -6\left[\frac{(n^2 - 1)^4}{(2n^2 + 1)^2(n^2 + 2)^2}\right]_{\text{solution}}\left[\frac{kB\Delta E}{\alpha}\right]_{\text{solute}} \tag{26}$$

In equation (26), α is the poarizability, ΔE is a transition energy roughly double the ionization energy, and k is an effective size factor. This equation has been used satisfactorily to correlate experimental chemical shifts.

From the cage model, Rummens *et al.*[105] have obtained the expression (27),

$$\sigma_W = -K\frac{3\pi B\alpha I}{(r_1 + r_2)^4 r_2{}^2}S \tag{27}$$

where S is a site factor, I is the ionization energy of the solvent, and K is an empirical scale factor. This equation satisfactorily predicts different σ_W values for protons at different sites in the same molecule. Rummens *et al.*[105] have also applied binary collision theory of gases to obtain σ_W for liquids by using the appropriate density.

Contributions to nuclear screening due to electric effects, σ_E, can be expressed in the form (28),[106] where E_z is the component of the electric field E in the bond

$$\sigma_E = -C_1\langle E_z\rangle - C_2\langle E^2\rangle \tag{28}$$

direction and C_1 and C_2 are constants which are determined by the nature of the bond and the magnetic nucleus concerned. Theoretical estimates of C_1 and C_2 are available for hydrogen,[97] but they are generally treated as empirical constants. In the continuum model, the solute is considered to be uniformly polarized by the reaction field as given by (29),[106] where n, μ, and α are the refractive index,

$$\langle R\rangle = \frac{2(D - 1)(n^2 - 1)}{3(2D + n^2)}\frac{\mu}{\alpha} \tag{29}$$

gas-phase dipole moment, and polarizability of the solute, respectively, and D is the static dielectric permittivity of the solvent. In the case of a fairly symmetrical solute, if $\langle R\rangle$ is parallel to μ, we can replace $\langle E_z\rangle$ in equation (28) by $R\cos\theta$ where θ is the angle between the bond containing the nucleus concerned and the direction of μ. While $\langle E^2\rangle$ in equation (28) is generally taken to be approximately $\langle R^2\rangle$, its contribution is sufficiently small to be ignored, particularly in the case of non-polar solvents. Buckingham[106] has also considered the importance of

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[103] V. P. Senthilnathan and S. Singh, *Chem. Phys. Letters*, 1973, **21**, 147.

[104] P. de Montgolfier, *J. Chim. phys.*, 1967, **64**, 639; 1968, **65**, 1618; 1969, **66**, 685.

[105] F. H. A Rummens, W. T. Raynes, and H. J. Bernstein, J. *Phys. Chem.*, 1968, **72**, 2111.

[106] A. D. Buckingham, *Canad. J. Chem.* ,1960, **38**, 300.

local solvent effects due to polar groups in a non-polar solute. In the case of a molecule with a quadrupole moment, ϕ, equation (30) applies.

$$R' = \frac{6(D-1)\phi}{(3D+2)r^5} \tag{30}$$

Buckingham *et al.*[98] have indeed found that relative shifts due to electric field effects vary linearly with $(D - 1)/(2D + 2.5)$ in the case of MeCN, as expected from equation (29). Diehl and Freeman[107] have proposed the proportionality (31), where ξ is a shape factor, based on the model of a point dipole residing

$$R'' \propto (D-1)/D + [n^2\xi/(1-\xi)] \tag{31}$$

at the centre of a spherical cavity. For a spherical molecule ($\xi = \frac{1}{3}$), (31) reduces to (29). By measuring solvent shifts of the methyl and methine proton resonances of paraldehyde, these workers essentially eliminated effects from σ_W, σ_A, and σ_S and showed that $\Delta\nu_{CH_3-CH}$ was linear with respect to $(D - 1)/(D + 2.86)$, as expected from (31).

There have been suggestions that equation (28) does not completely represent the electrical effects of solvents. For non-polar solutes in polar solvents, the field R_S has been described by equation (32),[104] where D and n refer to the solvent

$$\langle R_S{}^2\rangle = \frac{81}{16\pi^2}\,\frac{kT(D-n^2)(2D+n^2)}{D}\cdot\frac{1}{r^3} \tag{32}$$

and r is the radius of the solute cavity. This expression is not unlike the second term in equation (11), proposed by Nichol and co-workers[13,37] for the shifts of electronic absorption bands of non-polar solutes in polar solvents:

$$\langle R_S{}^2\rangle \propto \frac{(D-n^2)(2D+n^2)}{D(n^2+2)^2}$$

There are no appropriate expressions for polar solutes. Indeed, it is generally difficult to obtain reliable values for the contributions of the solute dipole to σ_E without making several assumptions. In this connection, studies of Chenon and co-workers[108] are noteworthy. They obtained experimental data involving polar effects by measuring shifts of acetone relative to hexane internal reference in a number of non-polar and polar solvents. To account for the differences in dispersion effect on the reference and the solute, they make use of the fact that a plot of de Montgolfier's function, $f(n) = (n^2 - 1)^4/(2n^2 + 1)^2(n^2 + 2)^2$ against Buckingham's function, $f(D) = (D - 1)(n^2 - 1)/(2D + n^2)$ is linear for non-polar solvents. For non-polar solutes, σ_W varies linearly with $f(n)$ and $\delta_{C_6H_{12}-Me_2CO}$ is also linear with respect to $f(n)$ for a few inert solvents. Therefore, it appears that σ_W and σ_E for a polar solute in non-polar solvents would vary linearly with $f(n)$ and $f(D)$, respectively. Deviation from such linearity would be found in the case of polar solvents owing to the inadequacy of $f(n)$ or $f(D)$ to account properly

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[107] P. Diehl and R. Freeman, *Mol. Phys.*, 1961, **4**, 39.

[108] M. T. Chenon, J. Bougnant, and N. Lumbroso-Bader, *J. Chim. phys.*, 1970, **67**, 1252, 1829.

for screening in such solvents. By making some approximations, σ_E in polar solvents has been estimated; the dipolar shift may exceed 0.3 p.p.m. for solvents of high dielectric permittivity. Becconsall and Hampson[109] have shown that differences in ^{13}C and ^{1}H shifts of MeI and MeCN in different solvents were almost entirely due to reaction field effects. The value of σ_E for ^{13}C is larger than for ^{1}H because of the larger number of electrons in the former.

From the above discussion, it becomes clear that even in the absence of specific interactions between solute and solvent molecules, there is considerable uncertainty in experimental and theoretical evaluations of the various screening constants (possibly with the exception of σ_W). The main difficulty is that we do not have a complete picture of the nature of the orientation of solvent molecules around a solute molecule. While the gas and cage models, particularly the former, have met with success, the continuum model is more readily employed because the solvent parameters employed are bulk properties of solvents. Systematic studies like those of Chenon *et al.*[108] and Weiner and Malinowski[110] would be most useful. Models similar to the ones mentioned above have also been employed to explain the effects of solvents on n.m.r. spin–spin coupling constants and e.s.r. hyperfine splitting constants.[96,111,112]

6 Specific Interactions

The various models and correlations of solvent effects on spectra discussed in the earlier sections are valid in the absence of specific interactions between solute and solvent molecules. Although in reality there would always be some specific interaction between solute and solvent molecules, the magnitude of interaction is usually small in the case of non-polar solutes and non-polar solvents. Thus, while benzene and CCl_4 are known to interact to form loose contact pairs,[52,53] we ignore such interactions while correlating solvent effects on spectra. This is because specific interactions in such systems are not appreciable and CCl_4 itself is the non-polar reference solvent employed in most studies. One can employ solvents which are more non-polar than CCl_4 or hydrocarbons like perfluoroethers[18] and so on to obtain a better reference point for the study of solvent effects and specific interactions.

Specific interactions between solute and/or solvent molecules increase when molecules are polar. Thus, there is evidence for association of ketones and nitrocompounds in non-polar solvents giving rise to spectral perturbations. I.r. and Raman studies of carbonyl compounds in the liquid state show the presence of high-frequency bands in the C=O stretching region due to alignment of the dipoles forming clusters.[113] The effect disappears on dilution with a solvent or with increase in temperature. Dipolar association between solute and solvent molecules is best studied by employing binary solvent mixtures. Thus, association

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[109] J. K. Becconsall and P. Hampson, *Mol. Phys.*, 1966, **10**, 21.
[110] P. H. Weiner and E. R. Malinowski, *J. Phys. Chem.*, 1971, **75**, 1207, 3160, 3971.
[111] J. Pannell, *Mol. Phys.*, 1964, **7**, 317.
[112] Y. Deguchi, *Bull. Chem. Soc. Japan*, 1962, **35**, 260.
[113] G. Fini and P. Mirone, *J.C.S. Faraday II*, 1973, **69**, 1243; 1974, **70**, 1776.

of ketones with nitriles can be studied in a non-polar solvent like hexane by employing electronic spectroscopy. Association phenomena due to hydrogen bonding or formation of EDA complexes are indeed well known and these have been studied by employing i.r., electronic, and n.m.r. spectroscopy.[53,70,81,96,97,114,115]

When spectral parameters of a solute dissolved in a binary solvent mixture are studied, two types of change are observed: (i) a new band whose intensity increases with increasing concentration of the polar component; (ii) shift of the original band of the solute to one side of the spectrum, the shift and intensity enhancement of the band being functions of the concentration of the polar component. The two spectral phenomena may be designated as the 'band change' and 'band shift', respectively. Typical examples of band change are found in the i.r. spectra of proton donor solutes in binary solvent mixtures exhibiting hydrogen-bonding and in the electronic spectra of EDA complexes. As the new band formed is due to new complex species (hydrogen-bonded, charge-transfer, *etc.*) methods for the evaluation of thermodynamic data of such equilibria (often employing the new bands) are well established. Frequency shifts of n–π^* transition bands due to solvent, charge-transfer-to-solvent (CTTS) band shifts of iodide ion with solvent, and changes in proton chemical shifts with varying concentration of the polar solvent can be considered to be cases representing band shifts. Even in such systems, one often sees isosbestic points (*e.g.* in electronic spectra) indicating the presence of equilibria.

Various authors have proposed expressions for the determination of equilibrium constants for hydrogen-bonding, charge-transfer, and dipole–dipole association employing n.m.r. chemical shifts of solutes in binary solvent mixtures.[53,70,96,97,114,115] Several authors have employed intensity enhancement of the blue-shifted n–π^* or the red-shifted π–π^* transition bands in electronic spectra for the determination of thermodynamic data for hydrogen-bonding and charge-transfer equilibria.[53,70,114,115] Becker[116] explained the effect of polar aprotic solvents (nitriles) on the n–π^* transition of benzophenone on the basis of formation of a dipolar complex. Isosbestic points in the absorbance–wavenumber plots confirmed the existence of an equilibrium. No attempt for the determination of equilibrium constants was, however, made. E.s.r. hyperfine splitting constants of substituted nitrobenzene and aromatic ketone radical-anions in binary solvent mixtures have been used for the determination of equilibrium constants of specific interactions by several workers.[117–121] Because of the inherent problems in i.r. band intensity measurements little work has been reported on the i.r. band intensities of solutes in binary solvent mixtures for systems showing band shifts.

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[114] A. S. N. Murthy and C. N. R. Rao, *Appl. Spectroscopy Rev.*, 1969, **2**, 69.
[115] R. Foster, 'Molecular Complexes', Elek Science, London, 1973.
[116] R. S. Becker, *J. Mol. Spectroscopy*, 1959, **3**, 1.
[117] J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2832.
[118] J. M. Gross and M. C. R. Symons, *Trans. Faraday Soc.*, 1967, **63**, 2117.
[119] E. W. Stone and A. H. Maki, *J. Amer. Chem. Soc.*, 1965, **87**, 454.
[120] M. T. Hetrich and T. Layloff, *J. Amer. Chem. Soc.*, 1969, **91**, 6910.
[121] V. P. Senthilnathan and S. Singh, *Indian J. Chem.*, 1974, **12**, 1311.

Ritchie *et al.*[122] as well as Senthilnathan and Singh[123] have determined equilibrium constants for the interaction of benzonitrile and benzophenone in various polar solvents by integrated i.r. band intensity measurements.

Data on spectral parameters of solutes in binary solvent mixtures can generally be treated in terms of equilibria (33) and (34), where S, P, and N denote the

$$\mathrm{S} + \mathrm{P} \rightleftharpoons \mathrm{SP} \tag{33}$$

$$\mathrm{SN}_q + \mathrm{P} \rightleftharpoons \mathrm{SN}_{q-1}\mathrm{P} + \mathrm{N} \tag{34}$$

solute, polar, and non-polar (or less polar than P) solvent molecules, respectively. Expressions (35) and (36), respectively, account for the variation of spectral parameters of solutes in binary solvent mixtures when the equilibria represented by (33) and (34) are considered; $\Delta\xi = \xi - \xi_0$ and $\Delta\xi^0 = \xi_c - \xi_0$, and the terms

$$\Delta\xi = \frac{K_P \Delta\xi^0 C_P}{1 + K_P C_P} \tag{35}$$

$$\Delta\xi = \frac{K \Delta\xi^0 \alpha}{1 + K\alpha} \tag{36}$$

ξ and ξ_0 are, respectively, the spectral parameters (i.r. and electronic spectral band shift or band intensity, n.m.r. chemical shift, e.s.r. hyperfine splitting constant, and so on) of the solute in the binary solvent mixture and in the non-polar solvent respectively, and ξ_c is the spectral parameter of the complex SP or SPN_{q-1} in the non-polar solvent; C_P and α are, respectively, the concentration of the solvent P and the ratio of the concentrations of P and N. Different forms of expressions (35) and (36) can be employed for the evaluation of equilibrium constants in a variety of weakly interacting systems.

7 Concluding Remarks

We have seen from the preceding discussion of solvent effects on electronic, i.r., and n.m.r. spectra of molecules that in the absence of specific interactions between solute and solvent molecules it is possible to correlate solvent-induced spectral shifts with bulk properties of solvents. Continuum theories appear to be uniformly effective in such correlations. While different expressions applicable to different types of solute–solvent interaction have been developed for each spectral parameter, we notice considerable similarities amongst them. Most of the expressions have $(n^2 - 1)/(2n^2 + 1)$, $(D - 1)/(2D + 1)$, or similar terms to represent solvent parameters. Thus, similarity between equation (32) applicable to n.m.r. spectra in polar solvents and equation (11) applicable to electronic spectra was pointed out. Such similarities become particularly striking when we examine the expressions for the effect of non-polar solvents on the spectra of non-polar solutes. The dispersion effect in such systems is almost always described by $(n^2 - 1)/$

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[122] C. D. Ritchie, B. A. Bierl, and R. J. Honour, *J. Amer. Chem. Soc.*, 1962, **84**, 4687.

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$(2n^2 + 1)$. Such a dependence of dispersion effect is also indicated by the recent theoretical study by Mahanty and Rao[124] on effect of solvents on molecular spectra from the point of view of dispersion self-energy. This study shows that the frequency shift due to non-polar solvents in the spectra of molecules is proportional to $[D(\omega_{nm}) - 1]/[2D(\omega_{nm}) + 1]$. Here, $D(\omega_{nm})$ is the dielectric permittivity measured at the absorption frequency, ω_{nm}. For all practical purposes, we may take $D(\omega_{nm}) = n^2$ and use $(n^2 - 1)/(2n^2 + 1)$ to describe dispersion effects.

The similarity between the effects of pressure and solvents in the case of electronic spectral bands and n.m.r. chemical shifts was pointed out earlier. An examination of the literature data indicates some similarity in the case of i.r. spectra as well. It would be worthwhile to examine more closely the analogy between pressure effects and solvent effects. In the case of n.m.r. spectra, the gas-to-liquid chemical shifts can be correlated with $(n^2 - 1)/(2n^2 + 1)$ of solvents,[125] just as in McRae's treatment[17] of solvent effects on electronic spectra. It is interesting that this refractive index term of McRae[17] and de Montgolfier's term[104] in equation (26) are related to each other by $(n^2 - 1)/(n^2 + 2)$, this last term itself being the basis for the well-known Lorenz–Lorentz equation for molar refraction. It is also interesting that ^{13}C chemical shifts of ketones have been correlated with their n–π^* transition energies,[126–128] the latter themselves being correlated C=O stretching frequencies.[18,19] Such correlations only reinforce the fact that solvent effects on these spectral parameters arise from similar interactions.

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