Comments Concerning Solvent Effects on Chemical Processes. Part 7. Quantitative Description of the Composition Dependence of the Solvent Polarity Measure $E_T(30)$ in Binary Aqueous–Organic Solvent Mixtures

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A recently published two-step solvational model for mathematically describing the spectral properties of the Dimroth–Reichardt betaine dye E_T in binary aqueous–organic solvent mixtures is critically examined in the light of fundamental spectroscopic principles. The published spectroscopic method is found to be inconsistent with the Beer–Lambert relationship with regard to absorption additivity in solutions containing multiple light-absorbing solvational chromophores. Two alternative data treatments are presented for describing the spectral properties of the E_T betaine dye. The first treatment is consistent with both the Khossravi–Connors–Skwierczynski two-step solvational model and fundamental spectroscopic principles. The second treatment assumes that only a single solvational chromophore is present in solution, and the observed absorption wavelength shift is described using the nearly ideal binary solvent (NIBS) model.

In a recent paper appearing in this *Journal*, Skwierczynski and Connors[1] assumed that reciprocal of the maximum absorption wavelength [λ_{max}/nm; E_T/kcal mol^{-1} = 28 591.5/(λ_{max}/nm)] of Dimroth–Reichardt betaine dye E_T dissolved in aqueous–organic mixtures is a weighted average of the contributions or fractions of betaine dye by the various solvated species, eqn. (1),

$$E_T(X_2) = F_{RWW}E_T(RWW) + F_{RWM}E_T(RWM) + F_{RMM}E_T(RMM) \quad (1)$$

with the E_T value of the 'mixed' solvational species RWM approximated as a simple arithmetic average of solute properties in the two pure solvents, E_T(RWW) and E_T(RMM) [eqn. (2)]. Stepwise competitive equilibria of water (component W) and organic solvent (component M) with solute R is used to model solute–solvent solvational effects as follows.

$$E_T(RWM) = (1/2)[E_T(RWW) + E_T(RMM)] \quad (2)$$

$$RW_2 + M \rightleftharpoons RWM + W \quad K_1 = X_{RWM}X_W/(X_{RW2}X_M)$$

$$RWM + M \rightleftharpoons RM_2 + W \quad K_2 = X_{RM2}X_W/(X_{RWM}X_M)$$

Fractions of the three solvational species are defined by eqns. (3)–(5), where X_1 and X_2 refer to bulk mole fractions of water and organic cosolvent, respectively. Through a series of algebraic manipulations, eqn. (1) was rearranged to a more convenient form [eqn. (6)] so as to enable computation of K_1 and K_2 by least-squares regression curve-fitting techniques.

$$F_{RWW} = X_1^2/(X_1^2 + K_1X_1X_2 + K_1K_2X_2^2) \quad (3)$$

$$F_{RWM} = K_1X_1X_2/(X_1^2 + K_1X_1X_2 + K_1K_2X_2^2) \quad (4)$$

$$F_{RMM} = K_1K_2X_2^2/(X_1^2 + K_1X_1X_2 + K_1K_2X_2^2) \quad (5)$$

$$[E_T(X_2) - E_T(WW)]/[E_T(MM) - E_T(WW)] = [0.5K_1X_1X_2 + K_1K_2X_2^2] \div (X_1^2 + K_1X_1X_2 + K_1K_2X_2^2) \quad (6)$$

The authors' mathematical treatment implied three discrete solvational species, each having its own spectral properties.

The intent here is not to criticize the authors' thermodynamic model,[1–6] but rather to suggest an alternative data treatment more consistent with basic spectroscopic principles for solutions containing two or more different, light absorbing solute solvational species. Our initial discussion thus assumes the identical two-step solvational exchange model, however, this may be an oversimplification of the true solvational picture. Thermodynamic mixing models, such as the UNIQUAC and UNIFAC models, assume much larger coordination numbers of 10 or more. Spectroscopic principles provide the basis for back-calculating a 'theoretical' absorption spectrum. Each theoretical spectrum can be compared against actual experimental spectral data to assess better the applications and limitations of the Skwierczynski and Connors spectroscopic probe method.

The Beer–Lambert law states that for monochromatic radiation the measured absorbance is directly proportional to chromophore concentration. For mixtures containing two or more chromophores the total absorbance of a solution at a given wavelength is equal to the sum of the absorbances of the individual components present. Applying the Beer–Lambert law to a solution having RW_2, RWM and RM_2 solute solvational species, the total measured absorbance is given by eqn. (7), where ε_i is the molar absorptivity of species i in dm^3 mol^{-1} cm^{-1}, [R] is the stoichiometric molar concentration of chromophore, and b is the path length. A similar expression holds for each wavelength. It can be shown that if all ε_i values are independent of solvent composition then the observed absorption spectrum over any wavelength region scanned must be equal to

$$A_{total} = F_{RWW}\varepsilon_{RWW}[R]b + F_{RWM}\varepsilon_{RWM}[R]b + F_{RMM}\varepsilon_{RMM}[R]b \quad (7)$$

$$\text{spectrum}\,(X_2) = F_{RWW}\,(\text{spectrum RW}_2) + F_{RWM}\,(\text{spectrum RWM}) + F_{RMM}\,(\text{spectrum RM}_2) \quad (8)$$

where (spectrum RW_2) and (spectrum RM_2) refer to the chromophore's absorption spectrum determined at fixed concentration $[R]_{constant}$ in pure water and organic cosolvent, respectively.

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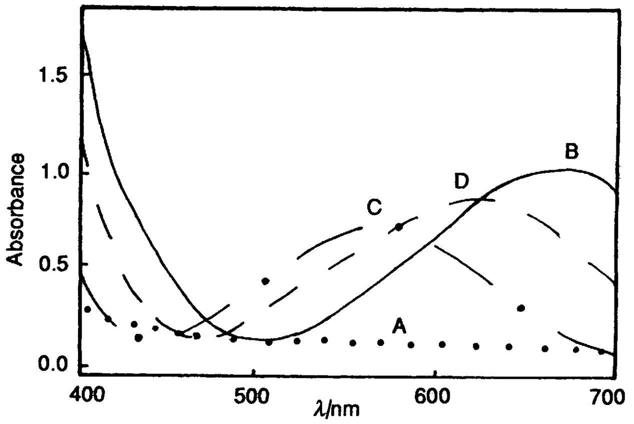

Fig. 1 Spectrum A is the measured absorbance of the two pure solvents and binary solvent mixtures without E_T dye. Spectra B and C correspond to the E_T dye's absorbance in the two pure solvents, and spectrum D represents the estimated absorption spectrum of the mixed solvational species RWM.

Eqns. (7) and (8) clearly show that there is no simple mathematical relationship with which to calculate the maximum absorption wavelength (or alternatively E_T) determined in a binary solvent mixture from values in the pure solvents as implied by eqns. (1) and (6). The mathematical treatment becomes more complicated if one or more of the molar absorptivities are solvent dependent. Moreover, the presence of three distinct chromophores in solution may result in three distinct absorption maxima, which may appear as shoulders in the case of a minor component. If eqn. (6) does define the wavelength of maximum absorption, and if RW_2, RM_2 and RWM are indeed present as originally postulated, then eqn. (6) must be derivable by differentiating the solution absorbance with respect to wavelength, setting the derivative equal to zero and solving the resulting mathematical expression for λ_{max}. Attempts to derive eqn. (6) along this line, showing how the various molar absorptivities, $\varepsilon_i(\lambda)$, or more specifically $\partial\varepsilon_i(\lambda)/\partial\lambda$, were eliminated have proved unsuccessful. Remember, ε_i is itself a function of wavelength. Eqn. (6) does not contain $\varepsilon_i(\lambda)$ functions or specific numerical values.

From an operational standpoint, and assuming that the two-step exchange model is to be used in lieu of published alternative models,[7,8] we feel that a better data treatment would have involved measuring the dye's absorption spectrum in each pure solvent and in the various binary solvent mixtures. The absorption spectrum of the 'postulated' mixed RWM solvational species could be approximated as having an intermediate general shape between spectrum RW_2 and spectrum RM_2, but with a maximum absorption wavelength of $(1/\lambda_{max})_{RWM} = 0.5\ [(1/\lambda_{max})_{RWW} + (1/\lambda_{max})_{RMM}]$, a maximum absorbance of $(A_{max})_{RWM} = 0.5\ [(A_{max})_{RWW} + (A_{max})_{RMM}]$, and a bandwidth at one-half A_{max} of $(\text{width})_{RWM} = 0.5\ [(\text{width})_{RWW} + (\text{width})_{RMM}]$, as indicated by the dashed line in Fig. 1. Location of $(1/\lambda_{max})_{RWM}$ in this fashion is consistent with basic thermodynamic mixing models, such as the nearly ideal binary solvent (NIBS) model,[9–11] which expresses the solute's energy as a mole fraction average of the measured solute properties in both pure solvents. For the mixed RWM solvational species, there is one molecule of each cosolvent located within the solute's solvational sphere, hence the simple arithmetic average. Simple arithmetic averages for $(A_{max})_{RWM}$ and $(\text{width})_{RWM}$ are suggested in the absence of a better approximation. To our knowledge, there is no rigorous, theoretical expression describing how these quantities vary with solvent composition. There is, however, experimental evidence in the chemical literature for several chromophores showing that ε_i remains fairly constant from one solvent to another as long as the solvent properties are not too dissimilar and provided that solute–solvent complexation does not occur. If better approximations for the spectral properties of RWM and/or for how ε_i varies with binary solvent composition are found, then these can be substituted into the more general eqn. (7) in place of the ones suggested here.

The preceding discussion assumed for whatever reason that the spectral properties of Dimroth–Reichardt betaine dye were to be described using the Khossravi–Connors–Skwierczynski two-step solvent exchange model. Inherent in this treatment were all spectral constraints imposed by the three presumed solvational species. Alternatively, one may assume that only a single solvational dye molecule is present. For modelling purposes, each solvational sphere is treated as a separate binary solvent microphase of composition Z_W^{GS} or Z_W^{ES}. The solute's energy in both the ground and excited state will be expressed *via* the NIBS model[9–11] as

$$E_{\text{chromo}}^{GS} = Z_W^{GS}E_{\text{chromo},W}^{GS} + (1 - Z_W^{GS})E_{\text{chromo},M}^{GS} - \Delta E_{WM}^{\text{mix}}(\text{at } Z_W^{GS}) \quad (9)$$

$$E_{\text{chromo}}^{ES} = Z_W^{ES}E_{\text{chromo},W}^{ES} + (1 - Z_W^{ES})E_{\text{chromo},M}^{ES} - \Delta E_{WM}^{\text{mix}}(\text{at } Z_W^{ES}) \quad (10)$$

a solvational mole fraction average of the corresponding fluorophore energies in the pure solvents, $E_{\text{chromo},i}^{GS}$ and $E_{\text{chromo},i}^{ES}$, minus the energy needed to create the 'solvent cavity' wherein the chromophore resides. The model assumes only pairwise interactions and that the probability of any given interaction is directly proportional to the mole fractions of each component.

The change in the energy corresponding to the ground state ⟶ excited state transition [eqns. (11) and (12)] depends

$$\text{chromo (at } Z_W^{GS}) + h\nu_{ex} \longrightarrow \text{chromo* (at } Z_W^{GS})$$
$$\Delta E_{\text{trans}} = Z_W^{GS}(E_{\text{chromo},W}^{ES} - E_{\text{chromo},W}^{GS}) + (1 - Z_W^{GS})(E_{\text{chromo},M}^{ES} - E_{\text{chromo},M}^{GS}) \quad (11)$$

$$\text{chromo (at } Z_W^{GS}) + h\nu_{ex} \longrightarrow \text{chromo* (at } Z_W^{ES})$$
$$\Delta E_{\text{trans}} = Z_W^{ES}E_{\text{chromo},W}^{ES} - Z_W^{GS}E_{\text{chromo},W}^{GS} + (1 - Z_W^{ES})E_{\text{chromo},M}^{ES} - (1 - Z_W^{GS})E_{\text{chromo},M}^{GS} - \Delta E_{WM}^{\text{mix}}(\text{at } Z_W^{ES}) + \Delta E_{WM}^{\text{mix}}(\text{at } Z_W^{GS}) \quad (12)$$

upon whether a change in the solvational sphere composition occurs during the excitation process. The latter transition is excluded on the basis of the Frank–Condon principle which states that an electronic transition is rapid compared with nuclear motion. Solvent molecules contain several atoms/nuclei which are 'fixed' in space with chemical bonds. Molecular diffusion, viewed as movement of several nuclei, should be much slower than an electronic transition. Absorption wavelength is inversely proportional to $|E_{\text{chromo}}^{ES} - E_{\text{chromo}}^{GS}|$. Eqn. (11) predicts that $1/\lambda_{ex}$ are additive on a preferential solvation basis. Interpretation of the spectral properties of the Dimroth–Reichardt betaine dye using the NIBS model leaves intact the Skwierczynski–Connors weighted average frequency postulate, eqn. (13), and at the same time removes the spectral additivity

$$1/\lambda_{ex} = Z_W^{GS}(1/\lambda_{ex})_W + (1 - Z_W^{GS})(1/\lambda_{ex})_M \quad (13)$$

constraint imposed by the Beer–Lambert law anytime that the solution contains multiple light-absorbing chromophores.

The observed absorption spectra of Dimroth–Reichardt betaine dye E_T dissolved in binary aqueous–organic mixtures appears to be only a single fairly broad band, lying somewhere between the two pure solvent bands. The observations are often complicated by strong absorption by bands at lower wavelengths, and by insufficient separation of absorption maxima in the pure solvents. Without supporting spectroscopic evidence to support the presence of discrete solvational species, it is felt that the spectral behaviour of the E_T dye molecule is probably best described in terms of eqns. (9)–(13). The success of eqns. (1) and (6) in describing the absorption maxima likely results from the model's ability mathematically to reproduce the variation of Z_W^{GS} (as calculated above) as a function of bulk liquid phase composition, X_W.

It is not our intent here completely to abandon the Khossravi–Connors–Skwierczynski two-step solvational exchange model as there may be instances where either (*a*) the experimental spectrum does show two or more absorption maxima or shoulders consistent with multiple solvational species, (*b*) the chemical nature of the probe (*i.e.*, transition metal–ligand coordination complex, RL_4) suggests formation of a series of well-defined ligand–solvent complexes (RL_4W_2, RL_4WM and RL_4M_2), or (*c*) the observed solvatochromic response depends upon intensities (or intensity ratios) rather than wavelength shifts. In this latter case multiple solvational species must be assumed in order to use spectroscopic principles to describe mathematically the intensity data.

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