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Spectral behavior and pH dependence of *N*-hexadecyl-5-iminomethyl-8-hydroxyquinoline

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Abstract

A new kind of amphiphile derived from 8-hydroxyquinoline, *N*-hexadecyl-5-iminomethyl-8-hydroxyquinoline (HIHQ) was synthesized and characterized by different physical methods. The influence of pH value on UV-vis absorption, fluorescence spectra were investigated and the surface pressure–area isotherms were recorded under different pH subphase. The linear response range between the emission intensity and the concentration of HIHQ was $1–4 \times 10^{-6}$ mol L^{-1}. The strongest emission of HIHQ about 460 nm was obtained at pH 8.2 and the acid–base equilibrium of HIHQ in monolayer and solution was also discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Amphiphile; pH dependence; Langmuir–Blodgett films; UV-Vis absorption; Fluorescence spectra

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1. Introduction

Since 1937, when Langmuir first reported the amphiphilic property of stearic acid at air–water interface [1], many kind of materials, such as dioctadecyldithiocarbamate, dialkyldimethylammonium and amphiphilic azobenzene, etc., have been studied in both theoretical and practical fields [2–4]. Recently, a great deal of novel compounds derived from 8-hydroxyquinoline were synthesized and used in this field. Usually 8-hydroxyquinoline and its derivatives have a rigid headgroup with nitrogen and oxygen atoms, which can coordinate with many metal ions. These amphiphilic complexes would be used in electroluminescence devices, oriented-crystallization and other practical applications [5–9]. In the present work, we have designed and synthesized an amphiphilic ligand, *N*-hexadecyl-5-iminomethyl-8-hydroxyquinoline (HIHQ), and investigated the characteristics of HIHQ monolayer at the air–water interface with different acidity in the subphase. The UV-visible spectra and fluorescence spectra of HIHQ in ethanol-water with different acidity were recorded and its acid–base equilibrium was also discussed.

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2. Experimental

2.1. Materials

8-Hydroxyquinoline (Shanghai Chemical Reagents) and hexadecylamine (Fluka Chemical) were used without any further purification. All solutions were purified by standard procedures. Deionized purified water from a Milli-Q System (Millipore) was used in all experiments.

2.2. Apparatus

C, H, N analyses were performed using a Perkin-Elmer Model 240C elemental analyzer. ^{1}H NMR spectra were obtained using a Bruker Am-500 NMR spectrometer. Infrared spectra were recorded on a Nicolet Model 170 SX FTIR spectrometer and the UV-Vis spectra were measured with a Shimadzu Model 3100 UV-VIS-NIR recording spectrophotometer. Fluorescence spectra were obtained from a LS 50B luminescence spectrometer controlled by a personal computer. The pH of solutions and subphases were determined by the pH sensor attached with the Langmuir trough.

2.3. Measurement of surface pressure–area isotherms

Measurement of surface pressure–area (π–A) isotherms was carried out with a KSV5000 Langmuir trough system. Solution of HIHQ (ca. 1×10^{-3} mol l^{-1} in chloroform) was added dropwise to the clean subphase surface by syringe. After the chloroform had evaporated for about 15 min, the monolayer was compressed by two Teflon barriers at 20 mm min^{-1}, and π–A isotherm was recorded automatically. Acidity of subphase were adjusted by addition of isopiestically distilled $HClO_4$ or NaOH solution. All work was carried out in a dust-free box at 14 ± 1°C and the experiments were repeated at least twice.

2.4. UV-visible spectra and fluorescence studies

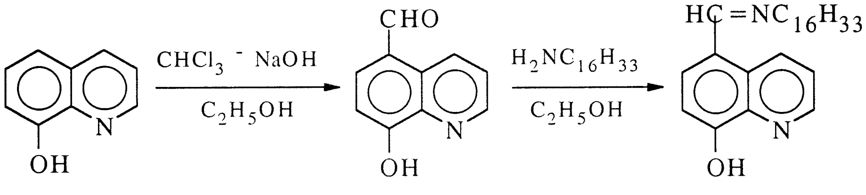
The studies of UV-visible absorption spectra and fluorescence spectra, were carried with an ethanol-water (V/V = 1:9) solution. The results were obtained at room temperature and the pH values of solution were adjusted as above mentioned. The fluorescence spectra were recorded using the Perkin–Elmer Fluorescence Data Manager software. Both excitation slit and emission slit were kept at 2.5 nm. The scan speed was 400 nm min^{-1}. The excitation monochromator was chosen at 257 nm. A cutoff filter of 290 nm was usually used in front of the emission monochromator to remove the second order scattering.

3. Results and discussion

3.1. Synthesis and conformation of title amphiphile

The synthesis procedure for the amphiphilic ligand, *N*-hexadecyl-5-iminomethyl-8-hydroxyquinoline (HIHQ) is illustrated in Scheme 1. This route involves the preparation of 5-formyl-8-hydroxyquinoline [10], and its condensation reaction with long chain alkylamine.

8-Hydroxyquinoline (10 g), ethanol (50 ml) and aqueous sodium hydroxide (20 g in 25 ml of water) were refluxed while chloroform (14 g) was added dropwise during 50 min. After refluxing for 12 h, ethanol and excess chloroform were distilled off, and the separated solid was dried and ex-



Scheme 1. Synthesis procedure of the amphiphilic molecule HIHQ.

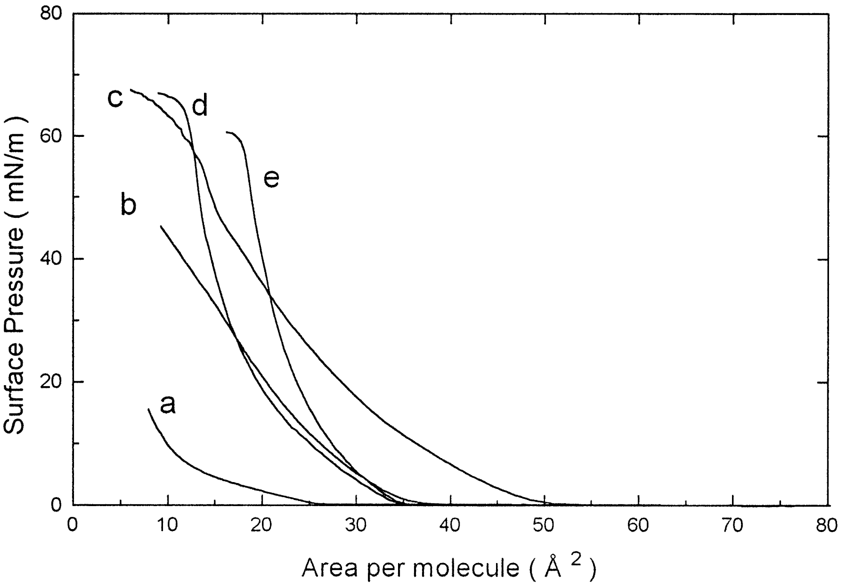


Fig. 1. Surface pressure–area (*π–A*) curves for HIHQ on aqueous subphases of different pH: a, 5.0; b, 6.0; c, 7.0; d, 8.3; e, 10.4.

tracted continuously with light petroleum (b.p. 60–90°C). The extract furnished 5-formyl-8-hydroxyquinoline (FHQ) as straw-coloured needles (m.p. 177–178°C). Analysis calculated for $C_{10}H_7NO_2$: C, 69.36; H, 4.07; N, 8.09%. Found: C, 69.13; H, 4.10; N, 7.86%. FTIR (KBr), v (cm^{-1}): 3188 (OH); 1663(C=O). UV-Vis, λ (nm): 388; 330; 262; 241. ^{1}H NMR ($CDCl_3$): 10.14 (1/2H, O–H); 9.68 (1H, Ar–H); 8.88 (1H, Ar–H); 8.00 (1H, Ar–H); 7.68 (1H, Ar–H); 7.48 (1H, H–C=N–).

5-Formyl-8-hydroxyquinoline (0.34 g) and hexadecylamine (0.75 g) were added in 40 ml ethanol and refluxed for about 10 min. Then solution was kept below 0°C. After evaporating of the solvent, yellow-green needles were obtained. The product gave a satisfactory analysis (m.p. 76–77°C). Analysis calculated for $C_{26}H_{40}N_2O$: C, 78.70; H, 10.11; N, 7.03%. Found: C, 78.71; H, 10.11; N, 7.03%. FTIR (KBr), v (cm^{-1}): 3188 (OH); 2916, 2849(CH_2, CH_3); 1646 (C=N); 786($(CH_2)_n$). UV-Vis, λ (nm): 427, 336, 265, 246. ^{1}H NMR ($CDCl_3$): 10.14 (1/3H, O–H); 9.73 (1H, Ar–H); 8.80 (1H, Ar–H); 8.60 (1H, Ar–H); 8.00 (1H, Ar–H); 7.67 (1H, Ar–H); 7.54 (1H, Ar–H); 3.65 (2H, N–CH_2); 1.76 (4H, N–C–CH_2–CH_2); 1.26 (24H, $(CH_2)_n$); 0.89 (3H, CH_3).

3.2. Formation of HIHQ monolayer on the subphases of different pH values

Fig. 1 shows the surface pressure–area isotherms of monolayer of HIHQ on the subphase of different pH values from 5.0 to 10.4. On a subphase of pH 7.0, the monolayer collapses when the surface pressure is increased to ca. 67 mN m^{-1}. The *π–A* isotherm has no plateau and only a condensed region appears. This indicates that neither a phase change nor a change in orientation of the head group fragment (quinoline ring) of HIHQ occurs in this situation. According to a space-filling molecular (CPK) model, the 8-hydroxyquinolinol ring can be approximated as a rectangular block with dimensions of about $8.4 \times 7.4 \times 3.6$ Å^3. A limiting area of about 26.5 Å^2 per molecule of HIHQ was obtained by extrapolating the surface pressure to zero in the compression region. Therefore, this value corresponds to the side area (7.4×3.6 Å^2) of the 8-hydroxyquinolinol ring of HIHQ.

The *π–A* isotherm of HIHQ depends remarkably on the pH value of the aqueous subphase. The pH dependence of the amphiphile should be attributed to the weakly acidic character of the phenolic group and the weakly basic character of the tertiary amine group. The addition of a small account of $HClO_4$ solution results in a great alteration of the π–A isotherm. For example, at pH 6.0, the collapse pressure is decreased to about 20 mN m^{-1}. Further decrease in the subphase pH leads to further reduction of collapse pressure. At pH 5.0, the π–A isotherm is a typical expanded isotherm with a very low collapse pressure of 13 mN m^{-1}. On the contrary, in basic subphases, with increasing pH values, the isotherm of HIHQ have a tendency to increasing the condensed phase, but the collapse pressure does not obviously change.

This means that HIHQ can form stable monolayers on neutral and basic subphases, but on acidic subphase the π–A isotherms are of the liquid expanded type and HIHQ cannot form stable monolayers. Usually, the imine group is unstable in basic solution, but the imine group of HIHQ confers an unusual stability on the monolayer on basic subphases, showing the difference between the air–water interface and the bulk solution. In 1951, Davies suggested that the surface pressure could be conceived of as the sum of two components, an electrostatic term and a nonelectrostatic term [11]. HIHQ exists as a deprotonated species in basic subphases, which can form a stable, diffuse electric double layer at air–water interface with the counterion (Na^+). Therefore, the electric double layers with a net zero charge reduce the electrostatic repulsion between the amphiphiles and facilitate the formation of a close-packed condensed film [12]. The protonated species cannot form a stable monolayer on acidic subphase. Increase of acidity in subphase would causes large change of collapse pressure. This may be explained by the increase of solubility of HIHQ, namely, the protonation of the nitrogen atom in the quinoline, which prevents HIHQ from forming a condensed film [13].

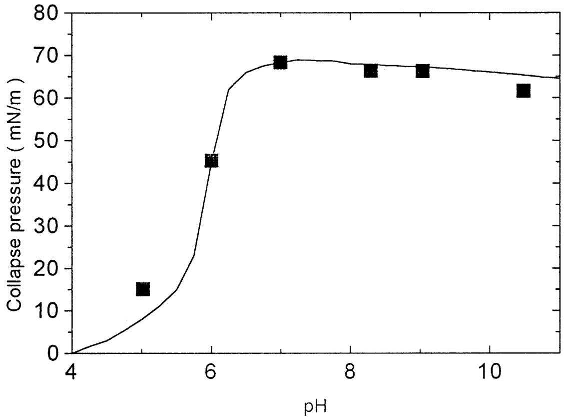


Fig. 2. Plot of collapse pressure versus pH values of subphase.

The collapse pressure (π_{max}) of an HIHQ monolayer at different pH values of aqueous subphases can be obtained from the π–A isotherms. Plotting the collapse pressure as a function of pH value of the subphase, (Fig. 2) shows the pronounced dependence of π_{max} on the pH values in the subphases. With increasing pH values, the π_{max} increases gradually, then a steep increase is observed at ca. pH 8.0. But the further increase of the pH value leads to a small decrease of π_{max}. From this result, we can see that HIHQ can be used as a material to form LB film only on the subphases with pH greater than 5.5, in which an HIHQ monolayer with a surface pressure greater than 20 mN m^{-1} can be obtained.

As mentioned above, in the pH range of 5–10, a small change of the pH values of the subphase can cause a large modification of the properties of the HIHQ monolayer. It can thus be deduced that the association-dissociation of two coordination groups N and OH of HIHQ with the H^+ ion occurs in the subphase pH range 5–10.

3.3. Influence of acidity on the absorption of HIHQ solution

The UV-visible spectra of HIHQ in ethanol at different medium are shown in Fig. 3. The most important features are the presence of three bands at ca. 255, 292 and 380 nm. They are assigned to the ^1B_b, ^1L_b and ^1L_a bands of the quinoline ring, respectively, and are due to $\pi \rightarrow \pi^*$ transitions. Although the position of the ^1B_b band hardly changes on going from low to high pH, the ^1L_a and ^1L_b bands are more sensitive both in terms of frequency and intensity. For example, the absorption of the ^1L_a band of HIHQ at various pH values is quite different (see Fig. 4). The absorption maximum at 381 nm was bathochromically

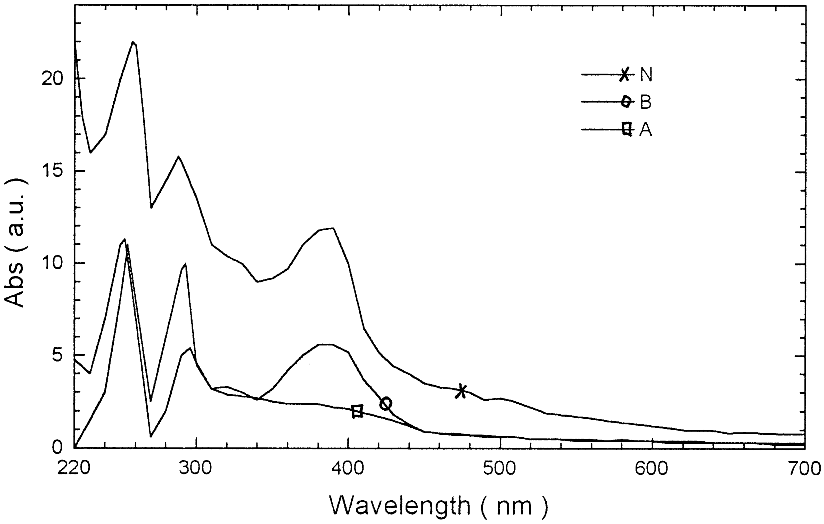


Fig. 3. Absorption of HIHQ in acidic (A), basic (B) and neutral (N) ethanol-water solution.

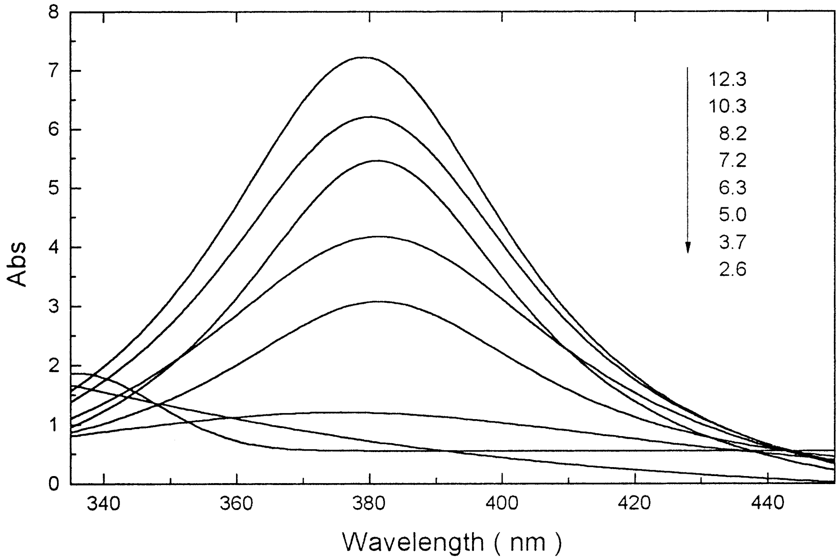


Fig. 4. Absorption of the ^1L_a band of HIHQ in different pH values.

shifted about 2.5 nm in the basic medium of pH 12.3, and the intensity of this peak is also raised with the increasing of the pH. Nevertheless, in acid medium, the $\pi \rightarrow \pi^*$ band at 380 nm was decreased greatly. According to Murrell's opinion [14,15], there is strong mixing of a charge-transfer transition, from the –CH$_2$– group to the ring, with the ^1L_a transition. Similarly, in the case of the alkaline media we can show empirically that the transition labeled ^1L_a also has considerable charge-transfer character, and the charge transfer is from the –O– to the heterocyclic, nitrogen-containing ring.

3.4. Fluorescence spectra of HIHQ solution at different pH values

The fluorescence emission spectra of HIHQ solution are shown in Fig. 5. Detected at 460 nm, a maximum excitation wavelength about 257 nm is obtained and choosen to excite the sample in the following experiments. Only a sign at ca. 460 nm is investigated in the emission spectrum. Usually, a high value of fluorescence efficiency is generally associated with a relatively rigid structure [15]. Therefore, the emission of HIHQ is much greater than that of 8-hydroxyquinoline in our experiments. The concentration dependence on the emission intensity of HIHQ is also examined and shown in Fig. 5. From our repeated experiments, we have seen that, as the concentration of HIHQ increases, the fluorescence intensity versus concentration becomes increasingly curved. However, the emission band does not enlarge when the concentration is higher than 4×10^{-6} mol dm^{-3}. The main reason for the additional curvature, observed at high concentration, is that each layer of the sample absorbs some of the incident radiation. Then we could deduce that the linear response range of the emission intensity versus the concentration of HIHQ would be obtained when the concentration is smaller than 4×10^{-6} mol dm^{-3}.

Fig. 6 shows the fluorescence emission spectra of HIHQ at various pH values ranging from 2.6 to 12.2. Although the fluorescence peaks do not change a lot in the HIHQ solutions with different pH values, the intensity of fluorescence emission band at ca. 460 nm changes remarkably. At pH 2.6, only a broad fluorescence emission about 400–500 nm is observed and the intensity of emission is not enhanced greatly until the pH value is higher than 5.3. A decrease of solution acidity leads to an enhancement of the emission. When the pH value is around 7, obvious changes are not observed neither in shapes nor intensity. On the other hand, the addition of the alkali also results in the decrement of the emission band. When the pH value is higher than 10.4, only a weak band is observed.

A plot of the fluorescence peak area (fluorescence intensity) as a function on the pH values is shown in Fig. 7. This figure shows that when a HIHQ solution of pH 8.2 is examined, an emis-

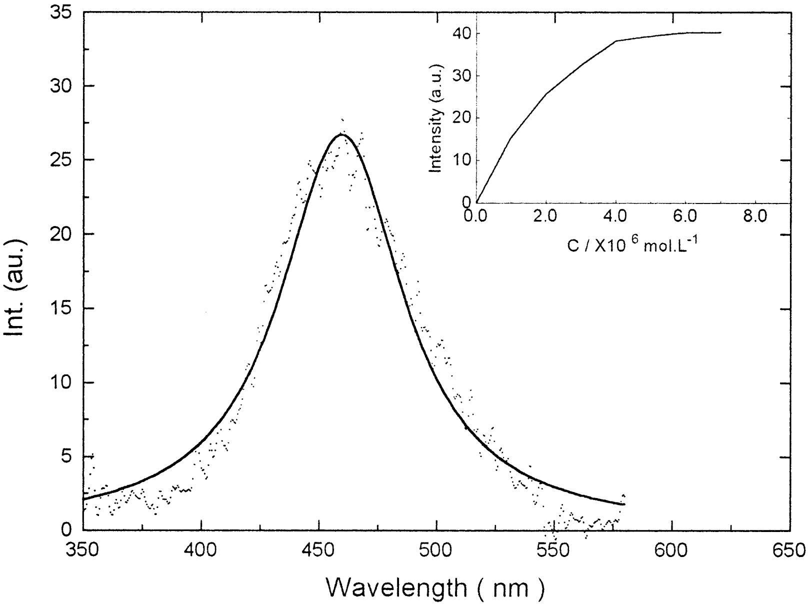


Fig. 5. Fluorescence emission spectra of HIHQ in ethanol solution. Inset: emission intensity as a function of HIHQ concentration in ethanol.

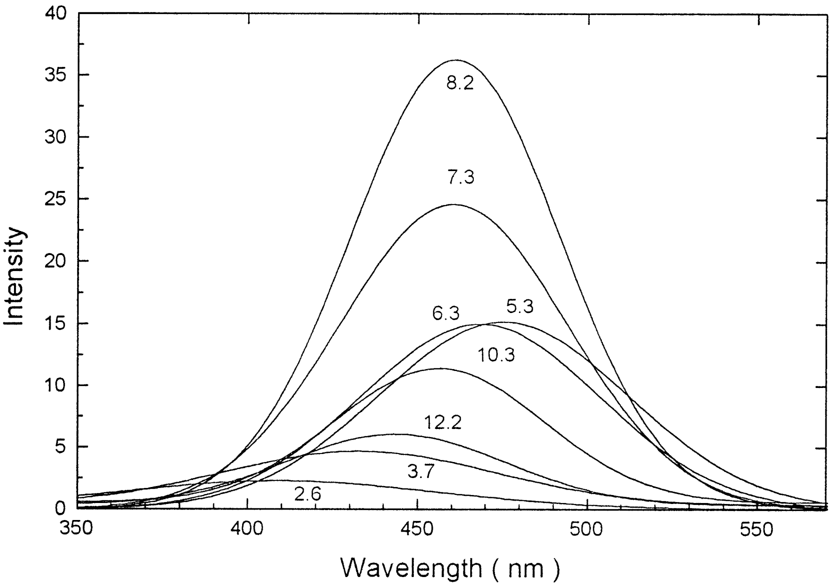


Fig. 6. Fluorescence emission spectra of HIHQ at various pH values.

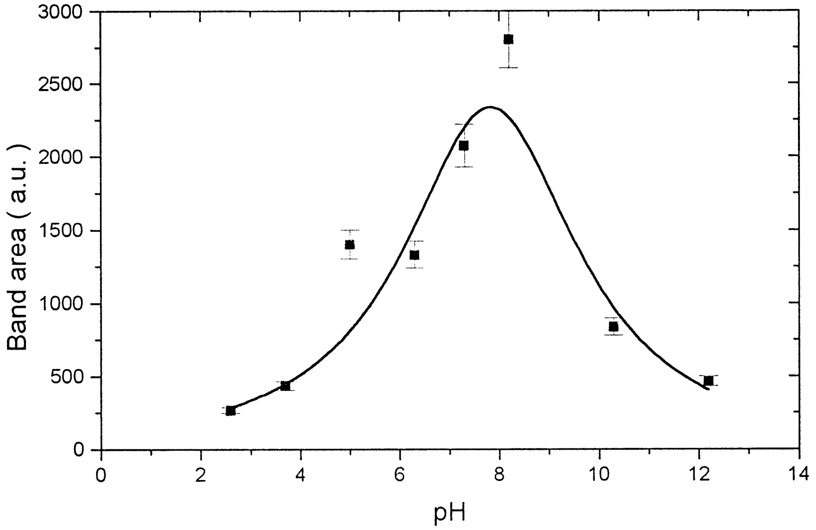


Fig. 7. Plot of area of fluorescence peak versus pH values of the solution.

sion band with very strong intensity is obtained at the same experimental condition. Its strength is about 15 times higher than that of pH 2.6 and the emission intensity is diminished with the increasing of the pH value. It means that the strongest fluorescence emission is obtained when the pH value is maintained at 8.2. In general, the explanation of the pH dependence of the fluorescence is dependent upon the prototypic form initially presented. But according to the opinions of Goldman and his co-workers [16], the neutral molecule is the fluorescent species while the cation is a nonfluorescent one. Perhaps their suggestion can be used to explain our experiments.

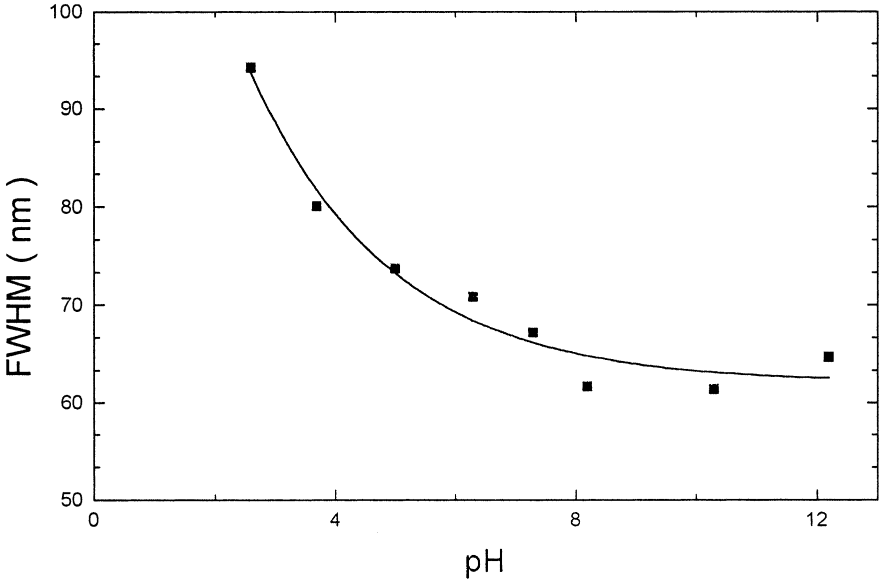


Fig. 8. Plot of FWHM (nm) versus pH of the solution.

Another interesting result found in our experiments is that the FWHM (Full width at half maximum) of the fluorescence emission at 460nm changes regularly with the change of the pH value. As shown in Fig. 8, the pH dependence of $W_{1/2}$ corresponds to the following equation,

$$W_{1/2} = 62.03 + 29.77\, e^{-{}^{X-2.74}/_{2.31}}$$

where $W_{1/2}$ is FWHM of the emission band and X is the pH value of the HIHQ solutions. This phenomenon may be considered as the pH dependence of the energy of excited singlet. Further details will be taken up in the future.

4. Conclusions

In this paper, a novel amphiphilic N-hexadecyl-5-iminomethyl-8-hydroxy-quinoline was synthesized and characterized by IR, UV-vis spectra and ^{1}H NMR. The π–A isotherm of HIHQ depends remarkably on the pH values of the aqueous subphase. The fluorescence of HIHQ changes greatly with different pH values and the strongest emission band at 460 nm is obtained at pH 8.2.

Acknowledgements

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