

Invariance of Activity Coefficients for the Hydrogen Ion with Charge-Type of Fluorescent Indicators in Aqueous-Methanol Solutions

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Steady-state fluorimetric pH titrations of three fluorescent indicators of differing charge-type were carried out in aqueous methanol solutions containing up to 64 mol% methanol. The plot of the ratio of the relative fluorescence efficiency of the indicator acid to that of its conjugate base versus the product of the formal hydrogen ion concentration and the appropriate Bronsted kinetic activity factor gives straight lines for titrations in each mixed solvent, just as it does in water, but only if the constant terms in the Bronsted factor are modified to account for the bulk dielectric constant in each solvent. The product of the formal charges on the proton and the particular conjugate base studied in each titration must also be included in the Bronsted factor. This supports the hypothesis that a valid operational pH can be defined and kinetic parameters related to proton transfer can be extracted from the fluorimetric titrations in mixed solvents.

KEY WORDS: Hydrogen ions; charge-type; aqueous methanol solutions; activity coefficients.

INTRODUCTION

In earlier reports from this laboratory⁽¹⁻³⁾ it was shown that in a number of acidic binary solvent systems which contain water as well as an organic cosolvent miscible with water, an operational pH, with presumably the same thermodynamic significance as that in dilute aqueous solutions, could be defined. The pH in the mixed solvents is calculated from the formal hydrogen ion concentration ($[H^+]$) and the activity coefficient of the hydrogen ion (f_{H^+}). The latter is calculated from the Bronsted kinetic activity relation,^(4,5) which is identical to the Debye-Hückel relationship⁽⁶⁾ in form. The range of validity of the calculated activity coefficients is es-

tablished from Weller's equation,^(7,8)

$$\frac{\phi/\phi_0}{\phi'/\phi'_0} = \frac{1}{k_a \tau_0} + \frac{k_b \tau'_0}{k_a \tau_0} F[H^+] \quad (1)$$

where ϕ/ϕ_0 and ϕ'/ϕ'_0 are, respectively, the relative quantum yields of fluorescence of a fluorescent indicator conjugate acid and base which demonstrate proton transfer during τ_0 and τ'_0 , the respective lifetimes of their lowest excited singlet states, and k_a and k_b are the rate constants for prototropic dissociation of the excited acid and reprotonation of the excited conjugate base, respectively. Also in Eq. (1), F is the Bronsted kinetic activity factor for the reprotonation reaction



where A^{-z} is the conjugate base (of charge $-Z$) of the fluorescent indicator and X^\ddagger is the encounter complex or transition state (both collision theory and transition state

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theory have the same form and yield identical results here), through which is regenerated the indicator acid HA^{1-z} . The form of F is

$$F = \frac{f_{H^+} f_{A^{-z}}}{f_{X^\#}} \quad (3)$$

where $f_{A^{-z}}$ and $f_{X^\#}$ are the respective activity coefficients of A^{-z} and $X^\#$. Now according to Bronsted,^(4,5)

$$-\log F = \frac{2A |Z| \sqrt{\mu}}{1 + aB\sqrt{\mu}} \quad (4)$$

where A and B are constants of the solution dependent on temperature (T) and dielectric constant (ϵ),

$$A = 1.826 \times 10^6 (\epsilon T)^{-3/2} \quad (5)$$

$$B = 5.031 \times 10^9 (\epsilon T)^{-1/2} \quad (6)$$

μ is the ionic strength of the solution, and a is an inter-ionic distance parameter which we have taken as the mean separation of H^+ and A^{-z} in the encounter complex.

An experimentally determined straight line fitting Eq. (1) for a fluorometric titration in a mixed solvent can be taken as proof of the aptness of F as a good Bronsted kinetic activity factor in that medium and, by induction, of the suitability of

$$-\log f_{H^+} = \frac{A\sqrt{\mu}}{1 + aB\sqrt{\mu}} \quad (7)$$

to represent f_{H^+} . Over the range in which Eq. (1) demonstrates linearity, then the pH can be defined in the conventional sense as

$$\text{pH} = -\log a_{H^+} = -\log f_{H^+} [H^+] \quad (8)$$

$$f_{H^+} = F^{1/2z} \quad (9)$$

To date, virtually all of our work in establishing ranges of solvent composition over which pH could be defined has entailed the fluorescent indicator 2-hydroxybiphenyl, which has a singly charged conjugate base. One means of testing the general applicability of Eq. (7) would be to show the linearity of several fluorimetric titrations, plotted in the form of Eq. (1), involving fluorescent conjugate pairs in which the conjugate base had $Z \neq -1$. Such linearity for conjugate pairs with different values of Z [in Eq. (4)] would constitute support for the validity of the pH so calculated [from Eqs. (8) and (9)] and the formal hydrogen ion concentration. With this in mind, fluorimetric titrations, in aqueous-methanol solutions, of 2,6-naphtholsulfonate (NSA), 2-naphthol-6,8-disulfonate (NDS), and 1-hydroxy-3,6,8-pyrenetrisulfonate (HPTS), were undertaken.

EXPERIMENTAL

Materials and Instruments

2-Naphthol-6-sulfonic acid (monosodium salt) and 2-naphthol-6,8-disulfonic acid (disodium salt) were purchased from Matheson, Coleman and Bell, East Rutherford, NJ. These compounds were purified by triple recrystallization 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, NY, and was used as received. Seventy percent perchloric acid and reagent-grade methanol were purchased from Fisher Scientific Co., FairLawn, NJ, and used as received. Fluorescence measurements were made on a Perkin Elmer LS-5 fluorescence spectrophotometer whose sample compartment was thermostated at $25.0 \pm 2.0^\circ\text{C}$ by means of a Lauda K2/R water bath. Fluorescence standards from Precision cells, Inc., were used to calibrate the excitation and emission monochromators. UV-visible measurements were made employing a Cary Model 219 spectrophotometer which had been calibrated using the absorbance peaks of a holmium oxide filter.

Methods

A 10^{-3} F ethanolic stock solution of each hydroxyaromatic indicator 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 solvent 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 desired mole fraction of the latter. The final concentration of indicator in each test solution was 2×10^{-6} F for NSA and NDS, while for HPTS it was 2×10^{-7} F . The probe concentrations were chosen to keep the absorbance at the excitation wavelengths below 0.02, thereby ensuring the proportionality between fluorescence intensity and concentration.

Excitation was effected at isosbestic points in the excitation spectrum, 325 nm for NSA and NDS and 327 nm for HPTS, using a 5-nm excitation band width. The band width passed by the emission slit was also 5 nm.

Titration were performed as follows: 2 ml of test solution of a known mole fraction of organic cosolvent was pipetted into a 1-cm cuvette having a 3.8-ml capacity and the emission spectrum was obtained. The above solution was titrated with a solution 1.17 F in perchloric

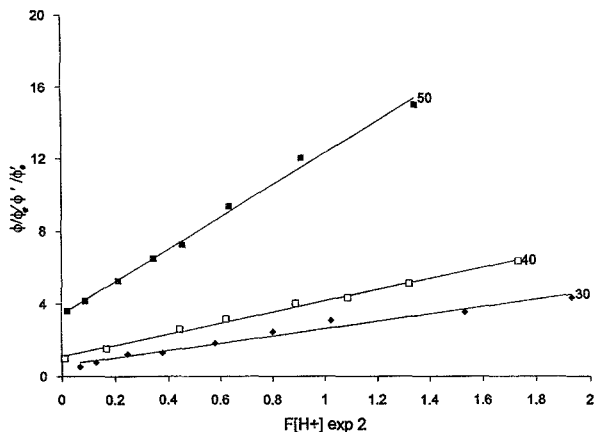


Fig. 1. Plot of $\phi/\phi_0/\phi'/\phi'_0$ (the ratio of the relative quantum yield of fluorescence of the conjugate acid to that of the conjugate base) for 2,6-naphthol sulfonate against $F[H^+]$ (the product of the Bronsted kinetic activity factor and the molar concentration of hydrogen ion in 30, 40, and 50 vol% methanol at 25°C ($X_{\text{meOH}} = 0.161, 0.229,$ and 0.308 , respectively).

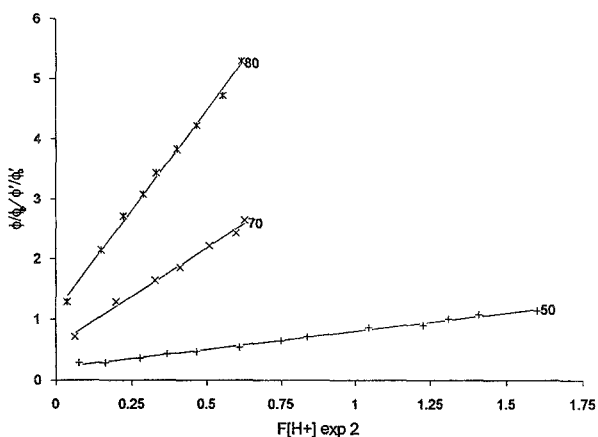


Fig. 2. Plot of $\phi/\phi_0/\phi'/\phi'_0$ for 2-naphthol-6,8-disulfonate against $F[H^+]$ in 50, 70, and 80 vol% methanol at 25°C ($X_{\text{meOH}} = 0.308, 0.510,$ and 0.640 , respectively).

acid and $2 \times 10^{-6} F$ in NSA, NDS, or ($2 \times 10^{-7} F$) HPTS, so that the concentration of the indicator remained constant throughout the titration. Fluorescence spectra were scanned after each increment of titrant had been added and the titration was carried out until the fluorescence of the indicator conjugate base could no longer be observed and the fluorescence of the conjugate acid was maximal and constant. Calculation of the ionic strength at each point in the titration was carried out using the formal concentration of the perchloric acid. The dielectric constants used for the methanol–water solutions were identical to those used in Ref. 3.

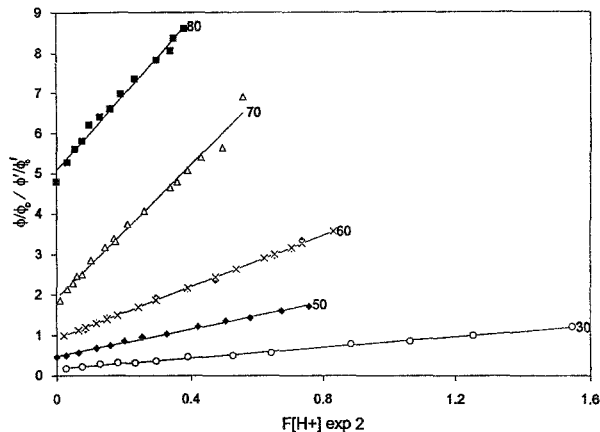


Fig. 3. Plot of $\phi/\phi_0/\phi'/\phi'_0$ for 1-hydroxypyrene-3,6,8-trisulfonate against $F[H^+]$ in 30, 50, 60, 70, and 80 vol% methanol at 25°C ($X_{\text{meOH}} = 0.161, 0.308, 0.401, 0.510,$ and 0.640 , respectively).

RESULTS AND DISCUSSION

The fluorimetric pH titrations of NSA, NDS, and HPTS in methanol–water solutions are typical of the behavior of hydroxyaromatics. At $\text{pH} > 4$ the relative quantum yields of fluorescence of acid and conjugate base are invariant with pH because of the small magnitude of $k_b\tau'_0 F[H^+]$. This is due to the very low values of $F[H^+]$ at $\text{pH} > 4$ ($0 \leq F[H^+] \leq 1 \times 10^{-4} M$). At $\text{pH} < 4$, $F[H^+]$ becomes larger and $k_b\tau'_0 F[H^+]$ becomes significant, causing a decrease in ϕ'/ϕ'_0 and an increase in ϕ/ϕ_0 . As the mole fraction of methanol is increased, the rate constant for dissociation, k_a , decreases for each of the compounds studied and the raw data from the fluorimetric titration curves ($\phi/\phi_0/\phi'/\phi'_0$ and $F[H^+]$) can be used to construct the plots conforming to Eq. (1), which are shown in Figs. 1–3. Values of the slopes and intercepts obtained from the plots in Figs. 1–3 are given in Table I along with the squares of the linear correlation coefficients representing the regions of linearity in the fluorimetric titrations.

Figures 1–3 show that the fluorimetric titration data fit Eq. (1) linearly (all points shown were included in the regression analyses) to a mole fraction of methanol as high as 0.64 and to $[H^+]$ values as high as $0.12 M$. As a rule, the greater the mole fraction of methanol, the smaller was the range over which linearity was maintained. This could be due to appreciable ion-pairing, which occurs to a greater extent as the dielectric constant falls. The linearities observed in Figs. 1–3 imply that F is a good kinetic activity factor for the reprotonation reactions and f_{H^+} a good activity coefficient for the hydrogen ion over at least the ranges of linearity of the

Table I. Debye–Hückel Terms (A and B) Calculated from Eqs. (5) and (6) at 25°C and Used in the Calculation of the Bronsted Activity Factor (F) at Various Methanol Mole Fractions (X_m), ordinate Intercepts and Slopes ($k_b\tau_0^2/k_a\tau_0$) as Well as Squares of the Linear Correlation Coefficients (r^2) Corresponding to the Lines Represented in Figs. 1–3

	Vol % methanol	x_m	A	$B \times 10^{-7}$	$1/k_a\tau_0$	$k_b\tau_0^2/k_a\tau_0$	r^2
2,6-Naphthol sulfonate	30	0.161	0.652	3.57	0.64 ± 0.12	1.99 ± 0.12	0.974
	40	0.229	0.723	3.69	1.12 ± 0.09	3.03 ± 0.09	0.995
	50	0.308	0.806	3.83	3.44 ± 0.17	8.83 ± 0.26	0.995
2-Naphthol-6,8-disulfonate	50	0.308	0.806	3.83	0.20 ± 0.01	0.60 ± 0.01	0.993
	70	0.510	1.078	4.22	0.57 ± 0.05	3.22 ± 0.12	0.993
	80	0.640	1.219	4.40	1.14 ± 0.06	6.66 ± 0.15	0.997
1-Hydroxypyrene-3,6,8-trisulfonate	30	0.161	0.652	3.57	0.18 ± 0.01	0.66 ± 0.01	0.995
	50	0.308	0.806	3.83	0.49 ± 0.01	1.67 ± 0.03	0.995
	60	0.401	0.924	4.01	0.93 ± 0.02	3.18 ± 0.04	0.998
	70	0.510	1.078	4.22	1.92 ± 0.06	8.24 ± 0.23	0.989
	80	0.640	1.219	4.40	5.08 ± 0.07	9.44 ± 0.32	0.987

curves in these figures. This is true for all the media studied here regardless of the formal charge the conjugate base anion.

The range of ionic strength ($0 \leq \mu \leq 0.1$) over which f_{H^+} is suitable as an activity coefficient for the hydrogen ion is comparable in the methanol–water solutions to that over which the Debye–Hückel relationship is valid in aqueous solutions. This supports the hypothesis that pH, as defined for aqueous solutions, is conceptually and thermodynamically valid for methanol–water solutions up to a mole fraction as high as 0.64. This is the highest methanol content which would permit the occurrence of excited-state proton transfer at a level at which the kinetics could be evaluated with less than

20% uncertainty. Experiments are currently under way using cosolvents other than methanol.

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