Resonance Raman Study on a Novel pH Property of Black Soap Films

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Resonance Raman spectra of the anionic azo dye brilliant yellow in the black soap films formed from aqueous solutions of cetyltrimethylammonium bromide and brilliant yellow at various bulk pHs, shows the aqueous core phase of the films has a buffer effect when the bulk pH is changing.

A black soap film can be easily formed by withdrawing a metal frame from a concentrated solution of surfactant through the air interface under suitable conditions.[1,2] Being ultrathin films with a sandwich structure consisting of an aqueous core between two surfactant monolayers, black soap films provide a microenvironment and molecular arrangement similar to those of biomembranes and have been referred to as an important mimetic agent for the investigation of structure and function of biomembranes.[3,4] However, spectroscopic investigations of black soap films are still limited because of their instability especially under irradiation by a laser beam. By the introduction of an anionic azo dye into the aqueous solution of a cationic surfactant, Jiang *et al.* have prepared more stable black soap films and succeeded in measuring their resonance Raman spectra.[2] Furthermore, by using brilliant yellow, another anionic azo dye containing double sulfate groups, as a spectroscopic probe, and cetyltrimethylammonium bromide (CTAB) as a film-forming surfactant, we have prepared very stable black soap films which can exist for two weeks at room temp. Here, we report the pH property of their aqueous core phase by studying the resonance Raman spectra of the black soap films.

Black soap films were prepared from CTAB solutions (0.01 mol dm^{-3}) by the addition of brilliant yellow (0.001 mol dm^{-3});[2] the Raman spectra were recorded on a Jobin Yvon HG 2S spectrometer.

In water, an acid–base equilibrium of brilliant yellow takes place with pK 8.75,[5] See Fig. 1. Its conjugated acid form (**A**) and conjugated base form (**B**) give maximum absorbance at 400 nm and 490 nm, respectively. Good overlap between the two bands suggests that Raman scattering of both **A** and **B** should be excited in resonance by the 457.9 excitation line. Fig. 2(*a*) shows the resonance Raman spectra of brilliant yellow solutions (0.0001 mol dm^{-3}) at different bulk pH. The two bands at 1385 and 1441 cm^{-1} are assigned to the –N=N– stretching modes of brilliant yellow corresponding to form **B** and form **A** respectively.[6] In the colour change interval, the relative intensity ratio between the two bands (I_B/I_A) is sensitive to the change of the bulk pH, see the curve (*a*) in Fig. 3. For the resonance Raman spectra of the black soap films in Fig. 2(*b*), however, the intensity ratio between the two bands does not change dramatically in a wide range of bulk pH [see Fig. 3(*b*)] in contrast to the solutions, which indicates the novel pH property of the films. In addition, the two –N=N– stretching vibration bands in the microenvironment of the black soap films shift to 1380 and 1430 cm^{-1} by analogy with the situation of brilliant yellow in the CTAB micellar solution.[6]

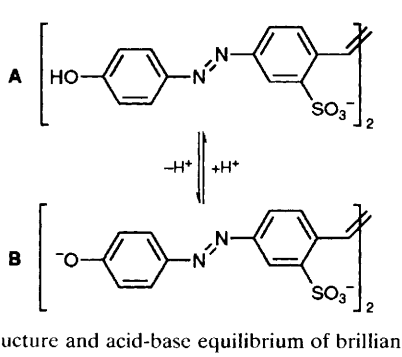

Fig. 1 Structure and acid-base equilibrium of brilliant yellow

In the bulk pH range (from pH 6.0 to 11.0), the ionic strength of the film-forming solutions is mainly decided by the critical micelle concentration of the solutions and the concentrations of brilliant yellow (0.001 mol dm^{-3}), thus the film thickness is approximately constant.[2] In order to obtain the relationship between the intrinsic pH (pH^i) of aqueous core phase of the films and the bulk pH of the film-forming solutions, two factors, *i.e.*, the intrinsic pK^i and log[**B**]/[**A**] of

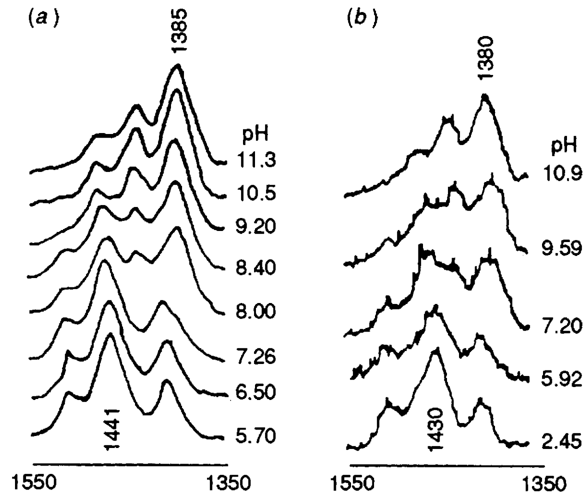

Fig. 2 Bulk pH-dependent resonance Raman spectra of (*a*) brilliant yellow in aqueous solutions (0.0001 mol dm^{-3}) and (*b*) black soap films formed from CTAB solutions (0.01 mol dm^{-3}) with the addition of brilliant yellow (0.001 mol dm^{-3})

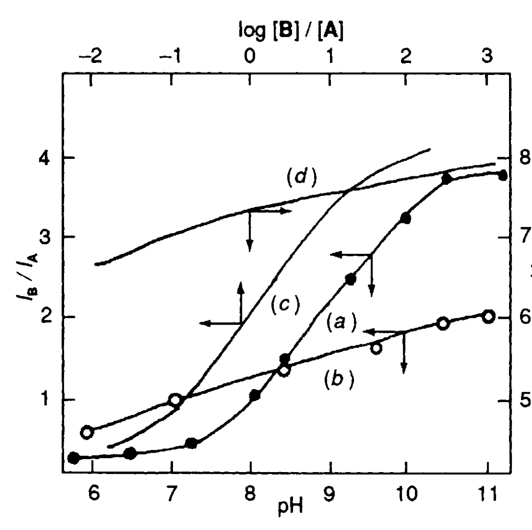

Fig. 3 Plot of I_B/I_A against bulk pH for (*a*) brilliant yellow in aqueous solution and (*b*) in the black soap films; (*c*) shows the working curve of I_B/I_A *vs.* log[**B**]/[**A**] and (*d*) the dependence of the intrinsic pH (pH^i) of the black soap films on the bulk pH

brilliant yellow in the films, must be known as according to eqn. (1).

$$\mathrm{pH}^i = \mathrm{p}K^i + \log[\mathbf{B}]/[\mathbf{A}] \qquad (1)$$

$$\log[\mathbf{B}]/[\mathbf{A}] = 8.75 - \mathrm{pH} \qquad (2)$$

In the brilliant yellow aqueous solutions, the value of log[**B**]/[**A**] can be calculated from eqn. (2) for a given pH. On the other hand, the value of I_B/I_A can be determined from Fig. 3(*a*) for the same pH. Thus, a working curve of I_B/I_A *vs.* log[**B**]/[**A**] can be drawn [Fig. 3(*c*)] and the value of log[**B**]/[**A**] for brilliant yellow in films at a given bulk pH can be obtained from its I_B/I_A *vs.* pH relationship [Fig. 3(*b*)] and the working curve of Fig. 3(*c*). Furthermore, if we reasonably assume that the intrinsic pK^i of brilliant yellow in the films is equal to the intrinsic pK^i of brilliant yellow on the surface of CTAB micelle (7.75[7]) then from eqn. (1) the pH^i at the given bulk pH can be obtained, see Fig. 3(*d*). This interesting result implies that when the bulk pH is changing from pH 6.0 to 11.0, the intrinsic pH of the aqueous core will have a small change between pH 6.5 to 8.0, indicating a pH-buffer effect of the thin layer water.

In previous studies on the acid–base equilibrium of dyes on the surface of a charged membrane or a similar interface,[8] much research has been directed towards determining the electrical potential at the surface.[9–13] It has been accepted that on charged membranes, including soap films with a thick layer of water (75–550 nm),[12] which have a semi-infinite dispersion layer compared with the Debye-length, the intrinsic pH is directly decided by the electrical potential and the bulk pH according to Boltzmann law. For black soap films, however, the thickness of the aqueous core (0.8–12.5 nm)[2] approaches or is even smaller than the Debye-length and the strong interaction of the double layer may result in the formation of a relatively stable microenvironment. The novel pH property discussed here may be one of the characteristics of such a microenvironment.

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References

1 J. Umemura, M. Matsumoto, T. Kawai and T. Takenaka, *Can. J. Chem.*, 1985, **63**, 1713.
2 Y. Jiang, Y. Tian and Y. Liang, *Science in China (Ser. B, Eng. Edn.)*, 1991, **34**, 1.
3 H. T. Tien, *Bilayer Lipid Membrane (BLM), Theory and Practice*, Marcel Dekker, New York, 1974.
4 J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley-Interscience, New York, 1982.
5 Y. Zhang and Y. Liang, *Acta Chim. Sinica*, 1993, **51**, 594.
6 Y. Zhang, Y. Tian and Y. Liang, *Chem. J. Chin. Univ., (Eng. Edn.)*, 1990, **6**, 232.
7 Y. Zhang and Y. Liang, *Proceedings of the First China Postdoctoral Academic Congress*, Beijiang, ed. E. Feng, 1993, p. 1573.
8 F. Grieser and C. J. Drummond, *J. Phys. Chem.*, 1988, **92**, 5580.
9 G. H. Hartely and J. W. Roe, *Trans. Faraday Soc.*, 1940, **36**, 101.
10 P. Mukerjee and K. Banerjee, *J. Phys. Chem.*, 1964, **68**, 3567.
11 M. S. Fenandez and P. Fromherz, *J. Phys. Chem.*, 1977, **81**, 1755.
12 P. Fromherz and R. Kotulla, *Ber. Bunsenges. Phys. Chem.*, 1984, **88**, 1106.
13 C. J. Drummond, F. Grieser and T. W. Healy, *J. Phys. Chem.*, 1988, **92**, 2604.