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Journal of Photochemistry and Photobiology A: Chemistry 113 (1998) 189–195

Journal of Photochemistry and Photobiology A:Chemistry

Paper acidity estimation: Application of pH-dependent fluorescence probes

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Received 17 September 1997; received in revised form 10 November 1997

Abstract

The use of pH-dependent fluorescence probes for paper acidity estimation has been explored. The changes in emission properties of the four probes (quinine bisulphate, fluorescein, pyranine and SNAFL-1, a seminaphthofluorescein dye) in buffer solutions of varying pHs are found to correlate with the respective changes observed for the probes applied on paper samples of varying acidity. The remarkable correlations suggest that the paper acidity ('pH_{app}') can be inferred by extrapolating the probe behavior on paper samples to that in aqueous solutions of varying pHs. Thus, with a judicious choice of pH-dependent fluorescence probes, a wider range of pH indicators of paper acidity are possible to be developed. This methodology promises a non-destructive alternative to measure acidity of paper.

Keywords: Fluorescence probe; Paper acidity; pH indicator

1. Introduction

Paper 'permanence' is of serious concern in the preservation and restoration of important documents, art works and library books of permanent value [1–3]. Among other factors, the acidity, which is imparted to the paper sheets during production and upon prolonged contact with the atmospheric pollutants (aging), has been shown to be highly detrimental to the mechanical properties of paper [1]. There is ample evidence to suggest that cellulose is degraded by acid hydrolysis leading to weakening of the fibers in the paper sheets [4]. Such a process manifests itself as a 'sheet brittleness' and causes the paper to fall apart. It is, therefore, not surprising that a great deal of research is focused on improving the paper permanence by deacidification [5].

In view of the deleterious effects of acidity, paper with low acidity content is desirable to assure a satisfactory degree of permanence for materials of long-lasting importance. Therefore, analytical methods which might permit a reliable assessment of paper acidity are desirable. Such methods will enable a clear-cut distinction to be made between papers of varying qualities. Although sporadic reports have dealt with the determination of acidity due to specific acid functionalities in pulp and paper fibers based on conductometric titrations [6,7], the method employed by the paper and pulp industry to estimate the paper acidity relies on the determination of pH of an aqueous extract of a defined quantity of paper [3,8]. Accordingly, 'pH of paper' is defined as the 'pH' of an aqueous extract of 1.0 g of paper in 50 or 70 ml of cold or hot water; the 'pH' in the range of 6.0–8.5 is specified for permanence. Although this method is presently practised by and large, a major disadvantage concerns the fact that it cannot be employed if the material is not to be destroyed during the acidity assay. It, therefore, appeared to us that the acidity estimation of paper based on a spectroscopic property might constitute a much simpler and practical solution. We herein report the utility of pH-dependent fluorescence probes, viz., quinine, fluorescein, pyranine and SNAFL-1, to assess the paper acidity. The pH-dependent emission/excitation intensity changes observed for the probes applied on paper samples of varying acidity (vide infra) are correlated with the respective changes observed in aqueous solutions of varying pHs. The results with a limited set of fluorescence probes suggest that pH indicators of paper acidity can be developed by appropriate selection of pH-dependent fluorescence probes with varying pK_as.

2. Experimental details

2.1. Materials and instrumentation

Quinine bisulphate (Fluka), fluorescein (Sigma), pyranine (Molecular Probes) and SNAFL-1 (Molecular Probes)

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1010-6030/98/$19.00
PII S1010-6030(97)00332-8

were used as received. Citric acid, disodium hydrogen phosphate and potassium dihydrogen phosphate were obtained from BDH Chemicals and used without further purification. The deionized water from a Sybron Barnsted system was used.

UV–vis absorption and diffuse-reflectance spectra were recorded on Cary 1 and Cary 5 systems at ca. 20°C. All the pH measurements for the buffer solutions were taken on Cole–Parmer pH Meter (Model No. 05669-20), which was calibrated prior to use by standard pH 4.0 and 7.0 buffer solutions (Fisher Scientific, Ontario). The steady-state fluorescence spectra were recorded on a PTI QM-2 spectrofluorimeter (20.0 ± 0.5°C). The slit widths for excitation and emission were typically 2–4 nm.

2.2. UV–vis absorption and fluorescence spectra in buffer solutions of various pHs

The buffer solutions (citric acid/Na_2HPO_4 and KH_2PO_4/NaOH) of various pHs were prepared [9] and the pHs were immediately determined. To 10 ml volumetric standard flasks containing these solutions were added 100 μl solution of the fluorescent probe ($2–5 \times 10^{-3}$ M in water) so that the overall concentration was in the range $2–5 \times 10^{-5}$ M. The UV–vis absorption and fluorescence spectra were recorded for these solutions.

2.3. Preparation, diffuse-reflectance and fluorescence spectra of paper samples

Paper samples (Whatman filter paper, diameter 110 mm) were soaked for 20–24 h in Petri dishes containing 25 ml buffer solutions (citric acid/Na_2HPO_4 and KH_2PO_4/NaOH) of varying pHs. During this process, the Petri dishes were completely covered to prevent any loss of water. Subsequently, the filter papers were removed and allowed to air dry for 2 days. The paper samples prepared likewise were used as the standards for papers of varying acidity. For one batch of paper samples, one half of the samples at each pH was sent for acidity estimation by the industrial method to Paprican, Pointe Claire, Canada and the other half was used for the fluorescence measurements.

For fluorimetric studies, a 50-μl solution of the fluorescent probe ($2–4 \times 10^{-4}$ M) was applied on to the filter paper strip (4×1.2 cm) with the aid of a micro syringe and allowed to air dry for 2–3 h; this period could be reduced to ca. 30 min by exposure to a gentle stream of air or by application of methanolic solution of the probe. Typically, the amount of probe applied was $2–4 \times 10^{-8}$ mol/cm^2. Subsequently, the paper strip was placed on a triangular metal block, which permitted the collection of fluorescence from front-face illumination upon insertion into the cell holder.

3. Results and discussion

In order to employ the fluorescence probes as indicators of paper acidity, one needs to establish (1) whether any emission from the probes applied on paper samples can be observed (presence of specific fluorescence quenchers in the paper matrix might prevent the fluorescence from being detected) and, (2) how well the changes in the emission intensity or maximum observed for probes in solutions of varying pHs correlate with those observed from probes applied on paper samples of varying acidity. Such a correlation is essential to infer the acidity of paper by extrapolation of the probe behavior to that in solution. We attempted to prepare the paper samples of varying acidity by deliberate soaking of near-neutral pH Whatman filter paper in buffer solutions of varying pHs for a substantial length of time (ca. 20–24 h) so that an equilibrium is achieved. It turned out that the acidity of paper samples, as estimated from the industrial method, depended on the pHs of the buffer solutions (citric acid/Na_2HPO_4) in which they were soaked. The pH values of the pre-soaked paper samples, as determined by the industrial method, are given in Table 1. Clearly, these values approximate the pHs of the solutions determined after soaking.

As will be evident later, we treat the pHs of the paper samples ('pH_{app}') as those of the values determined for the solutions after soaking with the assumption that the paper attains the acidity equivalent to the pH of the soaking solution. Thus, with a set of paper samples of varying acidity at hand, the pH-dependent fluorescence behavior has been examined in both aqueous solutions and paper samples for the probes with their pK_as ranging from ca. 4.9 to 7.8. The spectral changes are monitored through changes in the ratios, in a given spectrum, of emission or excitation intensities (ratiometric method) at two defined wavelengths, for which a progressive change with pH was observed. Subsequently, these changes in intensity ratios with pH are correlated for paper samples and buffer solutions of varying acidity. It should be noted that the monitoring of spectral changes through intensity ratios is advantageous in that any ambiguities as to the

Table 1
Industrial pH[a] values for the standard paper samples of varying acidity prepared by soaking in phosphate buffer solutions

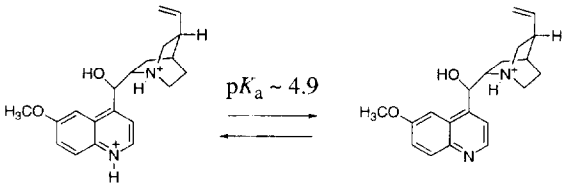
pH of the buffer solution		pH of paper (industrial method)[b]
Before soaking	After soaking	
2.90	2.93	3.32
3.53	3.57	3.74
4.10	4.15	4.18
4.71	4.76	5.10
5.34	5.40	5.66
5.72	5.79	6.08
6.35	6.40	6.57
7.00	7.02	7.17
7.42	7.47	7.56
8.04	8.06	8.21

[a]Cold method, Refs. [3] and [8].
[b]Determined by Pulp and Paper Research Institute of Canada, Pointe Claire, Quebec, Canada.

precise assignment of emission or excitation maxima are removed in cases where the latter can be employed to monitor the pH change. Moreover, the ratiometric method does not rely on absolute intensities, which is particularly important for the paper samples since considerable variations are observed in the measured intensities due to heterogeneous scattering properties.

3.1. Quinine bisulphate

This fluorophore is well-known to display two emission maxima corresponding to dicationic (ca. 440 nm) and monocationic (ca. 385 nm) species shown in



[10]. While the pK_a for deprotonation of the dicationic species has been reported to be 5.07 [11], Schulman et al. have reported as low a value as 4.30 [10]. In disagreement with the latter, we have independently determined this value to be 4.9 ± 0.2 (A. Magon and C. Bohne, unpublished results). In Fig. 1 (inset) are shown the emission spectra of quinine for excitation at 334 nm, an isobestic point, in H_2SO_4/NaOH solutions of various pHs. The isoemissive point was observed at 414 nm. Although the latter could not be observed in phosphate buffer (citric acid/Na_2HPO_4) solutions, the changes in the emission maxima and their intensities were clearly comparable. In Fig. 1 are also shown the normalized fluorescence spectra of quinine applied on paper samples of varying acidities ('pH_{app}'). Evidently, the expected changes in the emission occur for paper samples with decreasing acidity; the emission intensity corresponding to the monocationic species at 370–380 nm gradually increases with concomitant decrease in the emission of dicationic species at ca. 435–445 nm. It is noteworthy that the emission maxima for both the monocationic and dicationic species are blue-shifted by ca. 10–15 nm relative to those in the solution state. Such shifts, in general, are not surprising in going from a homogeneous medium to a rigid paper matrix and have been interpreted, in some cases, as a result of specific hydrogen-bonding interactions [12]. It should be noted that spectral shifts do not invalidate the ratiometric method as long as the intensities of emission or excitation are measured at wavelengths corresponding to acidic and basic species. Fig. 2 shows the plots of intensity ratios vs. pH for the buffer solutions and the paper samples. Clearly, an excellent correlation is revealed for the probe behavior on paper samples with that in buffer solutions, in particular at the pHs above the pK_a (ca. 5.0) of quinine bisulphate.

It is important to record the effects of concentration of the probe applied on the fluorescence spectra of paper samples.

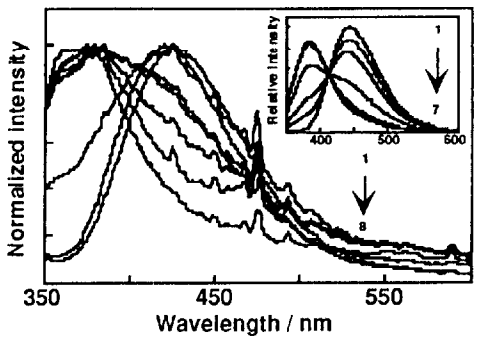


Fig. 1. Emission spectra ($\lambda_{exc} = 334$ nm) of quinine bisulphate applied on paper samples of varying 'pH_{app}' (1–8: 2.9, 3.5, 4.2, 4.7, 5.3, 5.8, 6.4, 7.0). The inset shows the respective spectra in phosphate buffer solutions of varying pHs (1–7: 3.0, 4.1, 4.5, 5.1, 5.5, 6.1, 7.0).

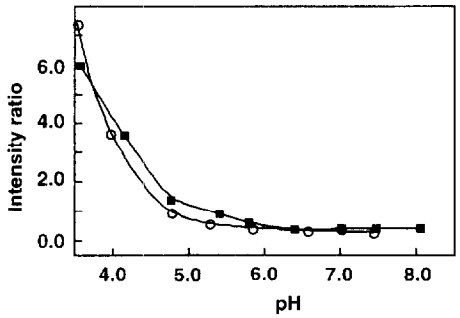
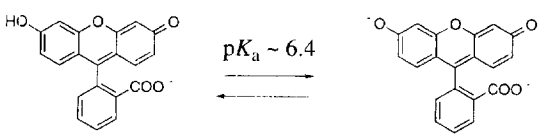


Fig. 2. Plot of intensity ratio vs. pH for quinine bisulphate: for phosphate buffer solutions (-○-) and paper samples (-■-). I_{444}/I_{384} and I_{435}/I_{374} were monitored, respectively.

At low loading concentrations of the probe ($< 2 \times 10^{-8}$ mol/cm^2), poor signal-to-noise ratios lead to significant errors in the measured intensities. On the other hand, at higher loading concentrations ($> 5 \times 10^{-7}$ mol/cm^2), considerable changes in the spectra are observed suggesting that significant proportion of the probe molecules are just deposited on the surface and contribute to the spectrum that does not reflect the true acidity of the paper. The optimum loading concentration of quinine and other probes employed in the present study was typically $2\text{–}4 \times 10^{-8}$ mol/cm^2.

3.2. Fluorescein

This compound and its derivatives exhibit multiple pH-dependent ionic equilibria [13]. For the equilibrium in



the wavelength of emission maxima and the shape of fluorescence spectra are independent of pH in the range ca. 5.5–7.5. However, the fluorescence intensity is dramatically reduced with increasing acidity. Since fluorescence intensities on paper are not reproducible, the fluorescence emission spectra cannot be employed as a means of monitoring the

change in acidity. Nevertheless, fluorescein is known to exhibit pH-dependent absorption spectra [14]; with increasing acidity, the absorption is blue shifted. We, therefore, decided to monitor such a change in the 'reflectance' of the probe applied on paper samples using diffuse-reflectance spectroscopy. At the employed concentrations of the probe, the technique is not sensitive enough to distinguish changes in the band shapes and the reflectance for paper samples of different acidities. However, the excitation spectra of paper samples (Fig. 3) revealed a discernible trend which could be readily compared to the corresponding changes in varying buffer solutions (Fig. 3, inset). The plots of intensity ratios at ca. 465 and 500 nm vs. pH are shown in Fig. 4; the intensity ratio is seen to be constant for both buffer solutions and paper samples above the pK_a of fluorescein (~6.4) [13]. Relatively poor correlation is revealed for strongly acidic solutions and paper samples. This appears to be due primarily to the differences in quenching of the fluorescein emission by phosphate ion in the solution state as compared to that in a rigid paper matrix. Indeed, the quenching of fluorescein emission by phosphate ions is well documented in the literature [13] and is particularly relevant here to exemplify how the presence of specific quenchers in the paper matrix might influence the probe emission properties.

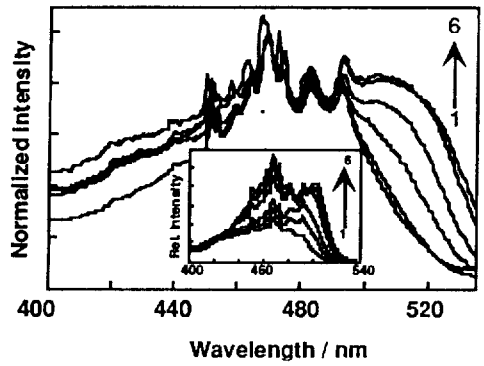


Fig. 3. Excitation spectra (λ_{em} = 550 nm) of fluorescein applied on paper samples of varying 'pH_{app}' (1–6: 4.2, 4.8, 5.7, 6.4, 7.0, 7.5). The inset shows the corresponding spectra in phosphate buffer solutions of varying pHs (1–6: 4.9, 5.5, 5.9, 6.5, 7.1, 7.5).

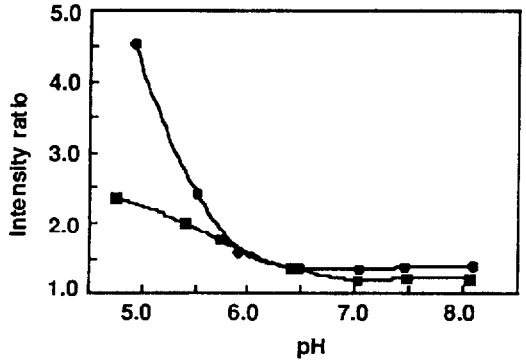


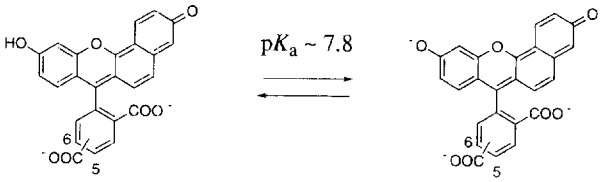
Fig. 4. Plot of intensity ratio vs. pH for fluorescein: for phosphate buffer solutions (-●-) and paper samples (-■-). I_{402}/I_{465} and I_{407}/I_{466} were monitored, respectively.

3.3. Pyranine (8-hydroxypyrene-1,3,6-trisulfonic acid, HPTS)

It is known to exhibit highly pH-dependent absorption shift corresponding to the species in

[12]. Since similar problems as those for fluorescein were encountered with diffuse-reflectance, changes in the excitation spectra with pH were monitored for paper samples and buffer solutions. The changes observed in the absorption spectra for solutions of various pHs clearly paralleled in the excitation spectra of pyranine in buffer solutions as well as the paper samples (Fig. 5). However, it is noteworthy that the spectra are highly structured in both the cases. Fig. 6 shows the plots of intensity ratios vs. pHs of the buffer solutions and paper samples, which reveals a remarkable correlation at all pHs.

3.4. 5-(and-6)-carboxy SNAFL-1



This compound belongs to the class of fluorescein dyes with a relatively higher pK_a of ca. 7.8 [15]. Excitation near the absorption maximum of the acidic form (ca. 515 nm) is known to result in strong emission from the acid and weak emission from the base, thereby enabling the changes in emission intensities to be used to monitor the acidity. In addition, it has been shown to be a dual-excitation probe when the emission is monitored at 620 nm. We have examined the changes in the latter property for paper samples and buffer solutions. In Fig. 7 are shown the normalized excitation spec-

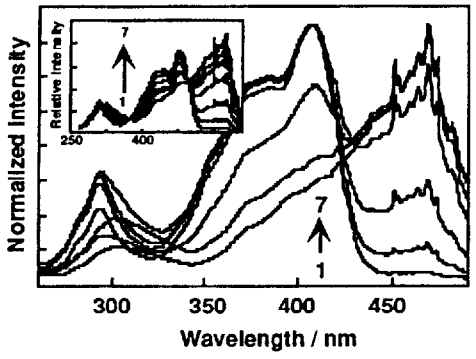


Fig. 5. Excitation spectra (λ_{em} = 510 nm) of pyranine applied on paper samples of varying 'pH_{app}' (1–7: 5.7, 6.3, 6.8, 7.2, 7.5, 8.0, 8.5). The inset shows the corresponding spectra in phosphate buffer solutions of varying pHs (1–7: 5.7, 6.3, 6.8, 7.2, 7.4, 7.6, 8.0).

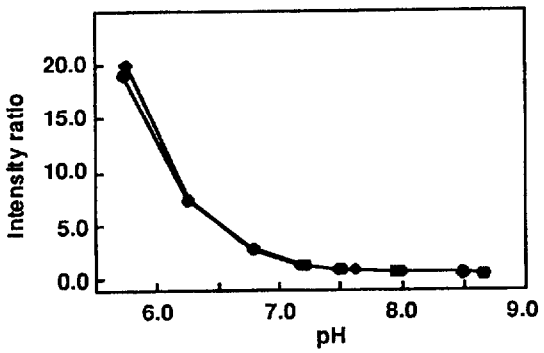


Fig. 6. Plot of intensity ratio vs. pH for pyranine: for phosphate buffer solutions (-◆-) and paper samples (-●-), I_{402}/I_{465} and I_{407}/I_{466} were monitored, respectively.

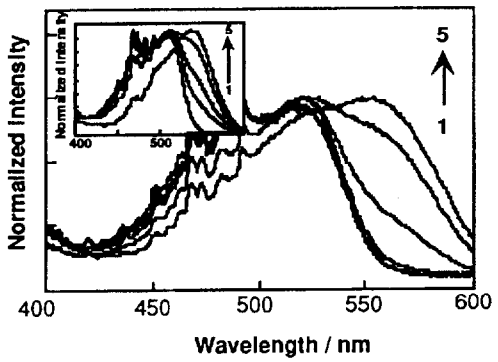


Fig. 7. Excitation spectra ($\lambda_{em}=620$ nm) of 5-(and-6)-carboxy SNAFL-1 applied on paper samples of varying 'pH_{app}' (1–5: 5.8, 6.4, 7.0, 7.5, 8.0). The inset shows the corresponding spectra in phosphate buffer solutions of varying pHs (5.7, 6.2, 7.6, 8.0, 9.1).

tra for the paper samples with the emission monitored at 620 nm. For comparison, the corresponding changes in phosphate buffers are shown in the inset. Fig. 8 shows the plots of intensity ratios vs. pH for buffer solutions and paper samples. Here again, one observes a satisfactory parallel for the behavior of the probe in buffer solutions and the paper samples. A similar trend was observed when the buffer was changed to KH_2PO_4/NaOH.

Ideally, if the fluorescent probe applied on the pre-soaked paper sample were to experience the environment similar to

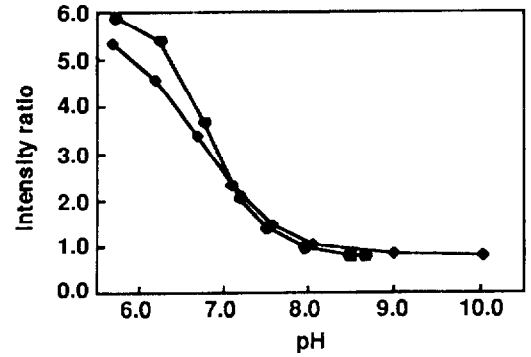


Fig. 8. Plot of intensity ratio vs. pH for 5-(and-6)-carboxy SNAFL-1: for phosphate buffer solutions (-◆-) and paper samples (-●-), I_{511}/I_{638} and I_{519}/I_{552} were monitored, respectively.

that of the solution in which it was soaked, the property considered to monitor the acidity should compare well for the two. In other words, one would expect similar intensity ratios for the buffer solutions and the paper samples, when ratiometric measurements of the emission intensities are employed to monitor the changes in acidity. Within the allowable limits, this expectation is met for pyranine and SNAFL-1 as may be seen from Figs. 6 and 8; the changes in the emission/excitation intensities for paper samples of varying acidity nicely correlate with those observed for buffer solutions of different pHs. Indeed, these changes are not severely deviated for quinine and fluorescein (Figs. 2 and 4) as well. Thus, the remarkable correlations observed for the buffer solutions and paper samples of varying 'pH_{app}'s prove the previous assumption that the latter attain the acidity equivalent to those of the solutions in which they are soaked. Since the 'pH_{app}'s refer to the pHs of the soaking solutions, we now define 'pH_{app} of paper' to refer to the pH of an aqueous solution in which the pH-dependent fluorescence probe displays changes in emission or excitation similar to those observed for a given paper sample. Astonishingly, the pH_{app}s do not significantly deviate from those measured by industrial method as evidenced from Table 1 and are complementary to industrial pH values.

A perusal of the Figs. 2, 4, 6 and 8 shows that the correlation of the probe behavior is particularly remarkable at the pHs close to their pK_as. Therefore, the intensity ratios at the pK_as of the fluorescence probes can be convincingly used to elicit information concerning the acidity of paper as extrapolated to the probe behavior in aqueous solution. Accordingly, the intensity ratio (I_{435}/I_{374}) of 1.0 ± 0.2 for quinine emission from paper samples (Fig. 2) can be diagnostic to decide whether the pH of a given paper is above or below its pK_a of 4.9 ± 0.2; e.g., if the intensity ratio for a given paper sample at the specified wavelengths is >1.2, its 'pH_{app}' is indicated to be lower than 4.9. Similarly, the intensity ratios of $I_{469}/I_{506}=1.3\pm0.2$ ($\lambda_{em}=550$ nm) for fluorescein (Fig. 4) and $I_{407}/I_{466}=1.4\pm0.1$ ($\lambda_{em}=550$ nm) for pyranine (Fig. 6) and $I_{519}/I_{552}=1.4\pm0.1$ ($\lambda_{em}=550$ nm) for SNAFL-1 (Fig. 8) serve to differentiate papers whose pHs fall in the range of ca. 4.9 to 7.8. For the blank filter paper (Whatman, 110 mm), a representative paper sample for which the acidity estimation is sought, the intensity ratio (I_{435}/I_{374}) for quinine emission was found to be 0.40, which suggested its pH to be >4.9. The intensity ratios for fluorescein, pyranine and SNAFL-1 at the aforementioned wavelengths were found to be 1.3, 5.7 and 5.7, respectively. Thus, the pH_{app} of Whatman filter paper is inferred to be 6.4 ± 0.2 (Fig. 9). It should be pointed here that the correlations for paper and buffer solutions have been established by ratiometric method and that the wavelengths at which the intensities are measured are critical. For any change in the monitoring wavelengths, the correlations must be re-established.

The probes chosen for this study cover a very narrow pH range and new probes with different pK_as will be required to extend the acidity range shown in Fig. 9. The acidity esti-

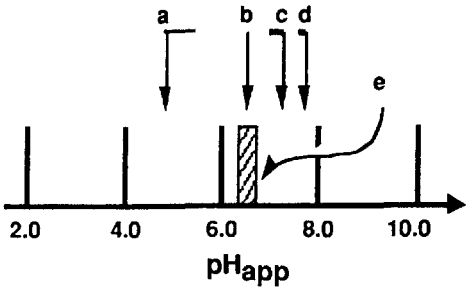


Fig. 9. The pH_{app} scale for the acidity of paper is shown by the lower arrow. The region determined by each probe for the blank Whatman filter paper is as follows: (a) quinine bisulphate >4.9, (b) fluorescein ~6.4, c) pyranine <7.3 and d) SNAFL-1 <7.8. The pH_{app} estimated for the blank Whatman filter paper is shown by the shaded box (e).

mation of paper by correlation with solution state behavior is based on the assumption that the pK_as of the probes in different environments (here the solution and the paper matrix) are not subject to significant changes, which is not always true [12,16]. For this reason, it is important that the correlation between the behavior in solution and on paper be established for each new probe to be employed. In addition, the probes should have high fluorescence quantum yields and emission or excitation spectra which markedly differ for the acidic and basic forms of the probes. The ratiometric method will be more precise if either the emission or excitation spectra are the same for both acidic and basic forms, but the complementary spectra show spectral differences. In this case, the intensity ratio will not be very dependent on the monitoring wavelengths. Otherwise, it is very important that the wavelength and slit widths established in the calibration procedure be used for all experiments. Constant slit widths are required when emission maxima are being measured. A high emission quantum yield is necessary in order to avoid application of large amounts of the probe and further to overcome the intrinsic fluorescence of paper [17–19].

The major disadvantage in using fluorescent acidity probes is that the constituents of paper can selectively quench the fluorescence of either the acidic or basic forms of the probe, leading to incorrect intensity ratios. In this respect, the Whatman filter paper that we have used is the ideal in that it does not contain significant amounts of additives. We are currently examining the behavior of various fluorescence probes on other grades of paper with a particular emphasis on the mechanical pulp, since this type of paper has not been accepted as a permanent grade and for this reason the acidity in lignin-rich papers is rather less investigated. Since lignin is a potential fluorescence quencher, it may limit the number of probes that one can employ.

The chief advantage in utilizing the fluorescent probes to measure acidity of paper is that the method is nondestructive. In addition, the probes could be used as acidity sensors, since application to only a small area is necessary. For example, the increased level of acidity due to exposure of the books stored in libraries to pollutants could be monitored periodically and such measurements would indicate the acidity levels which might be detrimental to the library collection. A further advantage of the fluorescent method is that the acidity can be measured under conditions different from those used for the industrial method. In the latter, the acidity is measured by extraction into the aqueous phase, and the paper is always exposed to an aqueous environment. This measurement may not represent the acidity under dry conditions. Fluorescent probes could be employed to measure the acidity under extreme conditions, such as those encountered in accelerated aging tests where high temperatures and humidity are employed or when paper is exposed to atmospheric pollutants.

Finally, the fact that the fluorescent probes, which have been developed for work in solution, can be used on paper opens up a new area in which the paper properties other than the acidity can be monitored. In particular, the large number of probes already developed for biological studies can be easily adapted to the studies of paper. For example, the fluorescence probes specific for certain ions such as Ca^{2+} are well known in cellular work and could be adapted to measure the metal-ion levels in pulp and paper. It is worth pointing out that in addition to the extrinsic probes, paper also has an intrinsic fluorescence [17–21], which could be applied for mechanistic and diagnostic purposes in combination with extrinsic probes.

4. Conclusion

The correlation of the behavior of fluorescence probes on paper with that in buffer solutions of various pHs suggests that pH-dependent fluorescence probes offer a reliable means of estimating the paper acidity; the emission properties of the probes (intensity ratios) can be employed to estimate the paper acidity ('pH_{app}') in a practically simple way without having to destroy the paper sample. Interestingly, the 'pH_{app}' inferred for the paper samples by extrapolation of the probe behavior to that in solution state compare very well with those of the values determined by industrial method. The results suggest that with a judicious choice of pH-dependent probes, the indicators for a wider range of pH can be developed.

Acknowledgements

The financial support for this work was provided by Networks of Centers of Excellence for Mechanical Woods and Pulps, Canada. We thank Luis Netter for his ready help in software development and usage.

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