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Steady-state fluorimetric studies of proton-transfer kinetics of some photoexcited hydroxyaromatics in DMSO-water solutions

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Abstract - Proton transfer kinetics of some photoexcited sulfonated hydroxyaromatics have been evaluated in DMSO-water solutions. An empirical linear relationship between the logarithm of the dissociation rate constant and the mole fraction of DMSO has been established. An attempt has also been made to relate the dissociation rate constant to the activity of water with limited success. The association rate constant has been confirmed to be relatively independent of solution composition.

INTRODUCTION

The acid-base chemistry of organic molecules in their lowest electronically excited singlet states has been a subject of interest for over three decades and is of direct relevance to the photochemical and photophysical dispositions of excited molecules. In 1952 Weller (ref. 1) showed that the dependences of the fluorescences of aromatic acids and bases, upon pH, are quantitatively related to the kinetics of proton transfer in their lowest excited singlet states as well as to the states of ionization of the absorbing species in their ground electronic states. This is a result of the fact that the lifetimes of the lowest excited singlet states of fluorescent molecules typically range from a few tenths of a nanosecond to perhaps 100 nanoseconds. This is the time frame in which proton transfer between acids and bases, in which oxygen or nitrogen atoms are the proton donors and acceptors, occurs.

The temporal competition of proton-transfer with fluorescence permits the study of those chemical processes occurring on the nanosecond time scale by fluorescence spectroscopy. Moreover, whereas several of the techniques used to study ground-state proton transfer kinetics are capable of determining the rate of reaction in only one direction, requiring the complimentary reaction rate to be calculated indirectly from the equilibrium constant, fluorimetric acid-base titrimetry often permits the direct observation of both protonation and proton-abstraction steps. In this regard, the fluorimetric approach to acid-base reaction kinetics, although directly involving electronically excited species, yields conclusions which are invaluable for the understanding of acid-base chemistry in general, but especially for those kinds of reactions which occur in the nanosecond time frame.

In the years since Weller initially developed the kinetic approach to excited state proton transfer there have been a large number of applications of his approach (refs. 2-7). With the advent of pulsed lasers and commercial flash-lamps in recent years, the instrumentation available for the quantitation of proton-transfer kinetics has become better and a complement to Weller's steady-state approach, in the form of time-correlated single-photon counting, has extended the treatment to some systems that were difficult to handle by the straightforward steady-state approach. With few exceptions (refs. 8,9) efforts have been directed at the determination of rate constants of proton-transfer in dilute aqueous solutions. Studies in aqueous solutions yield overall rate constants of protonation and proton abstraction which may be useful for evaluating acid-or base-catalyzed reactions in water but which yield very limited information about the proton-transfer process itself. Observation of proton-transfer kinetics in mixed aqueous organic solvents on the other hand might reveal more microscopic details of the reaction or of the nature of the solvent-solvent or solvent-solute interactions.

Recently, in this laboratory (ref. 10), it was shown that in moderately concentrated electrolyte solutions, changes in the rate constants for proton transfer in electronically excited organic acids could be accounted for by assuming that the rate of dissociation was limited by the rate at which the dissociating acid was hydrated to form the transition state (or the solvent-separated ion-pair which is the encounter complex of the fully hydrated proton and the fully hydrated conjugated base). This approach works well and is simple as long as there is sufficient water in the solution to fully hydrate all participants in the reaction as they are hydrated in dilute aqueous solutions. It would seem that a similar

approach would be useful for mixed water-organic solvent systems (with some modifications). Preliminary experiments in this laboratory, as well as the result of the few previous fluorimetric studies of proton-transfer kinetics in mixed aqueous-organic solvents (refs. 8,9), have shown that even in relatively high-dielectric, aprotic solvents weak organic acids (pKa >0) do not dissociate measurably during the lifetime of the lowest excited singlet state unless water is present. Moreover, the pseudo first-order rate constant for dissociation increases as the mole-fraction of water in the mixed solvent increases. The preliminary studies also show that the diffusion-controlled protonation of excited bases by the solvated proton occurs with a rate that is relatively unaffected by the macroscopic viscosity, even in highly viscous glycerol-water solutions (ref. 8). These observations suggested that additional study of excited-state proton transfer in mixed aqueous organic solvents would yield important information about the proton-transfer process and the participation of the solvent in the process.

EXPERIMENTAL

2-Naphthol, 2-naphthol-6-sulfonic acid (monosodium salt), 2-naphthol-6, 8-disulfonic acid (disodium salt), 2-naphthol-8-sulfonic acid (monosodium salt) and 2-naphthol-3,6-disulfonic acid (disodium salt) were purchased from Matheson, Coleman and Bell, East Rutherford, N.J. These compounds were purified by triple recystallization from ethanol-water and the purities of the recrystallized materials were confirmed by TLC. 8-Hydroxy-1,3,6-pyrenetrisulfonic acid (trisodium salt; laser grade) was purchased from Eastman Kodak Co., Rochester, N.Y. and was used as received. 70% perchloric acid and reagent-grade DMSO were purchased from Fisher Scientific Co., FairLawn, N.J. and used as received. Steady-state fluorescence measurements were made on either a Perkin Elmer MPF-2A, MPF-44 or LS-5 fluorescence spectrophotometer. Fluorescence decay-times were measured on a TRW model 31B decay time fluorometer and compared with literature valves. Fluorescence standards from Precision cells, Inc. were used to calibrate the excitation and emission monochromaters of these instruments. pH measurements were made with a Markson pH meter employing a Fisher silver/silver choride pencil glass combination electrode. UV-visible measurements were made employing either a Perkin Elmer Lambda-4 or a Beckman model 25 spectrophotometer which had been calibrated using the absorbance peaks of a holmium oxide filter.

SOLVENT TITRATIONS

Stock solutions of each of the compounds examined were made prior to each measurement. For 2-naphthol and sodium 2-naphthol-6-sulfonate these were 10^{-2} M methanolic solutions whereas aqueous 10^{-2} M solutions were prepared for the remaining compounds as necessitated by their poor solubility in methanol. Secondary 10^{-3} M, 10^{-4} M and 10^{-5} M stock solutions were prepared by serial dilution. The solutions used in the titrations consisted of an aqueous and a non-aqueous 5×10^{-6} M solution of the hydroxyaromatic, with one exception, prepared by micropipetting 50 µl of the 10^{-4} M secondary stock solution into each of two 10-ml volumetric flasks followed by dilution to the mark with deionized water to prepare the aqueous solution and DMSO to prepare the non-aqueous solution.

The fluorescent probe concentration of the solutions used in the titrations was chosen such that the absorbance at the isosbestic point used as the analytical wavelength in the fluorescence measurements would be less than 0.02 thereby reducing the probability of nonlinear fluorescence.

Because of the high molar absorptivity and quantum yield of fluorescence which characterize the photophysics of 8-hydroxy-1,3,6-pyrenetrisulfonate, it was necessary to reduce its concentration to 5×10^{-7} M in the solutions used in the titrations when this probe was employed. These solutions were prepared following the same procedure as for the preparation of the solutions containing 5×10^{-6} M probe with the exception that a 10^{-5} M 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt secondary stock solution was used.

Titrations were performed as follows. (1) 2 ml of the aqueous 5×10^{6} M solution was pipetted into a cuvette having a 4 ml capacity. (2) The fluorescence spectrum of the aqueous solution was recorded. (3) An aliquot of the non-aqueous 5×10^{-6} M solution was added to the cuvette. After thorough mixing, the spectrum of the solution was again recorded. This step was then repeated until a total of 2 ml of the non-aqueous solution had been added to the cuvette. At this point, 2 ml of the solution in the cuvette was removed permitting the continuance of the titration. Step 3 was repeated until emission from the excited conjugate base species could no longer be detected or until the mole fraction of the non-aqueous component of the resulting soution approached unity. (4) The fluorescence spectrum of 2 ml of the non-aqueous solution was recorded. (5) The fluorescence spectrum of the conjugate base, isolated by the addition of an appropriate amount of 1 M NaOH to 2 ml of aqueous solution, was recorded.

ACID/BASE TITRATION

500 ml stock solutions of approximately 0.5, 1, 3, 5, 7 and 9M $HClO_4$ were prepared by dilution of 70% (11 M) $HClO_4$ with distilled, deionized water. The exact molarity of each solution was determined by titration with standardized sodium hydroxide solutions. The acid solutions used in the titrations were prepared by micropipetting into each of 6 10-ml volumetric flasks 50 µl of the 10^{-4} M secondary stock solution of the probe employed, followed by dilution to the mark with the 0.5, 1, 3, 5, 7 and 9 M $HClO_4$ solutions respectively. The solutions of known mole fraction of organic cosolvent to be titrated were prepared by first micropipetting 500 µl of the 10^{-4} M secondary stock solution into 100 ml volumetric flasks and secondly by pipetting V ml of the organic co-solvent into the 100 ml flasks and finally by adding (100-V) ml of water. For reasons already stated, it was necessary to modify this procedure by reducing the concentration of probe in the case of 8-hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt by a factor of 10.

Titrations were performed as follows. (1) 10 ml of the fresh 100 ml solution were withdrawn from the flask. 2 ml of this solution were pipetted into a 1 cm^2 cuvette and the spectrum of this solution was taken. The remaining 8 ml were used in the determination of the solution pH. (2) After the pH reading was recorded the fractions were returned to the 100 ml volumetric flasks and an aliquot of the 0.5 M $HClO_4$ solution containing the probe was added. A Gilmont microburet was used for this purpose. After thorough mixing 10 ml were withdrawn and the cycle was repeated. In this manner a total of 1 ml of each of the 6 acid solutions containing the probe was added and the spectrum recorded after each addition. pH readings were continued until an indicated reading of pH 1.00 as the reliability of measurements below this value even in aqueous solutions is questionable. (3) In order to complete the titration, after the last addition of the 9 M $HClO_4$ probe solution, 2 ml of the solution was withdrawn from the flask and pipetted into the cuvette. Aliquots of the 9 M $HClO_4$ solution were then added directly to the cuvette and the spectrum recorded after each addition. (4) A 10 ml solution containing the same mole fraction of organic cosolvent and probe concentration as in the 100 ml solution was prepared by scaling down the procedure given above for the preparation of the 100 ml of solution. 2 ml of this solution was pipetted into a cuvette and the spectrum of this soution was then recorded. Microliter amounts of 1 M NaOH were thereafter added to the solution, the pH of the solution was monitored and the spectrum again recorded. This process was continued until the emission spectrum of the excited conjugate base was isolated.

DETERMINATION OF PROTON-TRANSFER RATE CONSTANTS

Proton-transfer reactions in the absence of buffer species in aqueous or partially aqueous solutions, in which water is the proton acceptor can be considered to occur according to the following scheme.

Scheme I

$$HA^n + rH_2O \underset{k_r}{\overset{k_i}{\rightleftharpoons}} H^+A^{n-1} \underset{k_a}{\overset{k_d}{\rightleftharpoons}} H^+ + A^{n-1}$$

Here, HA^n is the photoexcited conjugate acid, n the charge on the acid, H^+A^{n-1} is the solvent-separated ion-pair (or ion-molecule pair), A^{n-1} is the conjugate base of HA^n and k_i, k_r, k_d and k_a are the rate constants for ionization of HA^n (k_i appears here as a pseudo-first-order rate constant), recombination of H^+ and A^{n-1} in the separated ion-pair (encounter complex), dissociation of H^+A^{n-1} into free ions and association of H^+ and A^{n-1} to form the encounter complex, respectively.

The disappearances of HA^n, H^+A^{n-1} and A^{n-1} from the lowest excited singlet state subsequent to excitation under conditions where a steady state has been established in the excited state are described by

Scheme II

$$-d[HA^n]/dt = \left(\frac{1}{\tau_o} + k_i\right)[HA^n] - k_r[H^+A^{n-1}] \quad (1)$$

$$-d[H^+A^{n-1}]/dt = \left(\frac{1}{\tau'_o} + k_r + k_d\right)[H^+A^{n-1}] - k_i[HA^n] - ka\,[H^+][A^{n-1}] \quad (2)$$

and

$$-d[A^{n-1}]/dt = \left(\frac{1}{\tau_o'} + k_a [H^+]\right)[A^{n-1}] - k_d [H^+A^{n-1}] \tag{3}$$

These may be integrated from $[HA^n] = 1$, $[H^+A^{n-1}] = 0$ and $[A^{n-1}] = 0$ when $t = 0$ to $[HA^n] = 0$, $[H^+A^{n-1}] = 0$ and $[A^{n-1}] = 0$ when $t = \infty$ if the ground and excited-state pKa values differ by 4 or more units (as is the case for the phenolic molecules studied here, i.e., HA^n is excited exclusively). The result of this integration is

$$\frac{\varphi}{\varphi_o} = \frac{(k_r + k_d)\,\tau_o'' + k_r\tau_o''k_a\tau_o'\,[H^+]}{(k_r + k_d)\tau_o'' + (1 + k_d\tau_o')k_i\tau_o + (k_r\tau_o'' + k_i\tau_o)\,k_a\tau_o'\,[H^+]} \tag{4}$$

$$\frac{\varphi''}{\varphi_o''} = \frac{k_i\tau_o + (1 + k_a\tau_o'\,[H^+])}{(k_r + k_d)\tau_o'' + (1 + k_d\tau_o')k_i\tau_o + (k_r\tau_o'' + k_i\tau_o)\,k_a\tau_o\,[H^+]} \tag{5}$$

$$\frac{\varphi'}{\varphi_o'} = \frac{k_d\tau_o'\,k_i\tau_o}{(k_r + k_d)\tau_o'' + (1 + k_d\tau_o')k_i\tau_o + (k_r\tau_o'' + k_i\tau_o)\,k_a\tau_o\,[H^+]} \tag{6}$$

where φ/φ_o, φ''/φ_o'' and φ'/φ_o' are the respective relative quantum yields of fluorescence and τ_o, τ_o'' and τ_o' are the respective lifetimes of the lowest excited singlet states (in the absence of proton-transfer) of HA, H^+A^{n-1} and A^{n-1}.

If the numerators and denominators of equations (4) - (6) are divided by $(k_r + k_d)\tau_o''$ and we let

$$\vec{k} = \frac{k_d k_i}{k_r + k_d} \quad \text{and} \quad \overleftarrow{k} = \frac{k_r k_a}{k_r + k_d}$$

the steady-state equations become

$$\frac{\varphi}{\varphi_o} = \frac{1 + \overleftarrow{k}\tau_o'[H^+]}{(1 + \vec{k}\tau_o + \overleftarrow{k}\tau_o'\,[H+]) + \dfrac{\vec{k}\tau_o\,(1 + k_a\tau_o'\,[H^+])}{k_d\tau_o''}} \tag{7}$$

$$\frac{\varphi''}{\varphi_o''} = \frac{\dfrac{\vec{k}\tau_o\,(1 + k_a\tau_o\,[H^+])}{k_d\tau_o''}}{(1 + \vec{k}\tau_o + \overleftarrow{k}\tau_o'\,[H+]) + \dfrac{\vec{k}\tau_o\,(1 + k_a\tau_o'\,[H^+])}{k_d\tau_o''}} \tag{8}$$

$$\frac{\varphi'}{\varphi_o'} = \frac{\vec{k}\tau_o}{(1 + \vec{k}\tau_o + \overleftarrow{k}\tau_o'\,[H+]) + \dfrac{\vec{k}\tau_o\,(1 + k_a\tau_o'\,[H^+])}{k_d\tau_o''}} \tag{9}$$

wherein $\vec{k}$ and $\overleftarrow{k}$ are the overall rate constants for the forward and reverse reactions of schemes I and II, respectively. k_d and k_a can be estimated along the lines developed by Smoluchowski and Debye (refs. 10-11) and $\tau_o \sim \tau_o' \sim \tau$ (typically about 10 ns). If $k_d\tau_o''$ is very large (as in water), $\vec{k}\tau_o/k_d\tau_o''\,(1 + k_a\tau_o\,[H^+])$ will usually be very small and equations (7) - (9) become

$$\frac{\varphi}{\varphi_o} = \frac{1 + \overleftarrow{k}\tau_o'\,[H^+]}{1 + \vec{k}\tau_o + \overleftarrow{k}\tau_o'\,[H^+]} \tag{10}$$

$$\frac{\varphi''}{\varphi_o''} = 0 \tag{11}$$

$$\frac{\varphi'}{\varphi'_o} = \frac{\vec{k}\tau_o}{1 + \vec{k}\tau_o + \overleftarrow{k}\tau'_o[H^+]} \tag{12}$$

which are the steady state equations originally derived by Weller (ref. 1).

When $[H^+]$ is very small (i.e. pH> 4) $\overleftarrow{k}\tau'_o[H^+]$ and $\vec{k}\tau_o(1 + k\tau_o[H^+]k_d\tau''_o)$ become negligibly small in equations (7) - (9) and these then reduce to

$$(\varphi / \varphi_o)_c = \frac{1}{1 + \vec{k}\tau_o + \overleftarrow{k}\tau_o/k_d\tau''_o} \tag{13}$$

$$(\varphi''/\varphi''_o)_c = \frac{\vec{k}\tau_o/k_d\tau''_o}{1 + \vec{k}\tau_o + \vec{k}\tau_o/k_d\tau''_o} \tag{14}$$

$$(\varphi'/\varphi'_o)_c = \frac{\vec{k}\tau_o}{1 + \vec{k}\tau_o + \vec{k}\tau_o/k_d\tau''_o} \tag{15}$$

in which the relative fluorescence efficiencies are independent of pH (the subscript c stands for constant).

In a high dielectric medium such as water, $k_d\tau''_o >> 1$ and equations (13) - (15) become

$$(\varphi/\varphi_o)_c = \frac{1}{1 + \vec{k}\tau_o} \tag{16}$$

$$(\varphi''/\varphi''_o)_c = 0 \tag{17}$$

and

$$(\varphi'/\varphi_o)_c = \frac{\vec{k}\tau_o}{1 + \vec{k}\tau_o} \tag{18}$$

Now in equations (7) - (18), $\vec{k}$ and $\overleftarrow{k}$ are the observed rate constants for the overall pseudo-first-order forward reaction and second-order back reaction, respectively. If HA^n is a weak acid, as will be employed here ($pK_a > 0$), $\overleftarrow{k}$ corresponds to the rate constant of a diffusion-controlled reaction so that the rate constant, k_a, for ionic recombination is the overall rate constant $\overleftarrow{k}$. If $\overleftarrow{k} = k_r k_a/(k_r+k_d)$ it follows that if $k_a = \overleftarrow{k}$, $k_r >> k_d$.

Consequently, $\vec{k} = k_d k_i/k_r$ so that the ion-pairing term $\vec{k}\tau_o/k_d\tau''_o$ is equal to $k_i\tau_o/k_r\tau''_o$. If τ_o and τ''_o are of the same magnitude, since $k_i << k_r$ for a weak acid, $k_i\tau_o/k_r\tau''_o << 1$ and contributions to the fluorescence from the solvent-separated ion-pair will always be negligible, i.e. if the dielectric constant is low, no proton transfer during the lifetime of the excited state will be observed. This is, of course, not true for strong acids and bases where $k_i > k_r$.

For weak acids and bases then, equations (7)-(9) will always correspond to (10)-(12) as will equations (13)-(15) to (16)-(18). Combination of equations (16) and (18) yields

$$\frac{(\varphi'/\varphi'_o)_c}{(\varphi/\varphi_o)_c} = \frac{1 - (\varphi/\varphi_o)_c}{(\varphi/\varphi_o)_c} = \vec{k}\tau_o \tag{19}$$

which permits a rapid determination of $\vec{k}$ if τ_o can be measured or otherwise estimated. Moreover, combination of equations (10) and (12) yields

$$\frac{\varphi/\varphi_o}{\varphi/\varphi'_o} = \frac{\varphi/\varphi_o}{1 - \varphi/\varphi_o} = \frac{1}{\vec{k}\tau_o} + \frac{\overleftarrow{k}\tau'_o}{\vec{k}\tau_o}[H^+] \tag{20}$$

which permits evaluation $\vec{k}$ and $\overleftarrow{k}$ (or $\overleftarrow{k}$ alone if $\vec{k}$ has already been determined from equation (16). It should be noted that in a series of given solvents (or solvent mixtures) τ_o, τ'_o and φ'_o may vary so that for determination of τ_o and τ'_o, renormalization of φ/φ_o and φ/φ'_o in each may be necessary. This involves only adding a bit of mineral acid or base to a test solution in a given solvent system and measuring the fluorescence intensity or decay time.

RESULTS

Representative fluorimetric titrations (variations of the relative fluorescence efficiencies, φ/φ_o, with $[H^+]$ of 2-naphthol-8-sulfonate, at different mole fractions of DMSO are shown in Fig. 1. The line obtained when $\ln \vec{k}\tau_o$ was plotted against the mole fraction of DMSO is shown in Fig. 2 ($\vec{k}$ is the rate constant for dissociation in the S_1 state and τ_o the lifetime of the conjugate acid in S_1) and when $\ln \vec{k}\tau_o$ is plotted against $\ln a_w$ where a_w is the activity of water in the mixed DMSO-water solutions in Fig. 3. In Table 1 are presented the slopes of the lines obtained for the plots of $\ln \vec{k}\tau_o$ vs mole fraction of organic solvent for all of the DMSO-water solutions studied. Presented in Table 2 are the values of $\vec{k}\tau_o'$ taken from the slopes of the plots of $(\varphi/\varphi_o/1 - \varphi/\varphi_o)$ vs. $[H^+]$ for all compounds studied, along with the corresponding values of τ_o' and the calculated values of $\vec{k}$.

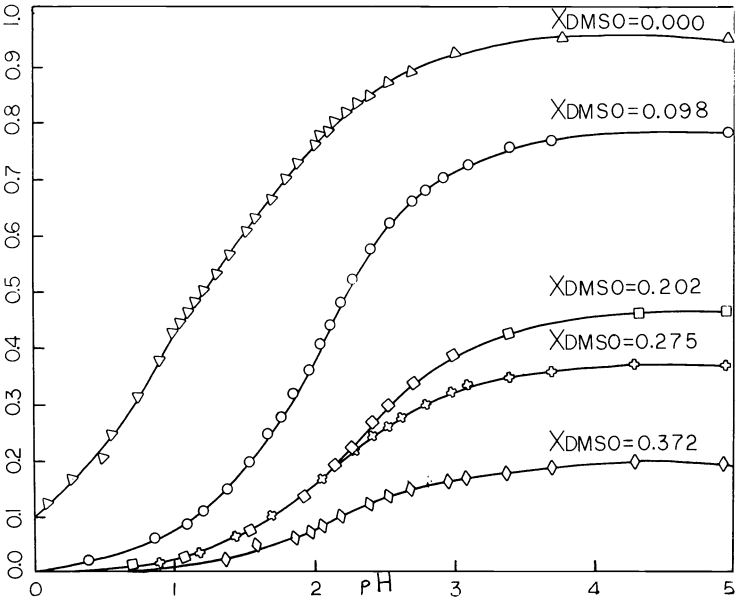

Fig. 1. Variation of the relative fluorescence efficiencies, φ/φ_o, with pH of the 2-naphthol-8-sulfonate dianion at different mole fractions of DMSO, X_{DMSO}.

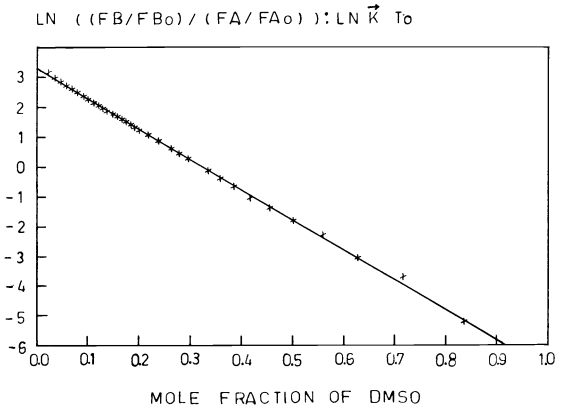

Fig. 2. Variation of $\ln \vec{k}\tau_o$, with X_{DMSO} for 2-naphthol-8-sulfonate.

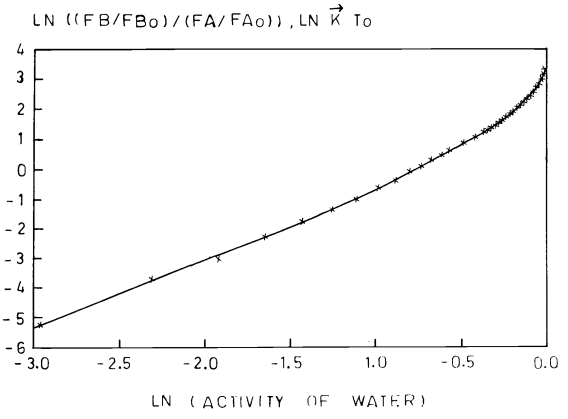

Fig. 3. Variation of $\ln \vec{k}\tau_o$, with $\ln a_w$ (a_w is the activity of water) in DMSO-water solutions.

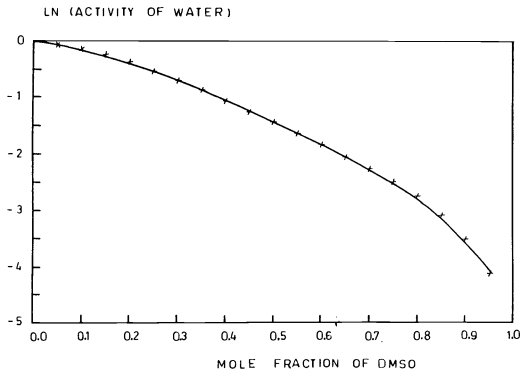

Fig. 4. Variation of $\ln a_w$ with X_{DMSO} in DMSO-water solutions.

TABLE 1. Slopes of the plots of $\ln \vec{k}\tau_o$ versus X_{DMSO}.

Slope	Fluorescent probe
-9.0 ± 0.5	2-Naphthol
-9.0 ± 0.3	2-Naphthol-6-sulfonate
-10.0 ± 0.2	2-Naphthol-8-sulfonate
-10.9 ± 0.3	2-Naphthol-3,6-disulfonate
-10.0 ± 0.2	2-Naphthol-6,8-disulfonate
-10.0 ± 0.2	8-Hydroxy-1,3,6-trisulfonate

TABLE 2. Rate constant for the protonation of some hydroxy aromatics in DMSO-water solutions.

Compound	Volume% DMSO	Mole fraction DMSO	$\vec{k}\tau'_o(M^{-1})$	τ'_o(N.S.)	$\vec{k}(M^{-1}s^{-1})$
2-Naphthol					
	0	0.000	413 ± 30	9.0 ± 0.2	4.6±0.4 x 10^{10}
	10	0.027	419 ± 12	9.0± 0.2	4.8±0.5 X 10^{10}
	20	0.060	603 ± 27	9.0± 0.2	6.0±0.6 X 10^{10}
	30	0.098	287 ± 13	9.0± 0.2	3.2± 0.7 X 10^{10}
	40	0.145	664 ± 85	9.0± 0.2	7.3±0.5 X 10^{10}
2-Naphthol-6-sulfonate					
	0	0.000	831 ± 40	16.6± 0.4	5.0±0.3 x 10^{10}
	50	0.202	618 ± 36	16.6± 0.4	3.7±0.4 x 10^{10}
	60	0.275	415 ± 24	16.6± 0.4	2.5±0.3 x 10^{10}
	70	0.372	166 ± 5	16.6± 0.4	1.0±0.1 x 10^{10}
2-Naphthol-8-sulfonate					
	0	0.000	654 ± 40	18.7 ± 0.4	3.5±0.2 x 10^{10}
	30	0.098	390 ± 7	18.7 ± 0.4	2.1±0.3 x 10^{10}
	50	0.202	355 ± 5	18.7 ± 0.4	1.9±0.4 x 10^{10}
	60	0.275	449 ± 8	18.7 ± 0.4	2.4±0.7 x 10^{10}
	70	0.372	187 ± 4	18.7 ± 0.4	1.0±0.1 x 10^{10}
2-Naphthol-6,8-disulfonate					
	0	0.000	419 ± 20	26.2 ± 1.1	1.6±0.1 x 10^{10}
	40	0.145	309 ± 57	26.2 ± 1.1	1.2±0.2 x 10^{10}
	50	0.202	314 ± 37	26.2 ± 1.1	1.2±0.1 x 10^{10}
	70	0.372	445 ± 40	26.2 ± 1.1	1.7±0.2 x 10^{10}
2-Naphthol-3,6-disulfonate					
	0	0.000	1627 ± 30	16.6 ± 0.6	9.8±1.1 x 10^{10}
	50	0.202	996 ± 40	16.6 ± 0.6	6.0±0.7 x 10^{10}
	60	0.275	498 ± 25	16.6 ± 0.6	3.0±0.3 x 10^{10}
	70	0.372	830 ± 37	16.6 ± 0.6	5.0±0.4 x 10^{10}
8-Hydroxypyrene-1,3,6-trisulfonate					
	0	0.000	433 ± 19	5.4 ± 0.3	8.0±0.4 x 10^{10}
	50	0.202	270 ± 21	5.4 ± 0.3	5.0±0.3 x 10^{10}
	60	0.275	216 ± 32	5.4 ± 0.3	4.0±0.3 x 10^{10}
	70	0.375	216 ± 17	5.4 ± 0.3	4.0±0.5 x 10^{10}

DISCUSSION

The plots of ln $\vec{k}\tau_o$ vs. mole fraction of DMSO are linear with excellent correlation coefficients. Slight deviations from linearity in the case of 2-naphthol at higher values of X_D are due to the nearly complete inhibition of excited-state dissociation and the attendant uncertainty in the determination of φ'/φ'_o under this circumstance. In the sulfonated 2-naphthols and the trisulfonated 1-hydroxypyrene, there is slight deviation from linearity at very low values of X_D as well because in pure or nearly pure water, these acids are so strong in the excited, state and dissociation is so extensive, that φ/φ_o cannot be determined with great accuracy or precision. Regardless of the hydroxyaromatic excited, the slope of the plot of ln $\vec{k}\tau_o$ vs X_D is between 9 and 10. The linearity of plots of $\vec{k}$ vs. mole fraction of organic cosolvent has been observed by Huppert et al. (ref. 9) in a variety of water-alcohol solutions and been suggested to infer the importance of the water structure in the proton-transfer process. That excited-state proton transfer is essentially unobservable at $X_D > 0.7$ certainly implies that a substantial amount of "free" water is necessary for proton-transfer to occur on the nanosecond time scale. This is rather interesting because even in neat DMSO prototropic equilibrium in the ground states of organic acids and bases is commonly observed as it is in a wide variety of organic solvents. The absence of excited-state (nanosecond) proton transfer in water-poor solutions suggests that the frictional diffusion mechanism (entailing translation of the solvated proton as well as the conjugate base) by which proton transfer occurs in most organic (certainly all aprotic) solvents must be too slow to allow dissociation to compete with ion recombination. Therefore, the much faster structural diffusion or Grotthus (proton jump through extended hydrogen-bonded network) mechanisms are necessary for proton-transfer to occur on the nanosecond time scale. The very small dependence of the reprotonation reaction on viscosity and dielectric constant in the mixed solvents, also observed by Trieff and Sundheim (ref. 8) in methanol water and glycerol-water solutions, indicates, moreover, that protonation as well as dissociation must occur by structural diffusion rather than by frictional diffusion.

The invariances of the slopes of the plots of ln $\vec{k}\tau_o$ vs. X_D with the formal charge on the conjugate base shows that the continuum dielectric properties of the DMSO-water solutions are irrelevant to the chemistry taking place in these solutions. In fact, the slope seems to be characteristic of the solvent system although it may contain factors related to the dissociation of the aromatic hydroxy group. At present the reason for the constancy of the slope is not fully clear. However, it probably represents some energetic parameter such as the heat of mixing of the two solvents. This is presently under investigation. In concentrated aqueous electrolyte solutions

$$\ln\vec{k} = \ln\vec{k}(o) + r\ln a_w \tag{21}$$

where $\vec{k}(o)$ is the rate constant for acid dissociation in the lowest excited singlet state in pure water and $\vec{k}$, that in a concentrated electrolyte solution, a_w is the activity of water and r has the same significance as in scheme I. Since it was found, empirically; in this study, that

$$\ln\vec{k} = \ln\vec{k}(o) + MX_D \tag{22}$$

where M is the slope of the plot of $\ln\vec{k}$ (or $\ln\vec{k}\tau_o$, if τ_o is invariant with respect to solvent composition), it seemed reasonable to equate

$$r \ln a_w = MX_D \tag{23}$$

Values of a_w for DMSO-water solutions have been published (refs. 12-13) and from these a plot of ln a_w vs X_D was constructed. As can be seen from Fig. 4 the plot is nearly but not quite linear. It would appear that ln a_w and X_D are related but the appropriate function of solvent composition or acid-base reactivity, necessary to modify equation (23) to make it exact has, so far, eluded us.

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