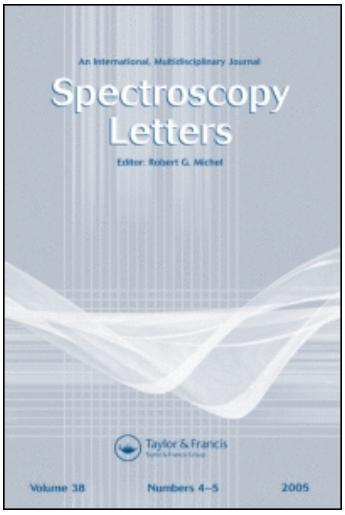

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Synthesis and Amphiphilic and Spectral Characters of N-Alkyl-8-hydroxy-2-quinolinecarboxamides

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SYNTHESIS AND AMPHIPHILIC AND SPECTRAL CHARACTERS OF N-ALKYL-8-HYDROXY-2-QUINOLINECARBOXAMIDES

Key Words: Absorption spectra; amphiphile; acid-base equilibrium; IR; ^{1}H NMR; Solvent effect; N-Alkyl-8-hydroxy-2-quinolinecarboxamides

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ABSTRACT

A series of amphiphilic derivatives of 8-hydroxyquinoline, N-alkyl-8-hydroxy-2-quinoline carboxamides (alkyl: dodecyl, tetradecyl, hexadecyl and octadecyl), were synthesized and characterized by IR, ^{1}H NMR and UV-visible spectroscopy. The positions of ^1L_a and ^1B_b bands of the derivatives were investigated as a function of solvent. Apparent concentration effect and acid-base equilibrium in polar solvents were observed. These amphiphilic molecules can form stable monolayer on pure water and salt solution.

INTRODUCTION

8-Hydroxyquinoline and its derivatives are known to be good chelating agents and can form chelates with many metal ions. Alkylated 8-hydroxyquinolines, such as 2-alkyl-8-hydroxyquinoline (alkyl: methyl, ethyl, propyl and butyl etc.)[1,2], Kelex100[3] and LIX26[4] were widely used to extract metal ions. But there is little information on the amphiphilic characteristic of long aliphatic chain

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derivatives of 8-hydroxyquinoline, and so far there has been no report on monolayer and LB film of 8-hydroxyquinoline amphiphiles. In this paper, a series of new amphiphilic derivatives of 8-hydroxyquinoline with a long alkyl chain, N-alkyl-8-hydroxy-2-quinolinecarboxamides (alkyl: dodecyl, tetradecyl, hexadecyl and octadecyl), were synthesized and characterized by elemental analysis, infrared, ^{1}H NMR and UV-visible spectral studies. The ability for these amphiphiles to form monolayer and to prepare LB film has also been discussed.

EXPERIMENTAL

Materials

8-Hydroxyquinaldine (the General Chemical and Pharmaceutical Co. Ltd. Sudbury Middlesex England) , hexadecylamine and octadecylamine (Fluka Chemical Co.) were used without any further purification. The other materials were purchased from Shanghai Chemical Reagent Co. All solvents were purified by standard procedures.

Measurements

Analyses of elements were performed using a CHN-O-RAPID Elemental Analyzer (Foss-Heraeus). Proton nuclear resonance spectra were obtained using a Bruker Am-500 NMR spectrometer with tetramethylsilane as an internal reference. Infrared spectra were recorded on a Nicolet Model 170 SX FTIR spectrometer. UV-visible absorption spectra were determined with a Shimadzu Model 3100 UV-VIS-NIR recording spectrophotometer.

Synthesis

The synthesis procedure for HHQ is illustrated in Figure 1. This route involves the preparation of 8-hydroxyquinaldinic acid and subsequent reaction with long chain alkylamine.

Preparation of 8-methoxyquinaldine (1)

To DMSO (40ml) was added powdered KOH (4.5g, 80mmol). After stirring for 10 min, 8-hydroxyquinadine (3.2g, 20mmol) was added, followed immediately by the CH_3I (4.3g, 30mmol). Stirring was continued for 1 h, the mixture was poured into water (400ml) and extracted with dichloromethane (3×100 ml). The combined organic extracts were washed with distilled water (5×30 ml), then the solvent was removed by rotary evaporation and the products (3.3g, yield: 95%) were collected by filtration. Recrystallized from ethyl acetate, a light yellow crystal, m.p. 126-127°C, were obtained. FTIR(KBr): 2940 (CH_3), 1230 (Ar-O-C), 1030cm^{-1} (Ar-O-C); ^{1}H NMR ($CDCl_3$): 8.08 (1H, Ar-H), 7.48-7.28 (3H, Ar-H), 7.05 (1H, Ar-H), 2.83 (3H, CH_3), 4.09 (3H,O-CH_3).

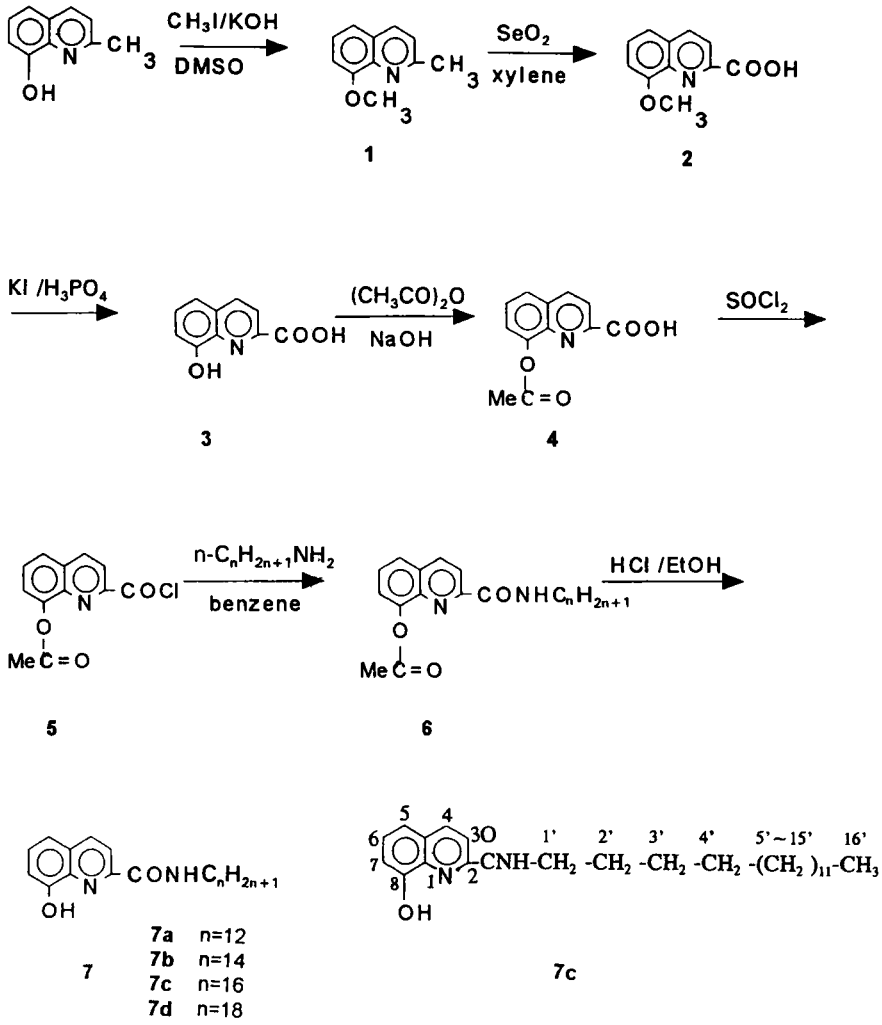

FIG. 1. The synthesis procedure of HHQ

Anal.calcd. for $C_{11}H_{11}NO$: C,76.3; H,6.36; N,8.09; found: C,76.2; H,6.57; N,7.88 .

Preparation of 8-methoxyquinaldinic acid (2) and 8-hydroxyquinaldinic acid (3)

2 and **3** were prepared in a modified method following H.Irving[5]. To a solution of 8-Methoxyquinadine (3.5g) in boiling xylene (30ml) was added during 30 min freshly sublimed, finely powdered selenium dioxide (3.5g). The selenium was immediately separated and filtered off from the boiling solution. After cooling a yellow crystal **2** (1.3g, m.p.155-157°C, yield: 27%) was separated from xylene solution, then it was recrystallized from benzene containing 5% ethanol, forming a yellow crystal of the monohydrate, m.p. 166-167°C. The yield is twice higher than that H.Irving[5] reported. FTIR (KBr) 3470 (OH), 2950(CH_3), 1700(C=O), 1220(Ar-O-C), 1040cm^{-1} (Ar-O-C). m/e: 203. ^1H NMR ($CDCl_3$): 8.39 (1H, Ar-H), 8.27 (1H, Ar-H), 7.65 (1H,Ar-H), 7.49 (1H, Ar-H), 7.15 (1H,Ar-H), 4.05 (3H,O- CH_3), 3.69-2.88 (2H, broad, H_2O). Anal. calcd. for $C_{11}H_9NO_3 \bullet H_2O$; C, 59.7; H, 4.98; N, 6.33; Found: C, 59.4; H, 5.05; N, 6.38.

3 is a golden needle (yield : 92%). The melting point of **3**, 221-222°C, is higher than that H.Schildknecht (210°C)[6], H.Irving (211°C)[5] and R.W.Hay (216-217°C)[7] reported. FTIR (KBr) 3230(OH), 1650cm^{-1}(C=O). ^1H NMR ($CDCl_3$) 10.25 (0.2H, OH), 8.58 (1H, Ar-H), 8.15 (1H, Ar-H), 7.65 (1H, Ar-H), 7.54 (1H, Ar-H), 7.23 (1H,Ar-H). Anal. calcd. for $C_{10}H_7NO_3$: C,63.4; H, 3.70; N, 7.41; Found: C, 63.9; H,3.74; N,7.65.

Preparation of 8-acetoxyquinoline-2-carboxylic acid (4)

4 was prepared by the method used by R.W.Hay[8]. It is a plate-like crystal (yield:83%), and melts at 140-141.5°C accompanied with decomposition. FTIR(KBr) 3300(OH), 1750(C=O in ester), 1700 (C=O in carboxylic acid), 1170cm^{-1} (Ar-O-C). Anal. calcd. for $C_{12}H_9NO_4 \bullet H_2O$: C, 57.8; H, 4.45; N,5.75; Found: C,57.6; H,4.60; N, 5.23.

Preparation of N-alkyl-8-hydroxy-2-quinoline carboxamide (7)

4 (160mg, 0.64mmol) and 2 ml of thionyl chloride were refluxed for 3 h. A yellow solution was resulted. Excess thionyl chloride was evaporated under vacuum and the residue dried under vacuum for 4 h. Freshly distilled benzene (20 ml) was added and the solution was treated with a slight excess of n-alkylamine and a few drops of triethylamine. The mixture was refluxed for 3 h more. After the solvent was evaporated off under reduced pressure, 20 ml HCl/ethanol solution was added to the residue. The mixture was slightly boiling for 3 h and the HCl/ethanol was driven off by rotary evaporation under vacuum,

the residue was recrystallized triple from hot benzene (animal charcoal), giving light grey powder of the monohydrate, **7**.

7a The yield was 50%. m.p. 36-37°C. FTIR(KBr) 3326(OH), 2923, 2855(CH_2,CH_3), 1650 (C=O), 722cm^{-1} ($(CH_2)_n$). UV-vis (in $CHCl_3$) 254, 307, 347nm. ^1H NMR ($CDCl_3$) 8.80 (1H, CONH), 8.05 (1H,Ar-H), 7.94 (1H,Ar-H), 7.58 (1H, Ar-H), 7.44 (1H, Ar-H), 7.33 (1H, Ar-H), 3.60 (2H, N-CH_2), 1.56-0.98 (20H, CH_2), 0.86 (3H, CH_3). Anal. calcd. for $C_{22}H_{32}N_2O_2 \bullet H_2O$: C,70.6; H, 9.09; N,7.49. Found: C, 70.4; H, 9.32; N,7.48.

7b The yield was 62%. m.p. 43-44.5°C. FTIR(KBr) 3312 (OH), 2924, 2855(CH_2 ,CH_3), 1649(C=O), 721cm^{-1} ($(CH_2)_n$). UV-vis (in $CHCl_3$) 254, 307, 348nm. ^1H NMR ($CDCl_3$) 8.70 (1H, CONH), 8.04 (1H,Ar-H), 7.94 (1H,Ar-H), 7.58 (1H, Ar-H),7.46 (1H, Ar-H), 7.33 (1H, Ar-H), 3.56 (2H, N-CH_2), 1.66 (4H, N-C-CH_2CH_2-) 1.43-1.00 (20H, CH_2), 0.86 (3H, CH_3). Anal. calcd. for $C_{24}H_{36}N_2O_2 \bullet H_2O$: C,71.6; H, 9.45; N,6.96. Found: C,71.3; H, 9.67; N,6.90.

7c The yield was 80%. m.p. 50.5-51.5°C. FTIR(KBr) 3306.2(OH), 2925, 2856(CH_2 ,CH_3), 1650(C=O), 722cm^{-1} ($(CH_2)_n$). UV-vis(in $CHCl_3$) 255, 308, 350nm. ^1H NMR ($CDCl_3$) 10.00 (0.15H, OH),8.35 (1H, CONH), 8.00 (1H,Ar-H), 7.92 (1H,Ar-H), 7.55 (1H, Ar-H),7.43 (1H, Ar-H), 7.32 (1H, Ar-H), 3.54 (2H, N-CH_2), 1.64 (4H, N-C-CH_2CH_2-) 1.45-0.98 (24H, CH_2), 0.86 (3H, CH_3). Anal. calcd. for $C_{26}H_{40}N_2O_2 \bullet H_2O$: C,72.6; H, 9.77; N,6.51. Found: C,72.8; H, 9.88; N,6.24.

7d The yield was 85%. m.p. 55-56°C. FTIR(KBr) 3315(OH), 2927, 2860(CH_2 ,CH_3), 1649(C=O), 721cm^{-1} ($(CH_2)_n$). UV-vis (in $CHCl_3$) 256, 308, 352nm. ^1H NMR ($CDCl_3$) 10.80(0.21H, OH), 8.40(1H, CONH), 8.01(1H,Ar-H), 7.90 (1H,Ar-H), 7.55 (1H, Ar-H),7.40 (1H, Ar-H), 7.32 (1H, Ar-H), 3.55 (2H, N-CH_2), 1.64 (4H, N-C-CH_2CH_2-) 1.44-0.97 (28H, CH_2), 0.85 (3H, CH_3). Anal. calcd. for $C_{28}H_{44}N_2O_2 \bullet H_2O$: C,73.4; H, 10.01; N,6.11. Found: C,73.0; H, 10.31; N,6.21.

RESULT AND DISCUSSION

IR Spectra

The IR spectra of **1**,**2**,**3**,**4** and **7** are very similar in the absorption of 1600-1500, 1300, 1150, 1000 and 850cm^{-1}, these bands are assigned to the absorption of quinoline ring and aromatic C-H bonds. All these spectra other than **1** show characteristic of OH group in 3230-3500cm^{-1}. Since free OH stretching modes occur in the range 3450-3550cm^{-1}, therefore, the absorption band appeared at 3230cm^{-1} in **3** may be likely the result of intramolecule hydrogen-bonding and / or hydrogen-bonding by water molecule. This argument is supported by the fact

that when the OH group of C-8 position in **3** was prevented by acetoxy group, the hydrogen bond was broken. Therefore, two C=O group absorption peaks at 1750 and 1700cm^{-1} were observed in **4**, 1750cm^{-1} is assigned to the absorption of aliphatic ester in C-8 position, 1698cm^{-1} is assigned to that of aromatic carboxyl acid group in C-2 position of quinoline ring (see Figure 1).

Elemental analysis indicated the presence of a water molecule in **7**. The IR spectrum of **7** with an intense broad band at 3306cm^{-1}, which is bathochromically shifted ca. 200cm^{-1} than that of free phenolic OH group, this band can be assigned to the hydration rather than the moisture contamination. Moisture bands usually occur at higher frequency (ca. 3400cm^{-1}) and they are considerably less broad and intense[9]. The absorption position of aromatic amide group $\nu_{C=O}$ (1650 cm^{-1}) is well consistent with the literature value, a characteristic of free aromatic amide group (C=O), which indicates that the hydration promotes the formation of hydrogen-bonding with OH group in C-8 position rather than with amide group. The strong sharp peaks at ca. 2925 and 2856 cm^{-1} are represented as the stretching absorption of long aliphatic chain. Another characteristic absorption to show the presence of long alkyl chain in **7** appeared at 722 cm^{-1}.

^{1}H NMR Spectra

In order to confirm the proposed structure for these derivatives of 8-hydroxyquinoline, the ^{1}H NMR spectra were observed. The spectra of compound 1, 2, and **3** are collected in Table 1, along with their assignments.

Comparing with the absorption of **1**, **2**, and **3**, the three spectra were very similar except that the peak at 2.83 ppm presented in **1** disappeared in **2** and **3**, and a new weak peak at low field (10.25 ppm) appeared in **3**. Since 2.83 ppm absorption, integrated for three protons, is ascribed to C-2 position methyl substituent, therefore, it indicated the oxidation of methyl in C-2 position was complete. The chemical shifts in the range 4.05-4.09 ppm for **1** and **2** were assigned to methoxy substituent in C-8 position.

The H^7 protons in quinoline ring are adjacent to the phenolic OH or phenolic OCH_3, they have been affected by these electron-giving groups, so they appear in highest field. Methyl substituent in the 2-position shield the meta-position proton (H^4) the most, so the H^4 absorption is present in the lowest field (see Table 1). A complex area of peak at 7.28-8.27ppm, integrating for three proton, can be ascribed to the protons H^3, H^5 and H^6. Since these three protons have similar chemical environment, they usually alternately appear together and can not be further distinguished. A very broad and low peak at ca. 2.88-3.69 ppm integrated for two protons in **2** can be assigned to water, and it differentiate apparently from the common proton peaks.

TABLE 1: ^{1}H-NMR Data for Quinoline Derivatives

	Chemical shift , ppm					
Derivative	H^2	H^4	H^3 H^5 H^6	H^7	H^8	H_{range}
1	2.83t*	8.08s+	7.48-7.28t	7.05s	4.09t*	
2		8.39s	8.27s,7.65s,7.49s	7.15s	4.05t*	3.69-2.88d+
3		8.58s	8.15s,7.64s,7.54s	7.23s	10.25++	

* chemical shifts of substituted CH_3 and OCH_3 in C-2 and C-8 position respectively.

+ s-single H, d-double H, t-triple H

++ had an integrated area one fifth that of the common proton

The decrease in the intensities of the corresponding peak at 10.25 ppm for **3** (relative to other bands in the spectrum) indicate the elimination of proton on OH or COOH by deuterium substitution. Since the hydrogens in OH, COOH and CONH groups are very active, these hydrogens can be easily dissociated and be partially or entirely substituted by deuterium in $CDCl_3$ solution. It makes the absorption of these protons partially sometimes entirely not be observed. In the spectrum of **2**, the hydrogen absorption in COOH group can not be observed. This fact indicates that the proton in COOH group was entirely substituted by deuterium in $CDCl_3$. In the spectrum of **3**, neither the proton signal in OH group nor the signal in COOH group can usually be observed. Only a weak peak (with an integrated area one fifth that of the ordinary proton) in the lower field (10.25 ppm) appeare. It is clear that four fifth hydrogen in OH group was substituted and the hydrogen in COOH group was entirely substituted by deuterium in $CDCl_3$.

From the results above, the ^{1}H NMR spectra of **7a-d** can be assigned. The chemical shifts presenting at higher field (ca. 8.00 ppm) and lower field (ca. 7.32 ppm) are assigned to H^4 and H^7 of quinoline ring, while signals at ca. 7.43, 7.55 and 7.92 ppm can be ascribed to H^3, H^5, and H^6. The peak appear at ca.8.80-8.35 ppm are assigned to the protons of amide groups (CONH) in C-2 position. They show a uncertain position in ^{1}H NMR spectra because of their activity. The hydrogen of OH group in C-8 position is more active than that of amide group. Therefore, most , sometimes all, of the OH protons were substituted by deuterium in $CDCl_3$. For example, no proton signal of OH is observed in **7a** and **7b**, and a very weak signal with an integrated area only one seventh and one fifth of that of a common proton are observed in **7c** and **7d**, which indicate six seventh and four fifth proton of OH group in **7c** and **7d** were substituted by deuterium in $CDCl_3$, respectively.

Besides, the proton absorption of long alkyl chain in C-2 position of quinoline ring can be assigned by comparing the values found in experiment with that calculated according reference [10] or Shoolery Law[11] (Table 2).

UV-VIS Spectra of **7a-d**

The UV-visible spectra of **7a-d** show marked similarities. The most important features of the spectra are the presence of two bands at ca. 255, 350 nm and one shoulder at ca. 308 nm (Figure 2). They are assigned to the ^1B_b,^1L_a and ^1L_b band of quinoline ring[12], respectively, due to $\pi \rightarrow \pi^*$ transition. The ^1L_a band is ascribed to the charge-transfer from the phenol ring to the heterocyclic[2].

Acidity shifts of absorption bands

A profound effect of acidic and alkaline conditions upon the absorption spectrum of **7a-d** are observed because of their zwitter property (see Figure 3). The absorption maxima of **7d** in neutral dioxane and in dioxane solutions with various acid / base concentrations are listed in Table 3.

The absorption maxima at 256, 308 and 352 nm of free **7d** in dioxane were bathochromically shifted to 274, 346 and 414 nm in 0.001 M NaOH medium, respectively. Variations in NaOH concentration between 0.0002 M and 1.0 M had no significant effect upon the spectra. It suggests the presence of only a single absorbing species in each NaOH concentration. In $HClO_4$ medium, these three absorption bands of **7d** were also bathochromically shifted, along with a change of the profiles. For the change of $HClO_4$ concentration from 1.0×10^{-5} M to 0.5 M, the absorption maxima at 256 (^1B_b) and 352 nm (^1L_a) were bathochromically shifted ca. 16 and 38 nm. Different from the quick change of absorption maxima of **7d** in basic media, the change of ^1B_b and ^1L_b bands in acidic media was gradual. Not only the absorption maxima gradually bathochromically shifted, but the profiles of absorption peaks gradually changed as well. Over the $HClO_4$ concentration region of 0.001 M to 0.5 M, the 308 nm (^1L_b) absorption band was splitted into two bands that appeared at ca.320 and 330 nm (Figure 2). This splitting seems to be a usual feature for the UV-vis spectra of 8-hydroxyquinoline families in acidic media.[13,14]

It can be seen from the argument above that with the pH values in dioxane solution going from low (ca. pH 1) to high (ca. pH 13), the absorption maxima of **7d** move from long to much shorter wavelength and then back to long wavelength.

When the NaOH concentration is larger than 1.5 M or the $HClO_4$ concentration is larger than 1.0 M, **7d** molecule begin to decompose by the breaking of amide bonding. In this case, the absorption band was found to be a

TABLE 2

Chemical Shifts (δ) for Aliphatic Chain in C-2 Position of Compound **7c** (ppm)

	proton		1'	2'-3'	4'-15'	16'
δ	calcd.	A^+	3.54	1.33	1.20	0.87
		B^{++}	3.17	1.57	1.37	1.07
	found.		3.54	1.64	1.45-0.98	0.86

$^+$ Chemical shifts calculated according reference.[10]

$^{++}$ Chemical shifts calculated according Shoolery Law.[11]

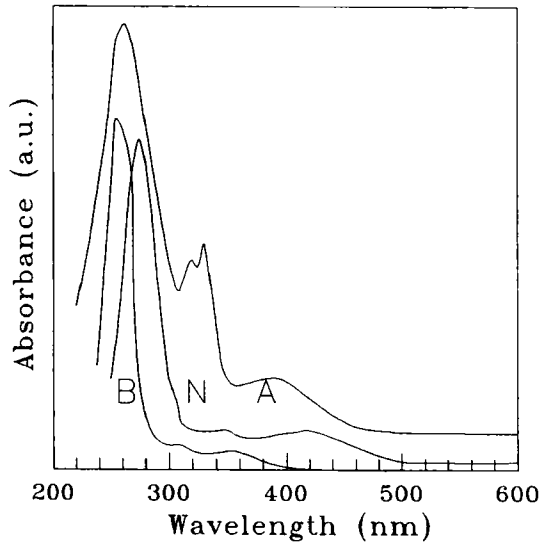

FIG. 2. The spectrum of **7d** in acidic (A), basic (B) and neutral (N) dioxane solution

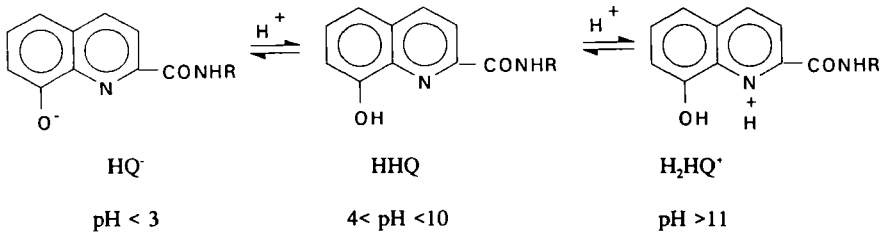

FIG. 3. Schematic illustration of the prototropic equilibrium of **7d**

TABLE 3

Summary of Absorption Data for 0.1 mM Solution of **7d** with Various Acidity

medium(in dioxane)	^1B_b (nm)	^1L_b(nm)		^1L_a(nm)
0.5 M NaOH	275	347		414
1×10^{-2}M NaOH	274	346		414
1×10^{-3}M NaOH	274	346		414
1×10^{-4}M NaOH	256	308		358
in neutral	256	308		352
1×10^{-5} M $HClO_4$	257	308		352
1×10^{-4} M $HClO_4$	258	308		359
1×10^{-3} M $HClO_4$	259	320	330	370
1×10^{-2} M $HClO_4$	261	320	330	383
0.1 M $HClO_4$	263	320	330	390
0.2 M $HClO_4$	265	320	332	390
0.5 M $HClO_4$	272	320	335	390

composition of absorption bands of 8-hydroxyquinaldic acid, n-octadecylamine and **7d**.

Concentration shifts of absorption bands

The effect of the concentration of **7d** on the absorption spectrum of **7d** has been investigated. The absorption maxima for **7d** at different concentration in ethanol are listed in Table 4. In this concentration range, with the decreasing of concentration of **7d**, the absorption maxima of ^1L_a and ^1L_b bands bathochromically shifted ca. 6 and 5 nm, respectively. This bathochromic shift is ascribed to that when the concentration of **7d** decreased, the amount of solvent

TABLE 4: Absorption Maxima for **7d** in Ethanol at Different Concentration.

conc. (M)	^1L_a (nm)	^1L_b (nm)	^1B_b (nm)	$n\rightarrow\pi^*$
1.0×10^{-3}	344	304	232~272	
5.0×10^{-4}	345	305	235~270	
2.5×10^{-4}	346	307	237~265	212
1.0×10^{-4}	347	308	247~256	211.5
7.0×10^{-5}	348	308.5	253	210
5.0×10^{-5}	350	309	253	209

molecules around every solute molecule increase, it is similar to the increasing of polarity of solvent, therefore, the dipole-dipole interaction between the polar solute (**7d**) and the polar solvent (ethanol) increased relatively, it more effectively lowered the energy of excited state (π^* orbital) and made the absorption of $\pi\rightarrow\pi^*$ transition (^1L_a and ^1L_b bands) appear at lower frequency.

In contrast with the $\pi\rightarrow\pi^*$ transition, the absorption band appeared near 210 nm has hypsochromically shifted ca. 3 nm with decreasing the concentration of **7d**. It corresponds to the $n\rightarrow\pi^*$ transition of alkylcarbamoyl group in C-2 position of quinoline ring. In the $n\rightarrow\pi^*$ transition, one of the electrons is removed from the n orbital (oxygen atom) and promoted to an empty anti-bonding π^* orbital. Hence the polar solvent should more effectively lowered the energry of the ground state (n orbital) than that of the excited state (π^* orbital). The more polar the solvent, the larger will be the energy lower. Therefore , with the decreasing of solute (**7d**) concentration, the $n\rightarrow\pi^*$ transition band blue shifted.

Solvent shifts of absorption bands

The absorption spectra of **7d** in various solvents were investigated. The study was extended over 26 solvents ranging in refractive indices (n) from 1.328 (methanol) to 1.557 (chlorobenzene) and in dielectric constant (ε) from 1.80 (n-heptane) to 37.7 (1,2-ethandiol)(see Table 5). The shifts of **7d** spectral bands in non-polar and low-polar solvents correspond to the equation derived by Bayliss (equation 1)[15]. It takes into consideration of the dispersive forces (the polarizability of the solvent) and is determined by refractive index:

$$\Delta\upsilon = \upsilon_0 - \upsilon_i = K\frac{n^2-1}{2n^2+1} \qquad (1)$$

$$\upsilon_i = \upsilon_0 - K\frac{n^2-1}{2n^2+1} \qquad (2)$$

where υ, υ_i,υ_0 are the frequencies, K is constant, and n is the refractive index of

TABLE 5

No	Solvent	n*	ε*
1	n-Pentane	1.360	1.84
2	n-Hexane	1.375	1.89
3	n-Octane	1.395	1.95
4	Cyclehexane	1.426	2.02
5	Carbon tetrachloride	1.457	2.24
6	Methyl benzene	1.497	2.38
7	Benzene	1.501	2.28
8	Xylene (mixt.)	1.520	2.30
9	Dioxane	1.422	2.21
10	Propionic acid	1.390	3.35
11	Phenylmethylether	1.517	4.33
12	Diethyl ether	1.352	4.34
13	Trichloromethane	1.443	4.81
14	1,1,1,-Trichloro ethane	1.438	5.24
15	Chlorobenzene	1.557	5.71
16	Tetrahydrofuran	1.407	7.58
17	Dichoromethane	1.424	8.93
18	n-Pentanol	1.410	15.0
19	n-Buthanol	1.399	17.5
20	Isopropanol	1.377	19.9
21	n-Propanol	1.386	20.4
22	Ethanol	1.361	24.6
23	Methanol	1.328	32.7
24	Nitromethane	1.381	35.9
25	Acetonitrile	1.344	37.5
26	1,2-Ethandiol	1.432	37.7

* ε and n values come from reference [16,17].

the solvent. As shown in Figure 4, a linear dependence between the $(n^2-1)/(2n^2+1)$ function of solvents and the frequencies of absorption bands maxima (^1L_a and $1B_b$ bands) was obtained. The points numbering in Figure 4 and in the following ones are identical with that of solvents listed in Table 5.The linear dependences obtained from Fig.4 can be described by the following equations:

$$\upsilon^{max}\,(^1L_a) = 29110 - 1500\ \frac{n^2-1}{2n^2+1} \qquad (3)$$

$$\upsilon^{max}\,(^1B_b) = 39900 - 2200\ \frac{n^2-1}{2n^2+1} \qquad (4)$$

But in polar solvents, equation (1) will cause a large deviation. Since polarization forces are the weakest intermolecular forces, interactions arising from them are likely to be overshadowed when the solvent and solute are polar. In these case, the simplified McRae equation[18,19] can be used to describe the shifts of absorption maxima for **7d** :

$$F(\varepsilon, n) = B\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] \qquad (5)$$

To ^1L_a and ^1B_b bands, the liner dependences between F (ε, n) function of solvents and the frequencies of absorption band maxima of **7d** satisfy the following equations:

$$\upsilon^{max}\,(^1L_a) = 28300 + 670\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] \qquad (6)$$

$$\upsilon^{max}\,(^1B_b) = 38890 + 730\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] \qquad (7)$$

with increasing values of the F(ε, n) function, the absorption maxima of ^1L_a and ^1L_b bands shift towards larger wave numbers (Figure 5).

Monolayer and LB Film of **7a-d**

For the trend of decreasing electronic device sizes, the interest in functional Langmuir-Blodgett (LB) film has increased considerably in recent years. LB films have been suggested as a route to the development of molecular dimension switches and storage elements used in energy conversion systems, sensors and microscopic communication systems[20,21]. Comparing with standard sensor technology, LB film sensor has the advantages that extremely small quantity of metal ion can be detected and an ordered molecular structure oriented specially to optimize complexation can be achieved[22]. With this in mind, a series of 8-quinolinol amiphiphiles were designed and synthesized, and some applications of

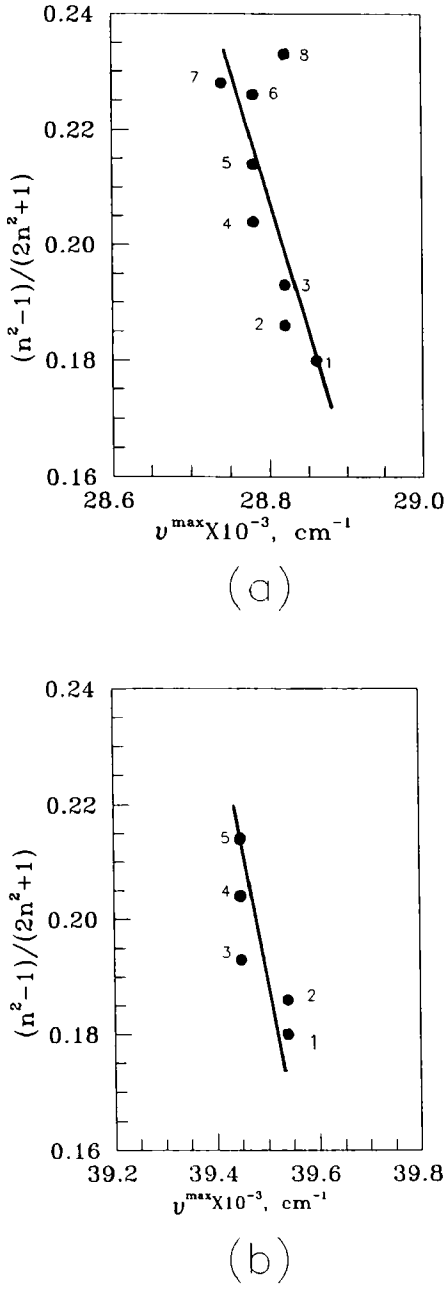

FIG. 4. The dependence between refractive indices of solvents and frequencies of absorption bands maxima of **7d** (a) ^1L_a band, (b) ^1B_b band

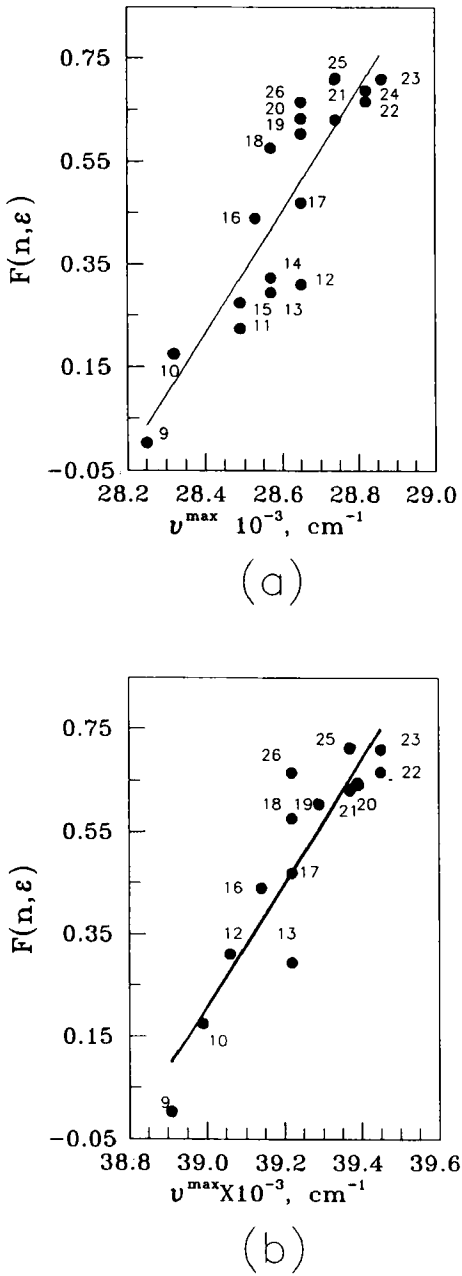

FIG. 5. The dependence between F(n,ε) function of solvents and frequencies of absorption band maxima of **7d** (a) ^1L_a band, (b) ^1B_b band

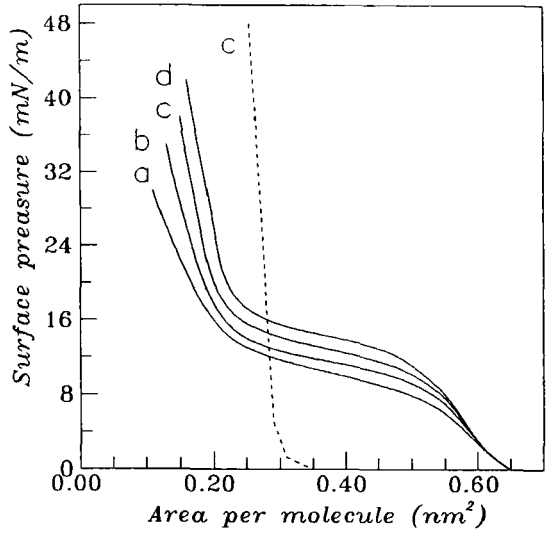

FIG. 6. Surface pressure-area isotherms of **7a-d** on pure water (solid line) and on 1.0×10^{-3} M $Co(OAc)_2$ solution (dashed line)

these amphiphiles in molecular electronic devices, in particular in metal ion sensors, have been expected.

7a-d can form stable monolayer on pure water and on aqueous subphase containing metal ions. The collapse pressure of **7a**, **7b**, **7c** and **7d** on pure water surface range from 30 to 45 mN/m (Figure 6). The extrapolated molecular areas, 0.63 and 0.28 nm^2, per **7d** molecule at the start and end of the plateau are corresponding to the face area and side area of quinoline ring, according to space-filling molecular (C.P.K) model. So the shape of the isotherms might be seen as that the hydrophilic head group (8-hydroxyquinoline) of **7d** originates in a 'lie flat on' to an ' edge on ' conformational transition initiated at 9 mN/m surface pressure upon compression. The dashed line in Figure 6 is the surface pressure-area isotherm of **7d** on 1.0×10^{-3} M $Co(OAc)_2$ solution. It is much steeper than that on pure water, and the limiting area of **7d** in this case is 0.30 nm^2, a little larger than that on pure water.

In order to investigate whether a coordinate compound had formed at the interface, UV-vis spectrum of 1-layer sample of **7d** deposited on quartz glass at

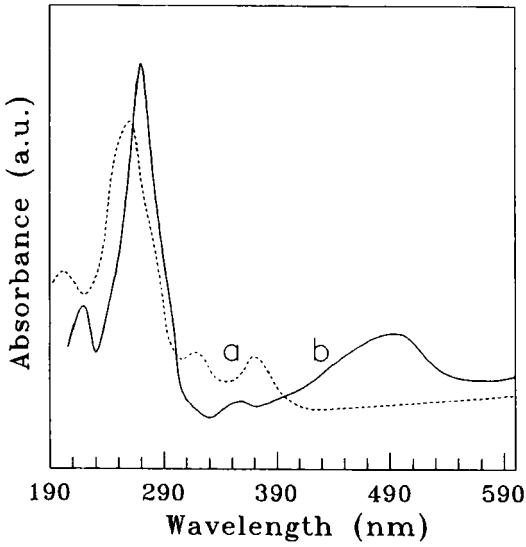

FIG. 7. UV-visible of **7d** LB film prepared from pure water(a)and from $Co(OAc)_2$ subsolution(b)

25 mN/m were recorded. The absorption maxima for LB film of **7d** on the water (2×10^{-4} M $NaHCO_3$) surface occurred at 261, 321 and 372 nm, but for the LB film prepared from $Co(OAc)_2$ subsolution, the strong band at 261 nm and the shoulder at 321 nm (see Figure 7) were bathochromically shifted to 270 and 365 nm respectively, and the 372 nm band disappeares and a new broad band centered at 498 nm is found. 498 nm band can be ascribed to the charge-transfer transition from ligand (**7d**) to metal ion (Co^{2+}). It indicates that an intensive interaction of d-orbital of Co(II) with the π-electron system of **7d** existed and coordination between **7d** and Co^{2+} has occurred at the air/water interface. So **7d** may be used as a chemical sensor for Co^{2+} ion. Further experiments are in progress.

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