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Observation of dielectric enrichment upon the formation of benzophenone radical anion in a binary solvent mixture

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In this paper we present results about the non-linear solvatochromic shift of the benzophenone radical anion absorption maximum in dimethyl sulfoxide–1,2-dichloroethane mixtures as a function of solvent mole fraction. Because of the non-hydrogen bonding character of the solvents, the observed absorption shift is attributed to dielectric enrichment only. The mathematical model which was developed for neutral dipolar solutes is extended to ionic species of charge q and molecular radius r; the preferential solvation index is proportional to $q^2 r^{-4}$. In the present case its value is larger than those observed in most cases of dipolar solutes.

It is well known that in general the solvatochromic shifts of the absorption or emission spectra of solute molecules present in binary solvent mixtures are not linear with the mole or volume fractions of the solvents.[1–3] This may result at least in part from the non-ideal behaviour of the mixture itself, but the most important factor is the preferential solvation which describes the association of one of the solvents with the solute. There are here two distinct mechanisms which involve specific and non-specific interactions. In the former, solute–solvent complexes of well defined stoichiometry and geometry are formed. This is not the case in the latter, which is described as dielectric enrichment when the two solvents have different static dielectric constants: the concentration of the more polar solvent then increases in the immediate vicinity of a dipolar solute molecule, and this can be described quantitatively by the balance between the electrostatic interaction and the entropy of mixing.[4] The mathematical model and the experimental data have so far dealt only with neutral dipolar solutes; here we extend these findings to an ion, specifically to the benzophenone radical anion (BP$^{\bullet-}$) in a mixture of two non-hydrogen-bonding solvents. The spectral shifts of some ions in single solvents have already been described,[5–8] but there is no simple general theory to account for them. When dealing with the free ions, there are severe limitations in the choice of solvents. It is of course essential to ensure that the BP$^{\bullet-}$ ions do not stay in contact with, in this case, the counter ions of diazabicyclo[2.2.2]octane, DABCO$^{\bullet+}$, since it is well established that the absorption spectrum of BP$^{\bullet-}$ in the ion pair depends on the nature of the counter ion.[9] In solvents of very low dielectric polarity (see below) charge separation does not take place, and these cannot be used as the 'non-polar' component of the mixture. We have therefore selected 1,2-dichloroethane (DCE) as the less polar (though not non-polar) solvent and dimethyl sulfoxide (DMSO) as the more polar component.

Experimental

1,2-Dichloroethane, DCE, (Aldrich), with a static relative permittivity value $D = 10.6$ at 20 °C and dimethyl sulfoxide, DMSO, (Aldrich), with $D = 48.9$ at 20 °C were of spectrophotometric grade and used as such. Benzophenone, BP, (Aldrich), and 1.4-diazabicyclo[2.2.2]octane (DABCO), (Fluka) were sublimed twice under vacuum before use.

BP anions were created *in situ* by populating first the triplet state through laser pulse excitation. The triplet is quenched in a diffusion controlled charge transfer process with DABCO as the electron donor. Subsequent separation yields the free BP anions. The $\varphi(D)$ values of the mixtures were calculated from the relative permittivities measured by the usual capacitor method, using the Dekameter WTW bridge. The excitation source was a nanosecond Nd : YAG laser (JK Lasers 2000) producing pulses of 22 ns at 355 nm. To monitor the transient absorption of the BP anion, the light of a 250 W halogen lamp was directed through the excited sample. The transmitted light was monochromated in a spectrograph (Applied Photophysics). Second harmonic transmission was avoided by the use of a cut-off filter placed in front of the spectrograph. At the exit a light-guide transmitted the signal to a photomultiplier (EMI 9785C). From there the signal was fed into an oscilloscope (Gould 4074) which permitted the transfer into a personal computer (Olivetti M240).

Results and Discussion

Theoretical

The theory of dielectric enrichment which was developed for the solvation neutral, dipolar solute molecules in binary solvent mixtures[4,10,11] is readily extended to the case of an ion by replacing the Onsager solvation equation by the Born equation of ion solvation.[12,13] The index of preferential solvation Z relates the mole ratio X in the undisturbed bulk of the mixture to the mole ratio Y in the first solvent shell at a distance r from the point charge q of the ion according to:

$$Y = Xe^{-Z} \tag{1}$$

where $X = x_N/x_P$ and $Y = y_N/y_P$, x_P and x_N being the mole fractions of the more polar (P) and less polar (N) solvents in the bulk mixture, respectively; and similarly y_P and y_N are the mole fractions in the solvent shell.

The preferential solvation index is then given by:

$$Z = \frac{Cq^2 \bar{M} \Delta F(D)_{N,P}}{\bar{\delta} R T r^4} \tag{2}$$

where $\bar{M}$ and $\bar{\delta}$ are the mean molecular weight and density of the solvents, respectively. The function $F(D)$ of the static relative permittivity is given by[12]

$$F(D) = 1 - (1/D) \tag{3}$$

C is a numerical constant formally equal to $1/8\pi$, although it may better be considered as an empirical parameter of the system. In the calculations reported here we used consistently $C = 1/8\pi$, and it should be pointed out that all equations imply the use of cgs units.
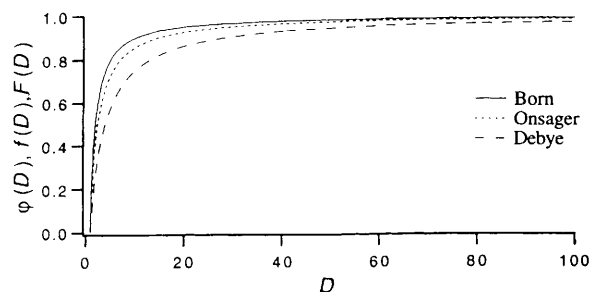
Fig. 1 Plot of the Debye-function $\varphi(D)$, the Onsager-function $f(D)$ and the Born-function $F(D)$ vs. the relative permittivity D

In any numerical calculation, the distance r is of rather critical importance since in the simple Born model it would be the ionic radius. There has been much discussion concerning the proper definition of this parameter, even for a spherical centred point charge ion.[14] The molecular volumes are best estimated from a cubic lattice model,[15] so that the molecular radius is

$$r = \frac{1}{2}\left(\frac{M}{\delta N_A}\right)^{1/3} \tag{4}$$

where M is the molecular weight, δ the density and N_A Avogadro's number. In the case of BP for instance, this yields $r = 3.54$ Å. In the single-shell approximation, however, this is clearly a lower estimate since r is defined as the sum of the solute and solvent radii.

The index of preferential solvation gives the mole ratios X and Y at equilibrium. The equilibration time depends on the diffusion of the solvents, in the absence of any electrostatic attraction beyond the first solvation shell. It is then given by:[4]

$$t = \frac{(y_P - x_P)\pi \bar{M} a^2}{k_D x_P \, 10^3 \bar{\delta} b^2} \tag{5}$$

where k_D is the second-order rate constant for diffusion-controlled encounters, a and b being the molecular radii of the solute and solvents (average), respectively. The equilibration time t can be of the order of 10–20 ns at low polar solvent mole fraction.[16] This must be borne in mind when dealing with observations of transient species such as electronically excited molecules and, as in the present case, molecular ions generated by flash photolysis.

Experimental observations

(a) Dielectric polarity functions of mixtures of DCE/DMSO.

The 'dielectric polarity' of a liquid is defined from its static relative permittivity D according to various functions which
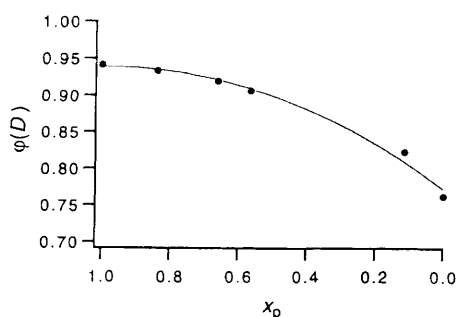
Fig. 2 Plot of the bulk polarity of DCE–DMSO mixtures as a function of increasing DMSO mole fraction (x_P)
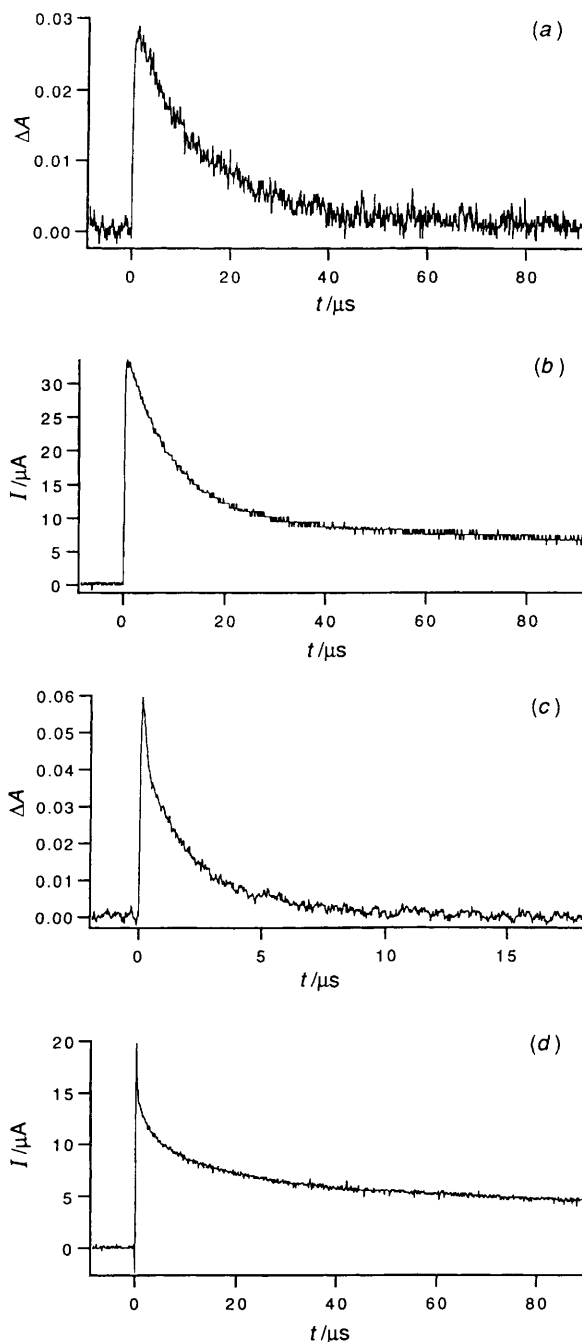
Fig. 3 (a) Trace of transient absorption of the system BP/DABCO in DMSO measured at 740 nm; (b) photocurrent trace of BP/DABCO in DMSO; (c) trace of transient absorption of the system BP/DABCO in DCE measured at 690 nm and (d) photocurrent trace of BP/DABCO in DCE

are:

$$\phi(D) = (D - 1)/(D + 2) \quad \text{(Debye)}^{17}$$

$$f(D) = 2(D - 1)/(2D + 1) \quad \text{(Onsager)}^{18}$$

$$F(D) = 1 - 1/D \quad \text{(Born)}^{12}$$

In a simple model of solvent mixtures the Debye polarity function is expected to follow a law of additivity according to the mole fractions of the two components N and P.

$$\phi(D)_{\text{mixt}} = x_N \, \phi(D_N) + x_P \, \phi(D_P) \tag{6}$$

A solvent mixture can be considered to follow ideal dielectric behaviour if this equation applies.

In the theory of dielectrics, it is clear that it is the function $\phi(D)$ which should be additive in mixtures which do not
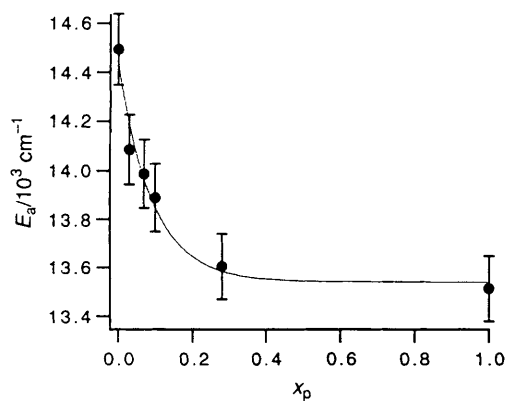
Fig. 4 Solvatochromic shift of the benzophenone anion absorption maximum in DCE–DMSO mixtures in function of increasing DMSO mole fraction (x_P)

contain any solute. The Onsager function $f(D)$ applies to solute dipoles, the Born function $F(D)$ to ionic solutes. They are so close numerically as to be practically indistinguishable (Fig. 1). In solvent mixtures which behave as ideal dielectrics, the additivity equation applies within experimental error to all three polarity functions.

We find that the $\varphi(D)$, $f(D)$ and $F(D)$ functions of the mixtures DCE/DMSO deviate from linearity as shown in Fig. 2, the non-linearity ratio being 0.38 defined according to eqn. (26) of ref. 4. This must of course be subtracted from the observed non-linearity ratio of the spectral shift of any solute in these mixtures.

In view of the known restricted localization of the charge on the carbonyl group, the expected sensitivity of the anion in terms of the environment is expected to be large. Because of the non-protic character of the solvents used, the resulting non-linear absorption shift is attributed to the process of dielectric enrichment only.

(b) Solvatochromic shifts of the benzophenone radical anion in mixtures of DCE–DMSO. As can be seen in Fig. 3 the lifetime of BP anions is of the order of several microseconds, as measured by transient absorption and by transient photoconductivity. It is therefore clear that the thermodynamic equilibrium is established in this case. The absorption spectrum of $BP^{\cdot -}$ shows the maximum of the $D_0 - D_1$ transition at 690 nm in DCE and 740 nm in DMSO. Fig. 4 shows the shift of this maximum as a function of DMSO mole fraction, and it is immediately clear that this shift is highly non-linear, with a non-linearity ratio $\rho = 0.81$ following its definition as:

$$\rho = \frac{2 \int_0^1 [F(D)_{\text{eff}} - F(D)_{\text{lin}}] \, dx}{\Delta F(D)_{\text{N, P}}} \tag{7}$$

The effective non-linearity ratio is then 0.43, and this corresponds to a value $Z = 1.4$ for the preferential sovation index

according to the calculated relationship between r and Z given in ref. 4, taking into account the non-linearity ratio of the solvent mixtures themselves.

This value of Z must be seen in the context of the rather small difference of dielectric polarities of the two solvents, $\Delta F(D) = 0.074$. It corresponds then to a value of $r = 3.4$ Å. The agreement between the observed and calculated values of Z is fairly satisfactory in view of the uncertainties linked to the parameters involved in eqn. (2), in particular the proper value of the ionic radius r. It lends support to the assumption that in an ion the process of dielectric enrichment is dominated by the solute charge–solvent dipole interaction.

Conclusions

The highly non-linear shift of the absorption spectrum of the benzophenone radical anion in mixtures of the non-protic solvents DCE and DMSO can be understood on the basis of a model of dielectric enrichment of an ion. The preferential solvation index depends on the square of the charge and on the inverse fourth power of the ionic radius. By considering the small polarity difference of the solvents used, the observed non-linearity is greater than that of most, if not all, neutral dipolar solutes investigated so far.

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