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Determination of pK_a by Luminescence Quenching Method. pK_a of Conjugated Acids of 1-Alkyl-4,4'-Bipyridinium Ions

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The pK_a value of an acid is the most important parameter for the interpretation of pH-dependent physico-chemical properties of chemical species. Variety of methods have been used for determination of pK_a. Luminescence method is a very sensitive tool for chemical analysis of luminescent molecules. However, this method is rarely used for the determination of pK_a, as the pK_a of an excited state is usually remarkably different from that of ground state.[1] In this communication, we present a novel method for determination of pK_a based on luminescence quenching results.

1-Alkyl-4,4'-bipyridinium (RBPY) ions undergo the following acid-base equilibria.

acidic form basic form

The acidic form of RBPY is chemically similar to 1,1'-dialkyl-4,4'-bipyridinium (viologen) compounds which are widely used as electron relays in chemical[2] and photo-sensitized reduction[3] of substrates, and as active materials in electrochromic displays.[4] The basic form is a substituted pyridinium and is considered as a coenzyme NAD^+ analog.[5] Because of these interesting characters, the pH-dependent electrochemical[6-8] and spectroscopic[7-9] behaviors of the compounds as well as their ability as electron carriers in redox reactions[10,11] have been investigated.

Eour 1-alkyl-4,4'-bipyridinium (RBPY: R=methyl (C_1), *n*-octyl(C_8), *n*-dodecyl (C_{12}), benzyl (Bn)) salts were prepared by reacting 4,4'-bipyridine with corresponding alkyl halides as described in ref 10. Solution media were 0.10 M HCl, 0.01 M NaOH+0.09 M NaCl, or 0.01 M Na_2HPO_4+0.07 M NaCl. By appropriate mixing of these solutions, we obtained solutions of desired pH. The maximum change of ionic strength between pH 1 and 10 was less than 10%. Quenching of tris(2,2'-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, luminescence by RBPY was studied by steady-state luminescence measurement at 25℃ in aqueous media. At a given pH, the quenching data gave good linearity following Stern-Volmer equation (Eq. (1)), indicating dynamic nature of the queching reaction.

$$I_o/I = 1 + K_{SV}[\text{RBPY}] \quad (1)$$

I_o and I are luminescence intensities in the absence and presence of the quencher, respectively. The K_{SV} values obtained at pH 2 and 8 are summarized in Table 1: RBPY are present mostly as acidic forms at pH 2 and basic forms at pH 8 (note that pK_a values are about 3.5 from Table 1).

Table 1. Stern-Volmer Constant (K_{sv}) for Luminescence Quenching of $Ru(bpy)_3^{2+}$ by 1-Alkyl-4,4'-bipyridinium (RBPY) Ions and pK_a Values of the RBPY in Aqueous Solutions of Ionic Strength 0.10 M at 25.0℃

Compounds	K_{sv}		pK_a	
	pH 2.0	pH 8.0	SDS-free	10 mM SDS
C_1BPY	355	108	3.42 (3.60[a])	4.50
C_8BPY	400	135	3.65	4.96
C_{12}BPY	590	245	3.61	4.62
BnBPY	490	401	3.51	4.38

[a] Reported value from UV spectroscopic method.[9]

The quenching reactions are transfer of electron from photo-excited $Ru(bpy)_3^{2+}$ to the quenchers.[10,11] The K_{SV} values of the acidic forms are very similar to those of corresponding methyl alkyl viologens[12] and much greater than those of basic forms, though reactions with acidic forms are less favorable when one considers only electrostatic effect. Thus, our result reflects clearly facile reduction of the protonated (acidic) form of RBPY: the reduction potential of the protonated RBPY is *ca.* −0.7 V (*vs.* SCE) and similar to that of dialkyl viologen, whereas that of basic form is about −1.0 V.[6,7]

Because of the intrinsic difference in quenching efficiency between the acidic and basic forms of RBPY, the luminescence titration of a solution containing $Ru(bpy)_3^{2+}$ and RBPY shows spectral change similar to that observed in spectroscopic titration of a dye. In Figure 1, we present absorption spectra of RBPY and luminescence spectra of $Ru(bpy)_3^{2+}$ in the presence of RBPY taken at pH 1 and 10. The relative change in emission intensity produced by lowering pH to 1 from 10 is much greater than the corresponding change in absorbance: exception to this is absorption at $\lambda > 290$ nm, which is tail absorption region. The relative changes in absorbance of RBPY solution and luminescence intensity of a solution of $Ru(bpy)_3^{2+}$ and RBPY with pH are displayed in Figure 2. Good agreement between the absorbance and luminescence titration data is indicative of that the spectral changes arise from acid-base eqilibria of RBPY. The pK_a values of the quenchers were obtained from the titration data by using the relationship, $pH = pK_a + \log[\Delta I/(\Delta I_{max} - \Delta I)]$: the ΔAbs can be substituted for ΔI for absorbance data. The results are given in Table 1.

We also determined pK_a of RBPY in the presence of 10 mM sodium dodecylsulfate (SDS) and the results are included in Table 1. The pK_a value in the SDS micellar solution is about 1 pH unit higher than that in SDS-free solution. This is a typical result observed when the acid is bound

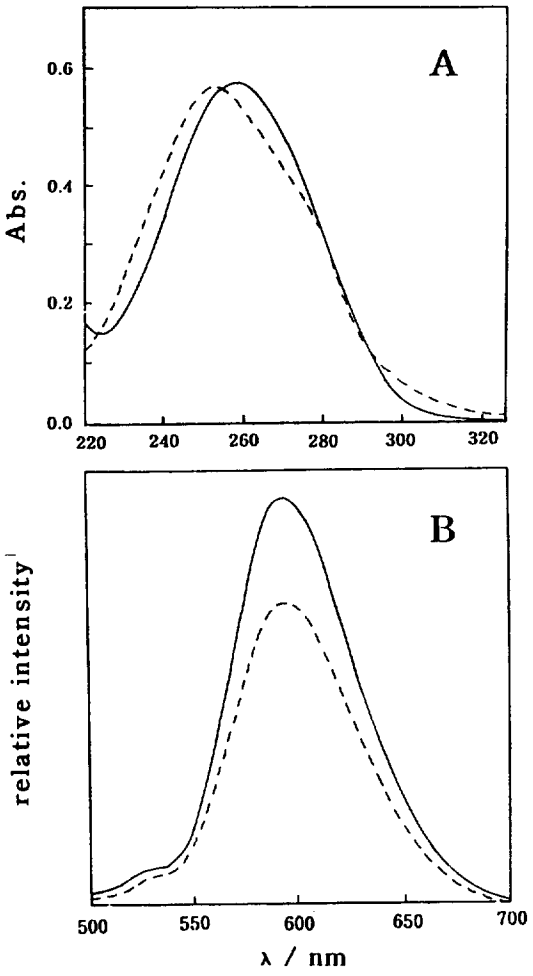

Figure 1. Absorption spectra of 3.8×10^{-4} M C_1BPY (A) and luminescence spectra of 5×10^{-5} M $Ru(bpy)_3^{2+}$ in the presence of 2.0×10^{-3} M C_1BPY (B) in aqueous 0.10 M NaCl or 0.10 M HCl solutions at 25℃; (——) pH 10; (------) pH 1.0. λ_{ex}= 450 nm.

to the anionic micelle.

The luminescence quenching method for the determination of pK_a of acids described in this communication can be applied to any systems where acidic and basic forms have different quenching efficiency. Also this method can be used to determine complex formation constant of a molecule provided that the complex and free molecule have different quenching effect. Works on these aspects and studies on the pH-dependent physico-chemical properties of RBPY relating their pK_a values are in progress.

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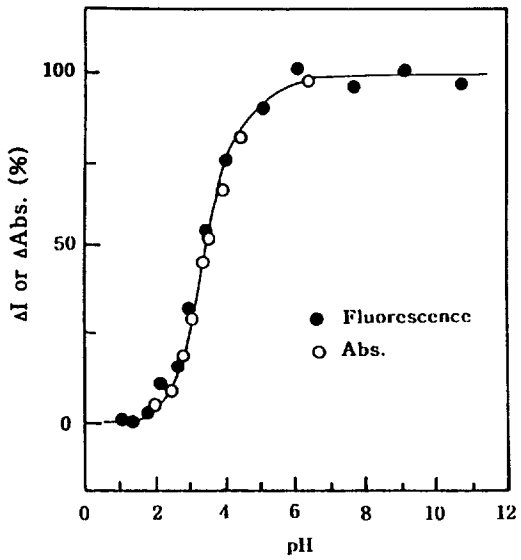

Figure 2. The percent change in absorbance of C_1BPY at 300 nm (○) and emission intensity of $Ru(bpy)_3^{2+}$ in the presence of C_1BPY at 595 nm (●) as a function of pH. Conditions are the same as Figure 1.