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Determination of pK^* in excited state proton transfer (ESPT) reaction: a rearrangement of Weller's equation; advantage of dual luminescence

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Abstract

The dual luminescence of certain fluorophores during excited state proton transfer (ESPT) reactions has been used for a convenient determination of the steady state equilibrium constants of the processes. From Weller's concept, a linear relationship has been developed between the logarithm of the relative fluorescence intensities of the deprotonated and protonated species and the pH of the solution; from this relationship, pK^* values have been determined for several compounds in aqueous medium in the presence of different proton-abstracting bases, such as NaOH, NH_3, $EtNH_2$, Et_2NH and Et_3N. Although the method overcomes some of the shortcomings of Weller's technique, it has its own limitations.

Keywords: Excited state proton transfer; Dual luminescence; Equilibrium constants; Carbazole

1. Introduction

Although it has recently been established, quite convincingly, that time-resolved studies are of major importance in understanding excited state proton transfer (ESPT) processes [1], steady state determination of pK^* for the reaction is still of use. Since the pioneering work of Weller [2] on the determination of the steady state equilibrium constants (pK^*) of ESPT reactions by fluorometric titration, ample work has been carried out in this field [3–8]. Weller's technique is based on the fluorometric titration of a chromophore by a prototropic quencher, leading to a plot of I/I_0 (where I and I_0 are the luminescence intensities of the chromophore in the presence and absence of the added quencher respectively) vs. the pH of the solution. The curve takes a sigmoidal shape and the steady state pK^* value is taken to be the pH value at the inflexion point. For compounds showing dual luminescence during prototropic reactions, pK^* is obtained from the pH at the cross-over point of the two curves, each resulting from a particular emitting species (protonated or deprotonated).

Like other steady state techniques, Weller's method faces some limitations. It is assumed that the prototropic reaction attains equilibrium within the lifetime of the excited species. However, recent time-resolved studies have established that the attainment of equilibrium is not a general outcome of an adiabatic ESPT process, and there are only a few examples in which an equilibrium is attained [1,9]. In addition, the "true pK^*" value determined from the direct measurement of individual rate constants may differ appreciably from the pK^* value obtained using the steady state method [9,10]. In spite of this, Weller's fluorescence quenching technique is still in use because of its overall simplicity and versatility.

In previous work [9–11], we used fluorometric and time-resolved techniques to establish different aspects of ESPT reactions of carbazole and related compounds. The compounds chosen were typical in the sense that both protonated and deprotonated forms were fluorescent. The method of determination of pK^*, reported in this paper, takes advantage of this dual luminescence and is based on a modified Weller's equation. The technique has been applied to sample compounds, such as carbazole (CAZL), indazole (INDZ) and 2-(*o*-hydroxyphenyl)benzimidazole (2HB), in the presence of aqueous external bases, such as NaOH, NH_3, $EtNH_2$, Et_2NH and Et_3N. The merits and shortcomings of the method are discussed.

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2. Experimental details

The purification of CAZL, INDZ and 2HB has been described elsewhere [8,12,13]. Sodium hydroxide, ethylamine, diethylamine and triethylamine (Ranbaxy, analytical reagent) were used as received. Triply distilled water was used as solvent. All the solutions were freshly prepared just before the experiment, and degassing of the solutions was found to be unnecessary for the steady state measurements.

The absorption and emission measurements were performed on a 17D spectrophotometer and a Perkin–Elmer MPF 44B spectrofluorometer respectively. The pH values were measured on a Toshniwal pH meter model Cl-44A.

3. Results and discussion

Weller's fluorescence quenching technique for the determination of pK^* in ESPT reactions involves the monitoring of either one of the dual luminescences exhibited by the compound under study in the presence of added prototropic quencher. The reliability of the method therefore depends strongly on the homogeneity and stability of the instrumental response at each data point. As the graphical plot is non-linear, the number of experimental data points also plays an important role. The larger the number of data points (particularly near the inflexion point), the more precise the inflexion point and, consequently, pK^*. In addition, it is often difficult to obtain accurate I_0 values for the species produced in the photoexcited state by the proton transfer process. High concentrations of prototropic quencher may cause an additional quenching effect (such as proton-induced quenching [6]) other than prototropic quenching. Lastly, the data points seem to be scattered more densely at either the beginning or the tail ends of the curves. This is because, in these regions, a small error in the numerator or denominator (which has a very low magnitude) leads to a large deviation.

A better method is to monitor both dual fluorescences simultaneously. Here, instead of I/I_0, the logarithm of I^-/I (where I and I^- are the fluorescence intensities of the protonated and deprotonated species respectively at a particular concentration of the prototropic quencher) is plotted against the pH of the solution. A simple mathematical treatment reveals that $\log(I^-/I)$ will be linear as a function of pH (see Appendix). The intercept of the straight line on the pH axis gives directly a measure of the steady state pK^* value.

Since we use the ratio of the intensities of two prototropic species within an experimental set, the instrumental artefacts are overcome to a large extent. However, if there is a difference in the fluorometric response with wavelength, the accuracy of the result will be compromised. The technique does not require the I_0 value for the excited state prototropic product, the measurement of which, as described above, is difficult. Moreover, due to the linear nature of the plot, we can safely avoid the data points at both the beginning and tail ends.

In spite of the procedural simplicity, a closer scrutiny of the new technique raises questions as to its versatility and the precision of the pK^* values thus determined. For example, for the relevant equation to be applicable, the fluorescence quantum yields of the two prototropic forms should be equal (this is rare). The equations for K^* and pK^* take the following forms

$$K^* = \frac{I^-}{I}\frac{\phi}{\phi^-}[H^+] \quad (1)$$

and

$$\log(I^-/I) = \mathrm{pH} - \mathrm{p}K^* + \log(\phi^-/\phi) \quad (2)$$

where ϕ and ϕ^- are the fluorescence quantum yields of the protonated and deprotonated species respectively. Thus, from a plot of $\log(I^-/I)$ vs. pH, we obtain the value of $[\mathrm{p}K^* + \log(\phi^-/\phi)]$ instead of pK^*. In order to obtain the exact pK^* value, measurement of the quantum yields of both forms is required. In effect, the modified method, which is intended to be simpler, is not for compounds for which the quantum yields of the two prototropic species are very different. For systems which have comparable yields for the two forms, this limitation is not serious since the term ϕ^-/ϕ is in logarithmic form.

Another interesting point of the technique is that Eq. (2) indicates that the slope ($\log(I^-/I)$ vs. pH) should be the same in every case, but the experimental results show that, for some systems, the slopes are the same, while for others they are quite different. This deviation in slope (from unity), although not predicted by the technique, points to the involvement of other fluorescence quenching processes competing with the proton transfer process [6].

Fig. 1 shows a set of plots of $\log(I^-/I)$ vs. the pH of the solution for the three different compounds in the presence of aqueous NaOH; the pK^* values are listed in Table 1. The table compares the estimated pK^* values from the new technique with those from Weller's method (based on the same experimental data in each case for the studied system); it can be seen that there is reasonable agreement between the two. The slopes of all the plots are equal to unity (deviation, ± 0.02), indicating that quenching processes other than prototropic quenching are insignificant for these systems.

Fig. 2 shows another set of plots reflecting a deviation of the slope from unity. The bases used here were aqueous solutions of ammonia and different aliphatic amines. This deviation in the presence of amines is probably indicative of the involvement of other fluor-

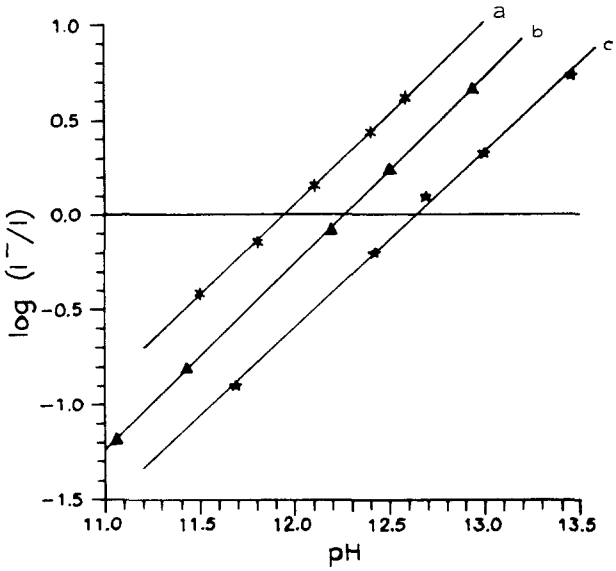

Fig. 1. Plot of $\log(I^-/I)$ vs. pH of the solution: (a) CAZL–NaOH; (b) INDZ–NaOH; (c) 2HB–NaOH.

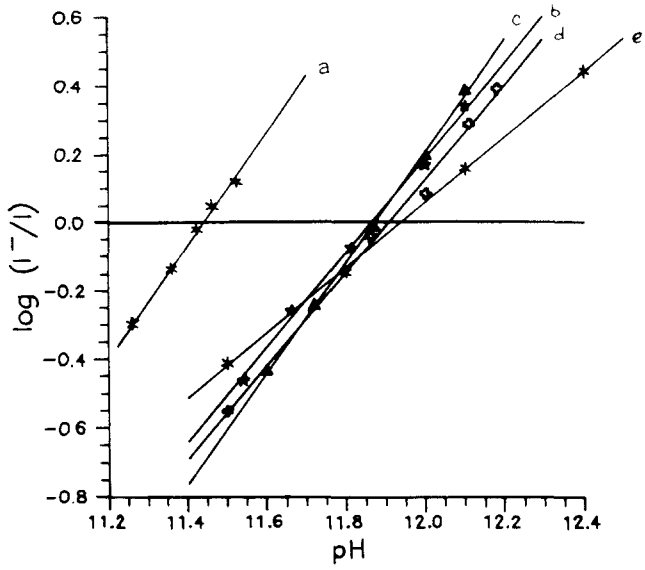

Fig. 2. Plot of $\log(I^-/I)$ vs. pH of the solution: (a) CAZL–NH_4OH; (b) CAZL–$EtNH_2$; (c) CAZL–Et_2NH; (d) CAZL–Et_3N; (e) CAZL–NaOH, for reference to show the deviation of the other slopes from unity.

Table 1
Steady state pK^* values determined in aqueous medium

Compound	Base used	pK^* value		
		This method	Weller's method	Reference
CAZL	NaOH	11.92	11.9	[9]
INDZ	NaOH	12.21	12.2	[12]
2HB	NaOH	12.62	12.6	[13]
CAZL	NH_4OH	11.45	11.24	[11c]
	$EtNH_2$	11.86	11.44	[11c]
	Et_2NH	11.87	11.47	[11c]
	Et_3N	11.91	11.64	[11c]

escence quenching processes in addition to prototropic quenching. The pK^* values extracted from these plots are reported in Table 1. It is obvious from the table that the deviation of these values from those obtained using Weller's method is greater than that of the previous set. The variation in the steady state pK^* value of a particular compound (e.g. CAZL), determined in the presence of different bases, results from the different transitory characters of the excited species in different environments [10].

Although the field of application is restricted to fluorophores showing dual luminescence during ESPT reactions and the quantum yields of the two prototropic forms should be the same, the technique described here is simple and reproducible. From the slope of the plot ($\log(I^-/I)$ vs. pH), it can be determined whether or not fluorescence quenching occurs by a process other than proton transfer induced by the quencher (base or acid). Finally, it is hoped that this technique of exploiting the dual luminescence from both prototropic forms may be applicable to intermolecular as well as intramolecular ESPT reactions.

Appendix

$$AH^* \rightleftharpoons A^{-*} + H^+ \quad K^* = \frac{[A^{-*}][H^+]}{[AH^*]}$$

$$BOH \rightleftharpoons B^+ + OH^- \quad K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$H^+ + OH^- \rightleftharpoons H_2O \quad K_w = \frac{[H^+][OH^-]}{[H_2O]}$$

Therefore,

$$AH^* + BOH \rightleftharpoons A^{-*} + B^+ + H_2O \quad K = \frac{K^* K_b}{K_w} \qquad \text{(A1)}$$

Or

$$K = \frac{[A^{-*}][B^+][H_2O]}{[AH^*][BOH]}$$

$$K = \frac{[A^{-*}]}{[AH^*]} \times \frac{[B^+][OH^-]}{[BOH]} \times \frac{[H_2O]}{[OH^-]} \qquad \text{(A2)}$$

Assuming that the fluorescence quantum yields of the two prototropic species are the same, we obtain from Eqs. (A1) and (A2)

$$K^* = \frac{I^-}{I} \times [H^+] \qquad \text{(A3)}$$

which gives the relation

$$\log(I^{-}/I) = \mathrm{pH} - \mathrm{p}K^{*} \quad \text{(A4)}$$

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