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Influences of Na^+ and H^+ on the spectroscopic properties and morphologies of a cyanine dye

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Abstract

In this paper, a cyanine dye was chosen to study the formation of J aggregates under the function of different ion sources (Na^+ and H^+). UV–vis spectra showed that adding either NaCl or HCl could promote dye to form J aggregates. So we investigated the different abilities of Na^+ and H^+ in forming J aggregates. The result indicated that the stimulative ability of H^+ was stronger than that of Na^+. Furthermore, we can also observe the morphology of the dye, which was coagulation of many gains before the addition of NaCl or HCl using Transmission Electron Microscopy (TEM). While it was changed to the short strands with a diameter of about 100 nm after adding NaCl to the dye aqueous solution, and comparably with the addition of HCl it became longer interlaced strands with an average diameter of about 200 nm.

Keywords: J aggregates; NaCl; HCl; Cyanine dye

1. Introduction

Organic molecular self-aggregation has been the focus of interest in both fundamental and applied fields due to their novel chemical, physical and optical properties in recent years. J aggregation is a typical example of self-aggregation in the photographic domain. Due to the delocalization of excitation over an aggregate by intermolecular interaction between two transition dipole moments [1,2] J aggregation band shows a new, especially narrow and red shifted band relative to the monomer absorption. There are usually several methods to form J aggregates effectively: adding inorganic salts into solution, lowering the temperature of the solution and/or changing other experimental conditions [3–5]. The addition of inorganic salt can cause an increase in the screening factor or effective dielectric constant and then promote dye aggregation [6,7]. Among the published papers many researchers studied the influence of adding inorganic salts to the dye on the formation of J aggregates by NMR [8], AFM [9] and other techniques. However, little attention was paid to the influence of HCl on the spectroscopic properties of the cyanine dye and the morphology of their J aggregates. In the present work, the effects of NaCl and HCl on the spectroscopic properties of the cyanine dye were characterized by UV–vis spectroscopy and the morphologies of J aggregates were investigated by Transmission Electron Microscopy (TEM).

2. Experiments

2.1. Material

All reagents were purchased from commercial sources and were used as received. The structure of the cyanine

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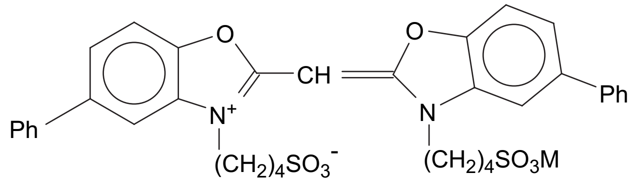

Scheme 1.

dye is shown in Scheme 1. Its maximum absorbance wavelength is 377 nm measured by UV–vis (solvent is water). For all experimental measurements the content of the dye is 1.0×10^{-4} mol/L and kept unchangeable. The concentration of HCl was obtained by pH meter (pHS-25). All experiments were carried out in room temperature.

2.2. Instruments

The absorption spectra were recorded with U-3000 spectrometer (HITACH Ltd., Toyato, Japan). And the samples for transmission electron microscopy (JEOL JEM-200CX) observation were prepared by dipping droplets of the solution on carbon-filmed grids and then dried at air temperature.

3. Results and discussions

3.1. UV–vis spectra of the cyanine dye in NaCl or HCl solution

UV–vis spectra show that the cyanine dye has two absorbance bands at 372 nm and 388 nm in aqueous solution. The absorptive property changed significantly after adding NaCl, as shown in Fig. 1(a). After adding NaCl, a decrease in the absorbance at 372 nm was observed and accompanied by a new absorbance at 412 nm, which is ascribed to the formation of J aggregates. Meanwhile, the absorbance of the band at 387 nm was independent of the NaCl/dye molar ratio, while slightly red-shifted due to the overlap with the other two bands. The similar phenomenon was observed with the addition of HCl (see Fig. 1(b)), indicating that H^+ could also promote the formation of J aggregation. We supposed that the reason for formation of J aggregation was due to HCl could transform the dye from sulphonate to sulfonic acid so that the intramolecular repulsion interaction of the dye was smaller and H bond maybe formed among molecules [10]. In most published papers, HCl was seldom investigated to make the cyanine dye self-aggregation. That is to say, a new material appeared to induce the cyanine dye to form J aggregation.

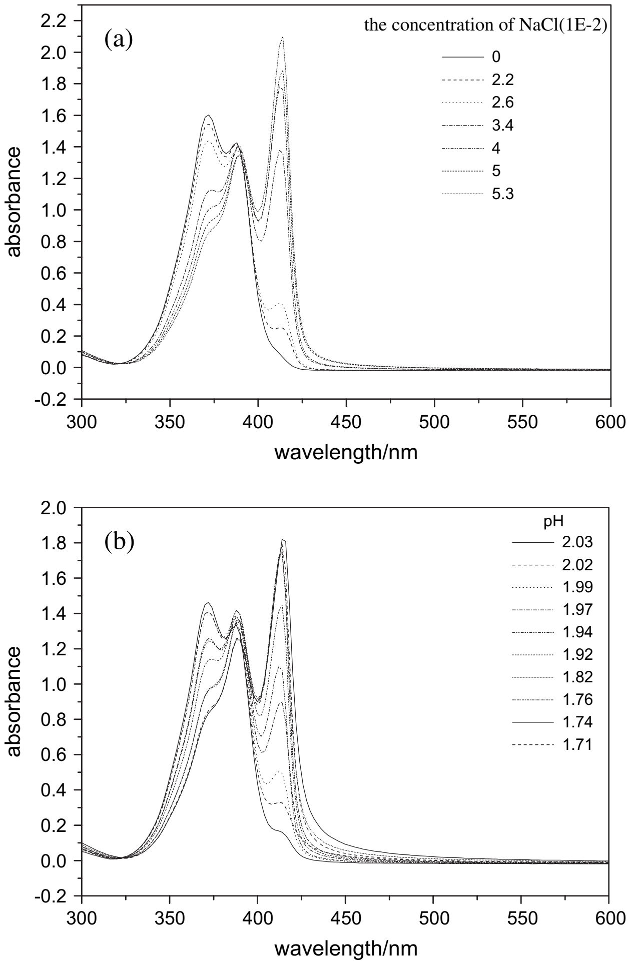

Fig. 1. Absorption spectroscopy of the dye: (a) in different concentration of NaCl solution; and (b) in different HCl solution.

3.2. The different ability of Na^+ and H^+ to form J aggregation

From the prior experimental results, it was suggested that either NaCl or HCl could promote the dye to form J aggregation. However, their abilities to form J aggregation may be different and were investigated in our present work. We denote the concentrations of NaCl or HCl as x-axis, and the value of J aggregation as y-axis to simply evaluate their abilities (seen in Fig. 2). From the curve it was found that the requisite concentration of H^+ is less than that of Na^+ under the condition of the same value of J aggregates forming. It indicates that the ability of H^+ to promote dye self-aggregation was stronger than that of Na^+.

3.3. TEM images of the cyanine dye

Since NaCl and HCl have different ability to form J aggregation, it is necessary to observe the morphologies of the two J aggregations, one is formed by NaCl

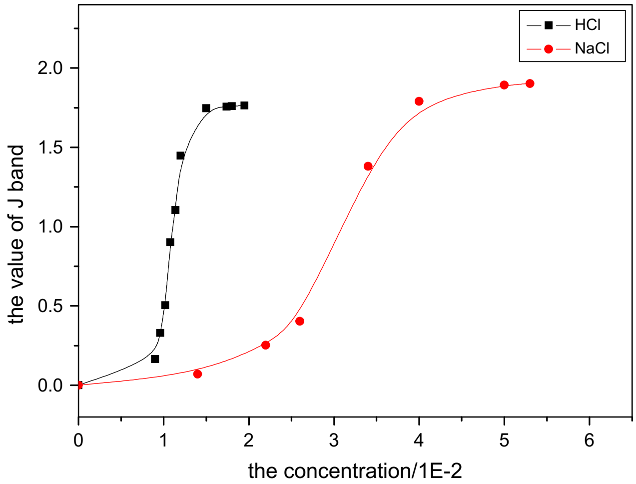

Fig. 2. The ability of Na^+ and H^+ to form J aggregation.

and the other by HCl. Fig. 3 shows the morphology of the cyanine dye in the absence of NaCl and HCl. The cyanine dye without forming J aggregation was the coagulation of many grains. However, the morphology of the cyanine dye, with the addition of NaCl changed dramatically, was discontinuous strands with a diameter of about 100 nm (see Fig. 4(a)). It maybe due to the formation of J aggregation. On the other hand, by treating with HCl, the cyanine dye shows the dissimilar morphology of interlaced and flexual fibrous threads with the average diameter of 200 nm (see Fig. 4(b)).

The TEM results clearly showed that the morphologies of J aggregation were greatly distinct due to the different ion sources. As we know, the effects of different ion sources on the morphology of J aggregation have not been reported up to now.

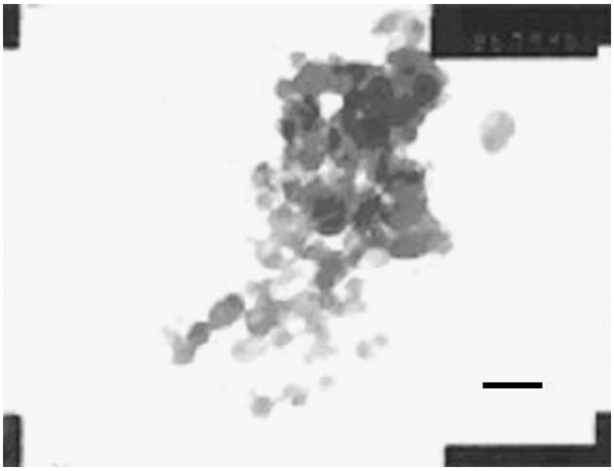

Fig. 3. TEM image of the cyanine dye before adding NaCl and HCl (bar = 125 nm).

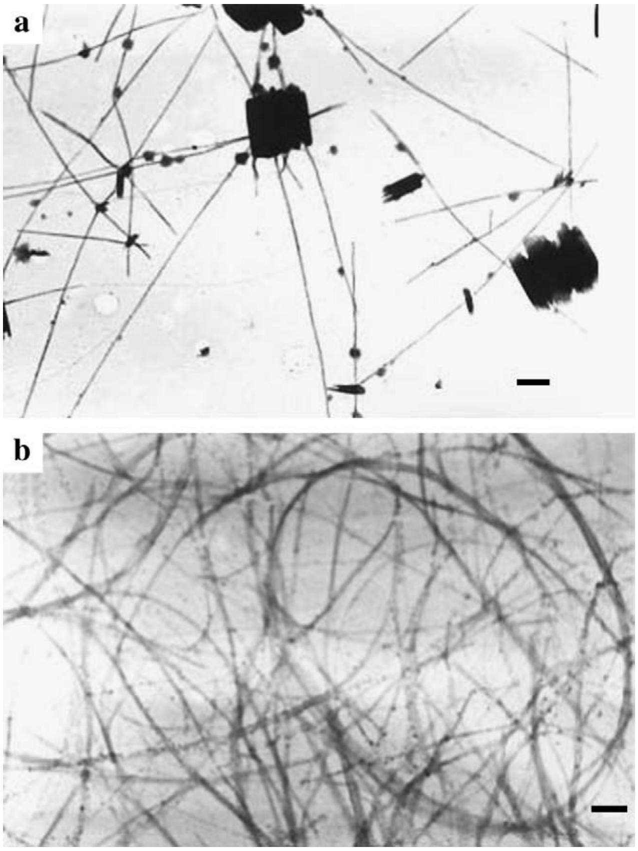

Fig. 4. (a) TEM images of the cyanine dye after adding NaCl (bar = 500 nm) and (b) adding HCl (bar = 500 nm).

4. Conclusions

In this paper we investigated the different effects of NaCl and HCl on the J aggregation of a cyanine dye. Through UV–vis spectra we found the cyanine dye easily formed J aggregates under the function of NaCl or HCl. But the ability of H^+ to form J aggregation was stronger than that of Na^+. Moreover we also observe the morphology of the cyanine dye, before forming J aggregation and after forming J aggregation induced by NaCl and HCl using TEM measurement. The results showed that the morphology of J aggregation fabricated by NaCl was completely different from that by HCl.

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Reference

[1] McRae EG, Kasha M. J Chem Phys 1958;28:721–2.
[2] Kasha M, Rawis HR, El-Baoumi MA. Pure Appl Chem 1965;11:371–92.

[3] Struganova. J Phys Chem A 2000;104:9670.
[4] Wang M, Silva GL, Armitage BA. J Am Chem Soc 2000;122:9977.
[5] Herz AH. Photogr Sci Eng 1974;18:323.
[6] Mukerjee P, Ghosh A. J Am Chem Soc 1970;92:6403.
[7] Robinson B, Loffler A, Schwarz G. J Chem Soc Farady Trans I 1973;69:56.
[8] Xiang Junfeng, Yang Xiaorong. J Colloid Interf Sci 2003;258:198–205.
[9] Yao H, Sugiyama S, Kawabata R, Ikeda H, Matsuoka O, Yamamoto S, et al. J Phys Chem B 1999;103:4452.
[10] Huiqing Zhao, Dongming Chen. Chin J Spect Lab 2000;3:3.