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An operational pH in aqueous dimethylsulfoxide based upon the acidity dependence of the rate of a simple ionic recombination reaction in the lowest excited singlet state

Rong Yang, Stephen G. Schulman *

Department of Medicinal Chemistry, College of Pharmacy, University of Florida, P.O. Box 100485, Gainesville, FL 32610-0485, USA

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Abstract

7-Hydroxy-1-naphthalenesulfonate (2-naphthol-8-sulfonate) monoanion demonstrates proton transfer in the lowest excited singlet state in DMSO–water mixtures as well as in pure water. The dissociation reaction of the directly excited monoanion is strongly solvent-dependent, and independent of solution acidity. The reprotonation of the conjugate base, however, depends predominantly on the acidity of the solution and only on the continuum properties of the solvent. The separability of the dissociation and reprotonation reactions, using steady-state methodology, allows the reprotonation to be treated independent of the dissociation. The linear relationship between the ratio of the relative fluorescence efficiencies of acid and conjugate base, and the hydrogen ion concentration is obtained only if proper Brönsted activity factors are included in the relationship. These factors can be calculated from classical electrostatics and are the fourth powers of the activity coefficients necessary to convert the formal hydrogen ion concentration to hydrogen ion activity. Using this approach, pH was calculated from hydrogen ion concentration in DMSO–water solutions, containing a mole fraction of DMSO up to about 0.4.

Keywords: Operational pH; Dimethylsulfoxide; Proton transfer; Excited singlet state

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Mixed aqueous-organic solvents are widely used in chemistry to enhance the reactivities, solubilities, biological absorption properties, and the chromatographic properties of a wide variety of chemical substances. As in aqueous solutions, the acidity or alkalinity of the solvent will be affected by solutes and its control will often be necessary to obtain optimal chemical results. The concept of pH where $\mathrm{pH} = -\log a_{\mathrm{H}^+}$, a_{H^+} being the activity of the solvated proton, has been an extremely useful one for the quantitative expression of acidity or alkalinity in aqueous solutions.

In principle, at least, it should also be possible to extend the pH concept to partially aqueous solution, although a rigorous definition of pH (or a_{H^+}) requires specification of the standard state of the proton [1], not an easy task in a mixed solvent (especially when the solvent composition is var-

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* Corresponding author. Tel.: +1-352-846-1953; fax: +1-352-392-9455.

E-mail address: schulman@cop.ufl.edu (S.G. Schulman).

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ied). The difficulties that arise when dealing with quantitative descriptions of acidity and alkalinity in mixed aqueous-organic solvents arise from experimental difficulties as well as from thermodynamic aspects insofar as the activity of the proton is concerned. It is, for example, well known that because of the overall electroneutrality of ionic solutions, single ion activities cannot be measured [1]. This pertains to pure aqueous systems as well as to those that are partially aqueous. The measurement of pH, as practiced in laboratories today, is based upon operational definitions of pH in which the true activity a_{H^+} is estimated as a mean activity based upon the charges on the ions derived from the compound yielding the hydrogen ion as well as on the concentrations of all ions in the solution. Usually, the operational pH is measured electrometrically [2], in which case errors due to non-equilibrium liquid junction potentials imposed upon the measurement, or medium effects upon the complimentary half-cell contribute to uncertainty in the true pH. Occasionally, pH is estimated by optical means via pH-dependent changes in the spectra of chemical indicators [3]. Here, uncertainties in the ratio of the activity coefficients and in the extent of hydration of reactants and products of the indicator reaction contribute to the difficulty of obtaining an accurate estimate of the true pH.

In dilute aqueous solutions, liquid junction errors are minimal, the ratios of the activity coefficients of indicator species can be made to approach unity or they can be estimated from the Debye–Hückel relationships [4], and the hydration of the various reaction partners is invariant so that the operational pH measured in water approximates, very well, the true pH.

In mixed aqueous-organic solvents, however, the correspondence between the measured and thermodynamic quantities is not as good. Larger liquid junction potentials and uncertain activity coefficients as well as uncertainty regarding the participation of the solvent in the reaction are the rule, in mixed solvents, although there have been some efforts to correct for those [5,6].

In this note, we would like to demonstrate that one can use a rather specialized area of fluorescence spectroscopy, namely excited-state proton transfer and its kinetic manifestation in the pH dependence of the fluorescence quantum yield (ϕ_0) of a fluorescent organic acid [7] or of its conjugate base (ϕ_0'), to establish a pH-scale in a mixed solvent. The solvent system chosen here was DMSO–water because of its wide use as a solvent in chemistry and biology. The fluorescent indicator chosen was 7-hydroxy-1-naphthalenesulfonate monoanion–dianion conjugate pair because it is soluble in the solvents employed here and because the fluorimetric titration characteristics of most hydroxyaromatics are such that one can separate the characteristics of the dissociation reaction (solvent-dependent, pH-independent) from those of the reprotonation reaction (pH-dependent, minimally solvent-dependent). The latter behavior allows the influence of the hydrogen ion upon the reaction to be quantitatively evaluated with minimal interference from macroscopic and microscopic properties of the solvent, which are, themselves, extremely difficult to assess.

1. Experimental

7-Hydroxy-1-naphthalenesulfonic acid potassium salt was purchased from TCI Organic Chemicals (Portland, OR) and used as supplied. Dimethylsulfoxide (HPLC grade), stored over Davison 4Å molecular sieves, 5.0 M sodium hydroxide, and sulfuric acid (reagent grade) were purchased form Fisher Scientific Co. (Fairlawn, NJ). A Fisher Accumet 950 pH meter employing a Fisher pencil gel-filled silver/silver chloride combination electrode was used for standardization of sulfuric acid and for aqueous pH measurements.

Absorption measurements were made on a Cary model 219 spectrophotometer. Steady-state fluorescence measurements were made on a Perkin–Elmer LS-5 fluorescence spectrophotometer whose monochromators were calibrated against the xenon line emission spectrum. An isobestic point at 309 nm was used for excitation of the naphtholsulfonate and its emission spectrum was monitored from 320 to 520 nm. A Gilmont Pipetman was employed to deliver volumetric amounts of water and cosolvent mixtures.

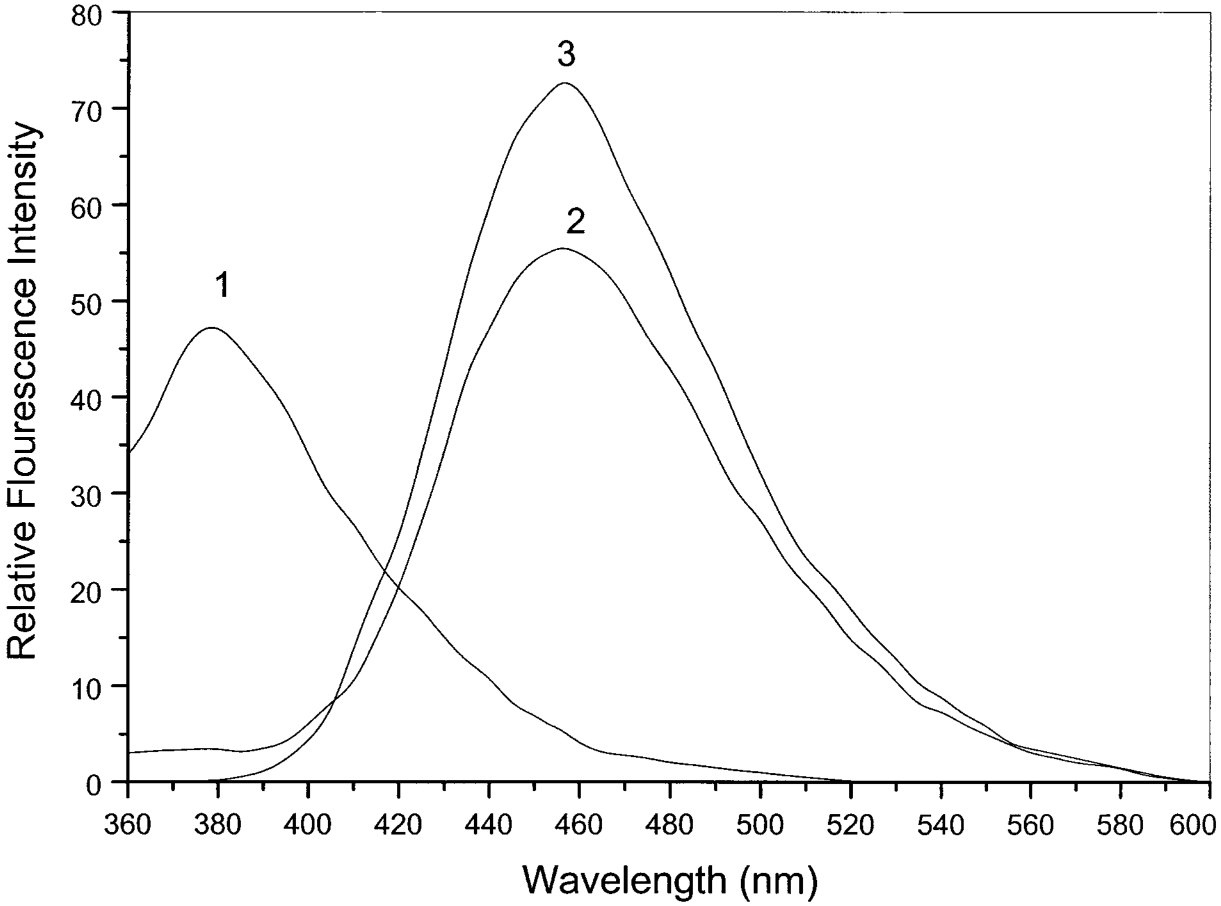

Fig. 1. Fluorescence spectra of the monoanion and dianion derived from 7-hydroxy-1-naphthalenesulfonic acid: (1) $H_0 = -1.25$; (2) pH = 4.03–9.02; and (3) pH = 11.8–14.0.

2. Methods

A 10^{-3} M methanolic stock solution of potassium 7-hydroxy-1-naphthalenesulfonate was prepared prior to experimentation. A known volume of the stock solution was then micropipetted into a series of 10-ml volumetric flasks, and the aliquot was evaporated under a stream of nitrogen gas. The residue was brought to volume by the addition of a known concentration of acid or base along with a specific volume of organic cosolvent to give the mole fraction of interest. The final concentration of naphtholsulfonate in each test solution was 2×10^{-6} M. The probe concentration was chosen to keep the absorbance at the excitation wavelength below 0.02 absorption units, thereby reducing the probability of nonlinear fluorescence.

Titrations were performed as follows:

1) Two milliliters of test solution of known mole fraction of organic cosolvent was pipetted into a 1 cm^2 cuvette having a 3 ml volume and the emission spectrum was obtained.
2) The above solution was titrated with a solution of 0.83 M in sulfuric acid and 2×10^{-6} M in naphtholsulfonate so that the concentration of the latter remained constant throughout the titration. Fluorescence spectra were scanned after each increment of titrant was added, and titration was carried out until the fluorescence of the naphtholsulfonate dianion could no

longer be observed and the fluorescence of the naphtholsulfonate monoanion was maximal and constant. Calculation of the ionic strength at each point in the titration was carried out using the formal concentration of the sulfuric acid at each point, and the pK_a of the bisulfate ion at 25 °C was taken to be 1.98. The relative (ratio of pH-dependent to pH-independent) quantum yields of fluorescence of the monoanion (ϕ/ϕ_0) and of its conjugate base (ϕ'/ϕ'_0) were calculated from the fluorescent intensities from

$$\frac{\phi}{\phi_0}=\frac{F-F'_0}{F_0-F'_0} \tag{1}$$

at the band maximum of the monoanion fluorescence of 379 nm and from

$$\frac{\phi'}{\phi'_0}=\frac{F_0-F}{F_0-F'_0} \tag{2}$$

at the band maximum of the dianion fluorescence of 459 nm, where F_0 is the fluorescence intensity at very low pH (>1 M H_2SO_4), F'_0 the fluorescence intensity at high pH (pH$>$ 12), and F the fluorescence intensity at intermediate pH.

3. Results and discussion

The fluoresences of the naphtholsulfonate dianion and monoanion in water are shown in Fig. 1. The dependencies of the relative quantum yields of fluorescence of the naphtholsulfonate dianion in solvents containing varying molar ratios of DMSO and water on the formal hydrogen ion concentration [H$^+$] are shown in Fig. 2. At formal hydroxide ion concentrations greater than 1×10^{-2} M, the dianion is the sole absorbing and emitting species. In the intervals 1×10^{-4} M$>$[H$^+$]$>1\times10^{-7}$ M and 1×10^{-6} M$>$[OH$^-$]$>1\times10^{-8}$ M, the monoanion is the sole absorber. However, fluorescence is observed from the dianion as well as from the monoanion. This results from the dissociation, in the lowest excited state, of the phenolic group of the directly excited monoanion. In this region of acidity or alkalinity, the relative quantum yields of fluorescence of the monoanion, ϕ/ϕ_0, and of the dianion, ϕ'/ϕ'_0, are invariant with respect to [H$^+$] and [OH$^-$] [7], and are related to the kinetics of dissociation in the excited state, in mixed aqueous-organic solvents as well as in water, by [7,8]

$$\frac{\phi'/\phi'_0}{\phi/\phi_0}=k_a\tau_0, \tag{3}$$

where k_a is the rate constant for prototropic dissociation of 7-hydroxy-1-naphthalenesulfonate monoanion and τ_0 the lifetime of the excited state. It was previously shown for some hydroxyaromatics in other organic solvents mixed with water that $(\phi'/\phi'_0)/(\phi/\phi_0)$ and therefore $k_a\tau_0$ varies exponentially with the mole fraction of organic cosolvent [8–10] and that the slope of the plot of log $k_a\tau_0$ against X_c, the mole fraction of cosolvent, is a function of the activity of water and the distance separating the fully hydrated hydrogen ion and the fully hydrated conjugate base in the encounter complex [11] (or solvent separated ion-pair).

At [H$^+$]$\geq1\times10^{-4}$ M, the fluorescence of the monoanion increased with increasing [H$^+$] in all solvent mixtures, becoming maximal and constant in about 2 M H_2SO_4. At the same time, the fluorescence of the conjugate base decreased and eventually disappeared, concomitant with the increase in fluorescence from the monoanion. This behavior is typical of a hydroxyaromatic compound and corresponds to reprotonation of the excited conjugate base subsequent to dissociation of the conjugated acid [7]. At [H$^+$]$<1\times10^{-4}$ M, the kinetics of reprotonation are such that there is no enough [H$^+$] present to reprotonate the dianion measurably during the lifetime of the excited state, τ'_0. In the acidity region, where ϕ/ϕ_0 and ϕ'/ϕ'_0 vary with [H$^+$], the relationship between them is given by [7,8]

$$\frac{\phi/\phi_0}{\phi'/\phi'_0}=\frac{1}{k_a\tau_0}+\frac{k_b\tau'_0}{k_a\tau_0}F[\mathrm{H}^+], \tag{4}$$

where k_b is the rate constant for reprotonation of the dianion (ArO$^=$) in the excited state and F is the Brönsted kinetic activity factor [12,13] which

Table 1
Debye–Hückel terms (A and B) calculated from Eqs. (4) and (5) at 25 °C and used in the calculation of the Brönsted activity factor (F) at various DMSO mole fractions (X_{DMSO}) having different dielectric strengths (ε) in DMSO–water solutions

DMSO (vol.%)	X_{DMSO}	ε	A	B ($\times 10^{-7}$)	$k_a\tau_0$ (from Eq. (3))	$k_a\tau_0$ (from Eq. (4))	$k_b\tau_0'$	Ionic strength over which $r^2 =$ 0.999
0	0	78.54	0.059	3.29	8.70	8.87	381	0–0.11
30	0.098	77.11	0.522	3.32	3.20	3.16	373	0–0.15
50	0.202	75.00	0.546	3.38	1.16	1.30	294	0–0.015
60	0.275	72.50	0.578	3.42	0.548	0.588	233	0–0.020
70	0.371	68.82	0.625	3.51	0.221	0.233	182	0–0.020

Presented are the products of the rate constants and corresponding fluorescence decay times, $k_a\tau_0$, calculated from Eq. (3), and $k_a\tau_0$ and $k_b\tau_0'$ determined from the intercepts of Fig. 3. All the lines in Fig. 3 had linear correlation coefficients $r^2 = 0.999$ or better.

corrects each experimental value of k_b to zero ionic strength in the solvent mixture chosen. F is derived along the same lines as the extended Debye–Hückel equation for the reaction

$$\mathrm{ArO}^{=} + \mathrm{H}^{+} \leftrightarrow \mathrm{X}^{\neq}$$

where $\mathrm{X}^{\neq}$ is the transition state (or activated complex) preceding the formation of ArOH^{-} and

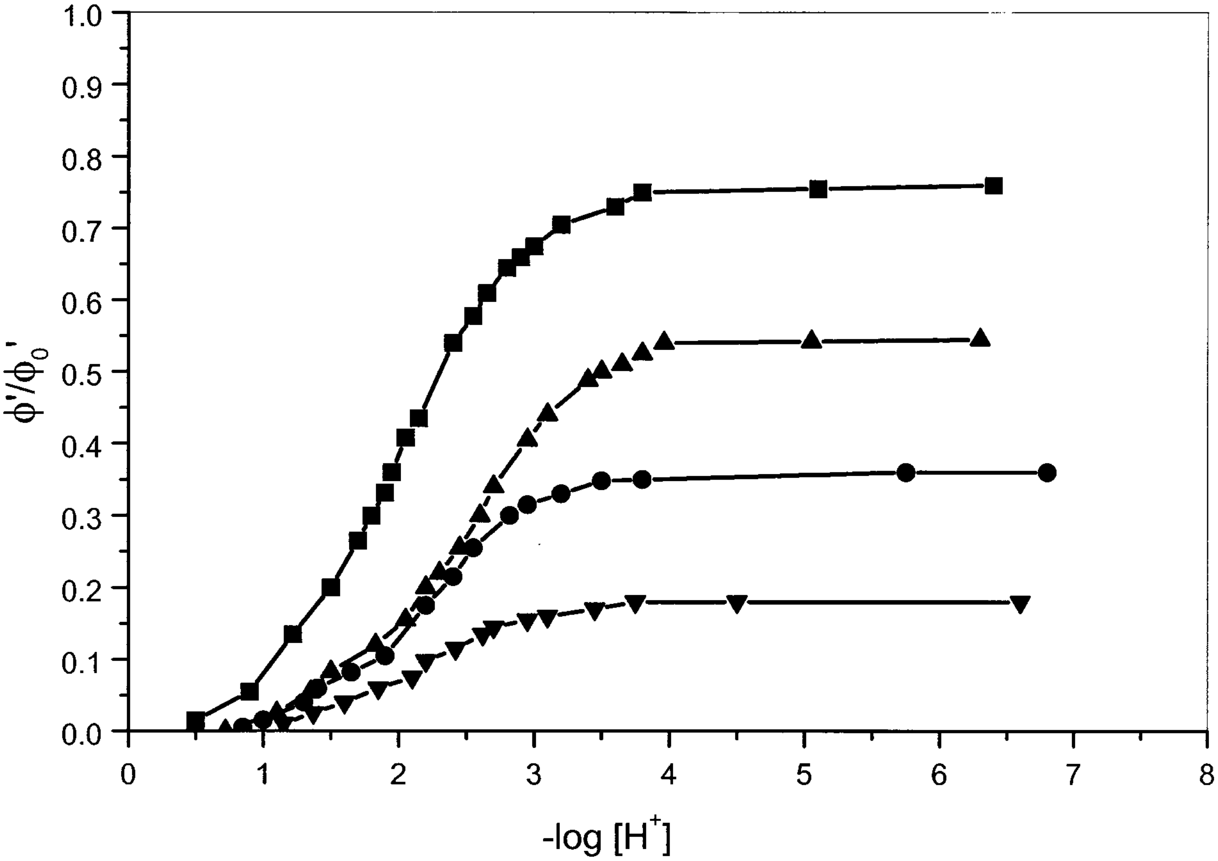

Fig. 2. Variation of the relative quantum yield of fluorescence (ϕ'/ϕ_0') of the dianion of 7-hydroxy-1-naphthalenesulfonate with logarithm of the formal hydrogen ion concentration ([H$^+$]) at various vol.% of DMSO in aqueous DMSO at 25 °C: (▼) 70 vol.% DMSO; (●) 60 vol.% DMSO; (▲) 50 vol.% DMSO; and (■) 30 vol.% DMSO.

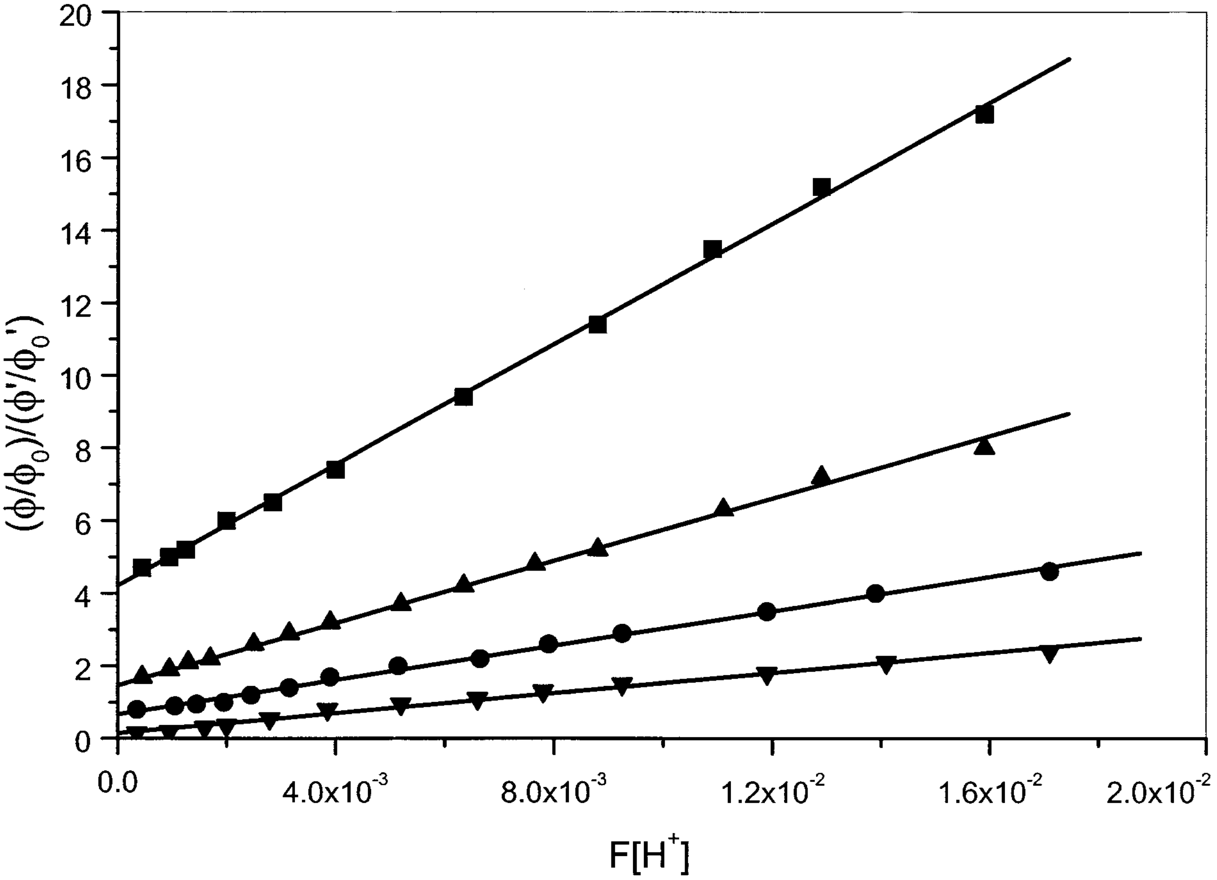

Fig. 3. Variation of $(\phi/\phi_0)/(\phi'/\phi_0')$, the ratio of the relative quantum yield of fluorescence of the monoanion to that of the dianion derived from 7-hydroxy-1-naphthalenesulfonate with $F[\mathrm{H}^+]$, the product of the Brönsted kinetic activity factor, and the formal hydrogen ion concentration at various vol.% DMSO in aqueous DMSO at 25 °C: (▼) 30 vol.% DMSO; (●) 50 vol.% DMSO; (▲) 60 vol.% DMSO; and (■) 70 vol.% DMSO.

is given, for an unidivalent ionic reaction such as the hydrogen ion dianion reaction, by

$$-\log F = \frac{4A\sqrt{\mu}}{1 + aB\sqrt{\mu}}, \tag{5}$$

where μ is the ionic strength. A is related to the dielectric constant, ε, and the absolute temperature, T, by [14,15]

$$A = 1.826 \times 10^6 (\varepsilon T)^{-3/2}, \tag{6}$$

and B is related to ε and by

$$B = 5.031 \times 10^9 (\varepsilon T)\varepsilon^{-1/2}, \tag{7}$$

and a is the mean distance of closest approach of the fully solvated proton and the dianion, taken for present purposes to be 6.5 Å.

Values of ε [16], A, and B for various DMSO–water mixtures at 25 °C, in which fluorimetric titrations were carried out, are listed in Table 1. As seen in Fig. 3, plots of $(\phi/\phi_0)/(\phi'/\phi_0')$ vs $F[\mathrm{H}^+]$ are linear up to at least $[\mathrm{H}^+] = 0.05$ M ($F[\mathrm{H}^+] \sim 0.02$ M). Note that it is not necessary to evaluate k_a and k_b explicitly for the present purposes, i.e. all fluorescence measurements can be made on steady-state equipment. Moreover, the ordinate intercepts of these lines according to Eq. (4), correspond to $(k_\mathrm{a}\tau_0)^{-1}$, agree well with the corresponding terms calculated from Eq. (3). The fluorescent decay time of the mono- and dication

Table 2
pH of dilute sulfuric acid solutions in aqueous DMSO as a function of the logarithm of the reciprocal hydrogen ion formal concentration ($-\log[H^+]$) and the mole fraction of DMSO (X_{DMSO})

-log[H^+]	pH ($X_{DMSO}=0$)	pH ($X_{DMSO}=0.098$)	pH ($X_{DMSO}=0.202$)	pH ($X_{DMSO}=0.275$)	pH ($X_{DMSO}=0.371$)
3.00	3.02	3.02	3.02	3.02	3.02
2.90	2.92	2.92	2.92	2.92	2.92
2.80	2.82	2.82	2.82	2.83	2.83
2.70	2.72	2.72	2.72	2.73	2.73
2.60	2.62	2.62	2.62	2.63	2.63
2.50	2.53	2.53	2.53	2.53	2.53
2.40	2.43	2.43	2.43	2.43	2.43
2.30	2.33	2.33	2.33	2.33	2.34
2.20	2.23	2.23	2.23	2.24	2.25
2.10	2.13	2.13	2.14	2.15	2.15
2.00	2.04	2.05	2.05	2.05	2.06
1.90	1.95	1.96	1.96	1.96	1.96
1.80	1.85	1.86	1.86	1.87	1.87
1.70	1.75	1.76	1.76	1.76	1.77
1.60	1.66	1.67	1.67	1.67	1.68
1.50	1.57	1.58	1.58	1.59	1.59
1.40	1.47	1.48	1.48	1.49	1.50
1.30	1.38	1.39	1.40	1.40	1.41

of 7-hydroxy-1-naphtholsulfonate are 8.7 ± 0.3 and 13.5 ± 0.5 ns, respectively, at H_0 −2 and pH 13, respectively, and were invariant with respect to the mixed solvents used here within the experimental uncertainty expressed above.

The linearities of the plots of $(\phi/\phi_0)/(\phi'/\phi'_0)$ vs $F[H^+]$ and the excellent agreement between the values of $k_a\tau_0$ obtained from these least-squares plots which are largely determined by the pH dependence of the back-reaction and those obtained from Eq. (3) which are calculated independent of any assumptions regarding pH lead us to conclude that the form of the Brönsted kinetic activity factor chosen here is a reasonably accurate means of correcting the parameters of the chosen reaction for non-ideal behavior (Fig. 3). Each fluorescence measurement has about 2% uncertainty so that each value of $(\phi/\phi_0)/(\phi'/\phi'_0)$ has about 4% uncertainty. Since this is the principal source of error in all measurements entailed, each value of $F[H^+]$ calculated can be assumed to be about 5% uncertain or each pH calculated is valid to ±0.02. It appears that while the solvent influence on the dissociation reaction cannot be described by continuum electrostatics [8], the influence of the solvent on the reprotonation reaction can. Accordingly, since F is a good factor for the overall reprotonation reaction up to an ionic strength of 0.05, $f_{H^+} = F^{1/4}$ should be a good activity coefficient for the solvated proton over the same range of ionic strength. In any of the DMSO–water mixtures, the activity of the hydrogen ion is

$$a_{H^+} = f_{H^+}[H^+], \tag{8}$$

and the pH is

$$\mathrm{pH} = -\log a_{H^+} = \frac{1.826\times10^{-6}(\varepsilon T)^{-3/2}\sqrt{\mu}}{1+558\sqrt{\mu/\varepsilon}^{T}} - \log[H^+]. \tag{9}$$

Tabulations of pH corresponding to $[H^+]$ for several DMSO–water mixtures at 25 °C are given in Table 2. According to Table 2, the influence of the cosolvent on the pH is remarkably small suggesting that H^+ is solvated exclusively by water.

The approach described here ought to be applicable to any aqueous-organic solvent system in which excited-state proton transfer of the kind demonstrated here is observed. It has already been successfully applied to mixtures of acetonitrile [17], 1,4-dioxane [18], and various alcohols [19] with water.

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