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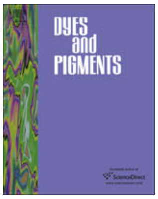

Spectroscopic study of dyes for pH and methanol sensing

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ABSTRACT

The spectral response of three dyes, in both pH and methanol in strongly acidic environments as examples of the inner media of a proton exchange membrane such as Nafion, was investigated. Picric acid responded predominantly to pH while C.I. Acid Orange 5 and C.I. Basic Green 4 each gave a combined response to both pH and methanol concentration. The spectroscopic results obtained show the feasibility of using a single dye for measuring pH without significant interference from methanol; the simultaneous determination of pH and methanol concentration using a binary combination of dyes is also feasible. These characteristics of the dyes allow their use as primary transducers for a fuel concentration sensor in a direct methanol fuel cell.

1. Introduction

Materials for fuel cells based on proton exchange membranes (PEMs) and powered by methanol–water mixtures are intensively studied [1]. The development of new materials with reduced methanol permeability and enhanced proton conductivity is an important direction of this research [2–6]. Direct estimation of proton and methanol concentration inside the PEM can facilitate the screening of newly developed materials. Performing these measurements by external sensor regardless of its operating principle [7,8] is a great problem because of microscopic size of hydrophilic proton conductivity channels [2] and the narrowness of the membrane. This problem can be solved by incorporation of suitable dye molecules into the PEM material. Such molecule can act as a probe which undergoes some reversible changes (for example, in absorption spectrum) induced by variation in proton and/or methanol concentration. Determination of relative humidity [9], pH [10] and ethanol [11] by dyes incorporated into PEM has been reported. Besides, dye molecules have been used for investigation of proton generation in thin photoresist layers [12] as well as for colorimetric detection of water pollution by metal cations and protons [13]. However, none of the cited papers discuss the possible interference between pH and alcohol concentration. It was found that alcohol concentration can be measured only in a very narrow range of about one percent [11]. Many pH sensitive dyes have been known for a long time [14], several dyes were synthesized recently [15,16] but there is still a lack in knowledge of their sensing behavior in mixtures with variable alcohol concentration. The aim of our study is to estimate the pH and methanol spectral response of different dyes in solution with composition and concentration expected for the inner media of a typical PEM such as Nafion.

2. Experimental

2.1. Selection of dyes

Some preliminary estimation of pH inside the PEM is required in order to choose the suitable dye correctly. It is well known that the pH inside the commonly used PEMs is defined by dissociation of sulphonate groups covalently attached to the polymer matrix. Therefore, we can assume that the PEM inner media is strongly acidic. More precisely, if the PEM ion exchange capacity is of about 1.3 meq/g we can expect the inner pH value between 0 and 1. Several commercially available dyes are known for pH measurement at such conditions. Their behavior in a wide range of methanol concentrations has not been sufficiently investigated to enable an informed choice between them. However, three dyes were chosen with different molecular structures from which distinctive sensing behavior could be expected. Thus Picric acid (C.I. 10 305), C.I. Acid Orange 5 and C.I. Basic Green 4 as representatives of nitro compounds, azo compounds and triphenylmethane compounds respectively were selected for this study. Their structural formulas are shown on Fig. 1. Recommended pH range for the above dyes is

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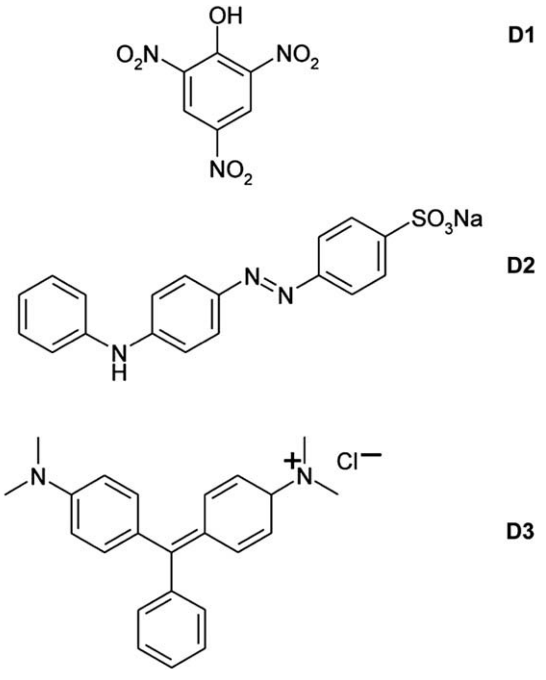

Fig. 1. Structural formulas of Picric acid (dye D1), C.I. Acid Orange 5 (dye D2) and C.I. Basic Green 4 (dye D3).

0–1.3; 1.4–2.6 and 0–2 respectively [14], which is considered as a good match for the conditions expected inside the PEM. Picric acid, C.I. Acid Orange 5 and C.I. Basic Green 4 were purchased from Sigma–Aldrich. [caution: picric acid is highly unstable; may detonate if struck or heated; highly flammable if dry; may explode if dry (keep wet at all times); flammable; incompatible with strong oxidants, alkalis, most metals reducing agents].

2.2. Spectrophotometric measurements

Optical absorption spectra of each dye in model solutions were measured using a UV–vis spectrophotometer Shimadzu UV1700 in the range from 300 nm to 700 nm. The concentrations of Picric acid, C.I. Acid Orange 5 and C.I. Basic Green 4 were 10^{-4} M, 10^{-5} M and 6×10^{-6} M respectively. This choice is resulting from the difference in molar extinction coefficients of the dyes (Fig. 2). It was assumed that a three component model solution comprising water, methanol and sulphuric acid was sufficient for preliminary estimation of dye behavior inside a PEM. For each dye its absorption spectra were measured in 24 solutions with 6 fixed values of methanol concentration and 4 fixed values of pH. Values of methanol concentration in volume percent were set to 0%, 20%, 50%, 80%, 85% and 90%. In the range of methanol concentration higher than 80% the measurements were carried out with a step of 5% because of strong pH dependence on methanol concentration in this range [17]. The pH value of model solutions was set to 0.1; 1.1; 2.1 and 3.1 by addition of sulphuric acid with constant monitoring using a glass pH electrode. The accuracy of pH setting was not worse than 0.1 pH unit. Methanol and sulphuric acid were of p.a. grade. Double distilled water was used throughout all experiments.

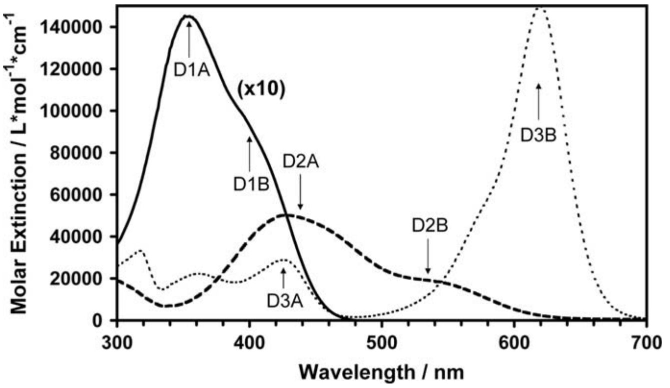

Fig. 2. The overall view of the absorption spectrum for Picric acid, C.I. Acid Orange 5 and C.I. Basic Green 4 in 80 vol.% methanol–water mixture at pH 1.1: D1A – absorption band A of Picric acid; D1B – absorption band B of Picric acid; D2A – absorption band A of C.I. Acid Orange 5; D2B – absorption band B of C.I. Acid Orange 5; D3A – absorption band A of C.I. Basic Green 4; D3B – absorption band B of C.I. Basic Green 4.

3. Results and discussion

3.1. Main features of dye spectra

Each dye under investigation is identified by two alphanumeric characters: Picric acid (D1), C.I. Acid Orange 5 (D2) and C.I. Basic Green 4 (D3), which will be used in the discussion. The overall view of the absorption spectrum for dyes D1, D2 and D3 in 80 vol.% methanol–water mixture at pH 1.1 is shown on Fig. 2. From this figure it can be seen that for each dye two wide bands appear in the absorption spectrum. This approximate consideration of the absorption bands is sufficient for the stated purpose. Each absorption band is identified on Fig. 2 by three alphanumeric characters, the first two of which unambiguously point to the dye the given band is related to. The third character is an identifier of the band itself. For example, D1A means absorption band A of dye D1.

In Section 3.2 we describe the dependence of absorption bands on pH and methanol concentration for each dye under investigation.

3.2. Sensing properties of single dye absorption bands

Dependence of optical density on pH and methanol concentration for absorption band D1A is depicted on Fig. 3. This figure represents a two-dimensional surface of optical density in coordinates

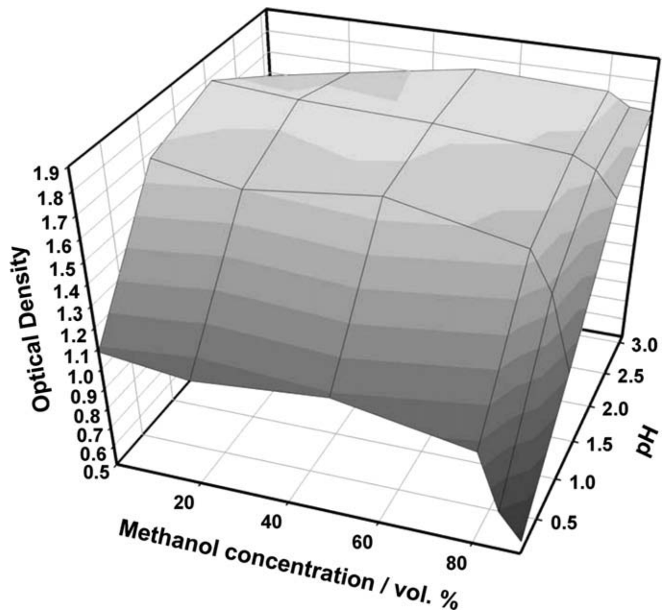

Fig. 3. Optical density dependence on pH and methanol concentration for absorption band A of Picric acid (D1A).

pH–methanol concentration. It is evident that this band is sensitive to pH. The isolines which represent the constant level of optical density are almost parallel to the methanol concentration axis in the range from 0 to 80%. This means that the response of band D1A to pH is not significantly influenced by methanol if methanol concentration does not exceed 80%. Absorption band D1B (not shown) behaves similarly and can also be considered as suitable for pH determination in the presence of methanol.

Sensing properties of dye D2 differ markedly from sensing properties of dye D1 (Fig. 4 and Fig. 5). The arrangement of isolines clearly shows that optical density in the bands D2A and D2B changes with pH and also with methanol concentration. This demonstrates combined sensitivity of both absorption bands of this dye to pH and methanol concentration. However, the optical density of bands D2A and D2B depend on these parameters differently. For example, optical density of D2A increases with pH while optical density of D2B decreases.

Both absorption bands of dye D3 also have combined sensitivity to pH and methanol concentration. However, unlike to dye D2 their sensing properties are similar to each other. The surface of optical density for band D3A in coordinates pH–methanol concentration is shown in Fig. 6.

For each dye considered there is some threshold value of methanol concentration. The sensing properties of absorption bands change if this threshold is exceeded. For example, direct relationship between optical density and methanol concentration can change to an inverse relationship (D3, Fig. 6) and vice versa (D2, Fig. 5). Another example is the change from a weak to a strong dependence (D1, Fig. 3). Thus, we can select in the whole investigated range of methanol concentration two intervals each of which results in different sensing properties of the given dye. The interface between these intervals is located nearly 80% methanol by volume for all three dyes D1, D2 and D3. For direct methanol fuel cells described in the literature methanol concentration in the fuel does not exceed 40% even for specially designed device with highly concentrated solutions [18]. Therefore the change in sensing properties of the dyes takes place outside of practically important range of methanol concentration.

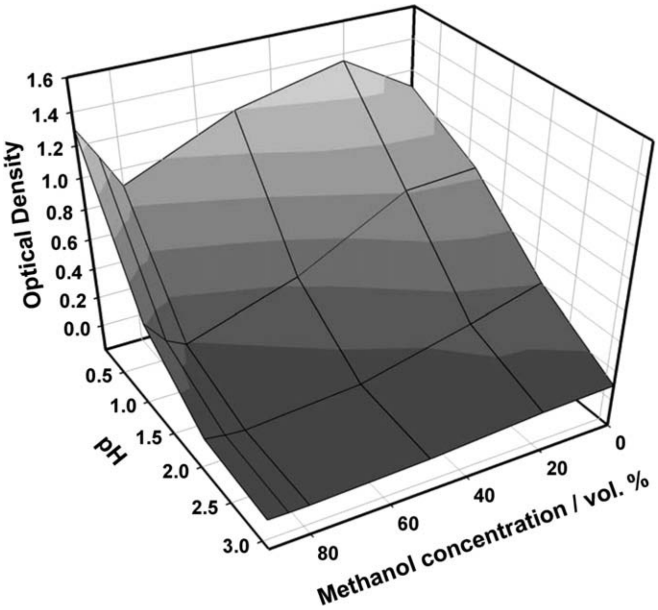

Fig. 5. Optical density dependence on pH and methanol concentration for absorption band B of C.I. Acid Orange 5 (D2B).

3.3. Sensing properties of absorption bands in the dye mixture

In the previous Section 3.2 it was shown that dye D1 exhibits a predominant response to pH in the range of methanol concentration up to 80% while dyes D2 and D3 have combined response to pH and methanol. In this connection there is a reason to verify the possibility of simultaneous sensing both pH and methanol by using a binary combination of dyes (D1 + D2 or D1 + D3). Such binary combination might be feasible if possible interactions between the dyes do not lead to an unacceptable change of their sensing properties. An example of such interaction is possible formation of an ion associate between picrate anion and C.I. Basic Green 4 cation [19]. Another example is the bonding of protonated Picric acid to the amino group of C.I. Acid Orange 5 [20]. It is known that the

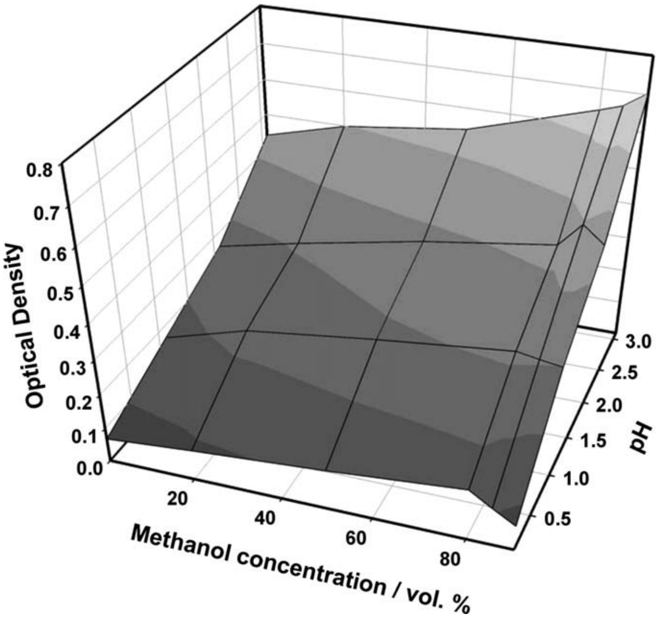

Fig. 4. Optical density dependence on pH and methanol concentration for absorption band A of C.I. Acid Orange 5 (D2A).

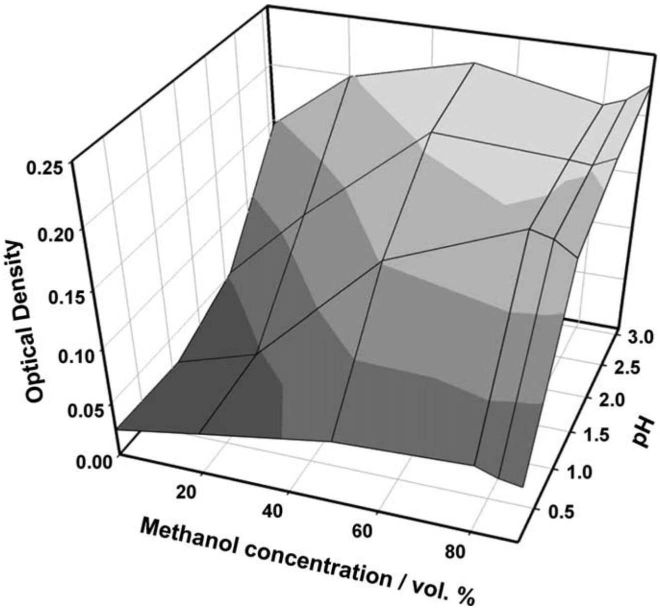

Fig. 6. Optical density dependence on pH and methanol concentration for absorption band A of C.I. Basic Green 4 (D3A).

absorption spectrum of Picric acid or picrate anion can be altered by their association with other species [21]. In order to investigate this assumption the absorption spectra of both binary combinations D1 + D2 and D1 + D3 in the same set of model solutions with predefined pH and methanol concentration as described in Section 2.2 were measured.

From the consideration of the combination D1 + D3 it can be seen that the relative position of absorption bands D1A and D3B allow their simultaneous observation without any complicated processing of the whole spectrum for their extraction. On the contrary, absorption bands D1B and D3A overlap so strongly that their sensing properties are difficult to use in a binary combination. Behavior of absorption band D1A as pH sensor for combination D1 + D3 is similar to behavior of this band for the single dye D1. Weak sensitivity of this band to methanol concentration up to 80% also remains intact in this combination. Response of absorption band D3B to methanol concentration is kept at the same level and concentration range.

From the consideration of the dye combination D1 + D2 it can be concluded that the relative position of absorption bands in this case looks similar to that described above and substantial changes in their sensing properties are not found. Thus, bands D1A and D2B can be used for simultaneous determination of pH and methanol. However, the band D2B looks less attractive than band D3B as a methanol sensor because its optical density alters the response from rise to fall even if methanol concentration does not exceed 80%.

The results described in this section show that binary combinations of dyes under investigation can be used for the simultaneous determination of pH and methanol concentration in model solution. For practical implementation of such measurements the principle of multivariate calibration can be applied [22].

3.4. Possible reason for the observed difference in sensing properties of the dyes

There are some general concepts about the mechanism responsible for the changes in absorption spectrum of dyes. For example, we can mention reversible protonation/deprotonation of the dye molecule [12] and formation of multimolecular aggregates [11,23]. However, the above models cannot adequately explain the details of the molecular probe response mechanism in methanol–water mixture. We can suppose that the predominant response of dye D1 to pH and combined response of dyes D2 and D3 to both pH and methanol concentration is affected by the formation of a solvate shell around the dye molecule. In the framework of this concept the predominant response to pH can be explained by formation of such shell mainly from water. Combined response to pH and methanol can be related to formation of solvate shell from comparable amounts of methanol and water. In order to verify this assumption we plan to perform quantum-chemistry simulation of dye absorption spectrum in model solutions described in this paper. Identification of a response mechanism of the dyes to pH and methanol can be useful for design of molecular probes adapted to particular applications.

4. Conclusions

Picric acid has a predominant response to proton concentration (pH) at moderate methanol concentration. This feature makes it feasible for pH determination in mixed methanol–water solutions.

At methanol concentration higher than 80% the significant interference pH–methanol appears for Picric acid that limits its application as pH sensitive probe in mixed solutions.

C.I. Acid Orange 5 and C.I. Basic Green 4 demonstrate combined response to both pH and methanol concentration in the full investigated range of these parameters. Thus, each of these dyes can be used for determination of methanol if pH is estimated independently.

Sensing properties of each dye in investigated binary combinations Picric acid + C.I. Acid Orange 5 and Picric acid + C.I. Basic Green 4 are feasible for simultaneous determination of acidic pH in the range of about from 0.1 to 2 and a wide range of methanol concentration (up to 80%).

The results obtained can be useful in research related to polymeric materials for Proton Exchange Membranes as well as in the development of dye-based optical sensor for simultaneous determination of pH and methanol concentration in the fuel for Direct Methanol Fuel Cells.

Acknowledgements

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