Monatshefte für Chemie 128, 23–28 (1997)

Monatshefte für Chemie
Chemical Monthly

Spectrophotometric Studies of 4-(2-Hydroxy-4-substituted-azobenzene)-2-methyl-quinolines as Reagents for the Determination of Silver

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Summary. The spectroscopic behaviour of some quinoline azo dyes has been studied. A simple, rapid, accurate, and sensitive method for the spectrophotometric microdetermination of Ag(I) ions using the title compounds is given. The conditions for the formation of the coloured complexes are obeyed up to $26\,\mu g \cdot ml^{-1}$; the optimum concentration range for application of the *Ringbom* method is 2.5–$23\,\mu g \cdot ml^{-1}$. The molar absorptivity and the *Sandell* sensitivity have also been calculated. The method proved to be successful in determining Ag^+ in photography fixing solutions. The results agreed satisfactorily with those obtained using standard atomic absorption spectroscopy.

Keywords. 4-(2-Hydroxy-4-substituted-azobenzene)-2-methyl-quinoline; IR; ^{1}H NMR; Electronic spectra; Spectrophotomentric determination of Ag^+ ions.

Spectrophotometrische Untersuchungen von 4-(2-Hydroxy-4-subst.-azobenzol)-2-methylchinolinen als Reagentien zur Silberbestimmung

Zusammenfassung. Das spektroskopische Verhalten einiger Chinolin-Azofarbstoffe wurde untersucht. Eine einfache, rasche, genaue und empfindliche Methode zur spektrophotometrischen Mikrobestimmung von Silber(I)-Ionen mittels der Titelverbindungen wird vorgestellt. Die Bedingungen zur Bildung der gefärbten Komplexe werden bis zu einer Maximalkonzentration von $26\,\mu g \cdot ml^{-1}$ erfüllt; der optimale Konzentrationsbereich zur Anwendung der *Ringbom*-Methode liegt zwischen 2.5 und $23\,\mu g \cdot ml^{-1}$. Die molare Absorption und die Empfindlichkeit nach *Sandell* wurden ebenfalls berechnet. Die Methode wurde erfolgreich zur Bestimmung von Ag^+ in photographischen Fixierlösungen eingesetzt. Die Ergebnisse stimmen in zufriedenstellender Weise mit durch Atomabsorptionsspektroskopie erhaltenen überein.

Introduction

The absorption spectra of azobenzene and its derivatives have been the subject of many investigations [1, 2]. However, little attention has been paid to heterocyclic azo dyes [3] despite the importance of this compounds.

The known methods for the determination of silver employing formation of binary complexes suffer from drawbacks [4] like lack of reproducibility, low sensitivity, *etc* [4]. The lithizone complex of silver is photosensitive, and the corresponding method extensive standardization, whereas other reagents like pyrogallol red [5, 6] 2-amino-6-methylthio-4-pyrimidine carboxylic acid [7], 5-(4-(2-methyl-3-hydrox-5-hydroxymethyl)-pyridylene) rhodanine [8] and 5-(4-hydroxy-3-methoxybenzylidene) rhodamine [9] *etc.* suffer from many interferences. The most common reagent used for the determination of silver, *p*- dimethylaminobenzylidene rhodanine, is very sensitive to changes of acidity [10].

The present study deals with the elucidation of the molecular structure of the litle compounds and their analytical applications for the determination of silver at a sub-microgram level. The proposed method has been applied for the determination of silver ions in photography fixing solutions with good results.

Results and Discussion

Electronic absorption spectra

The UV/Vis absorption spectra of the compounds under investigation display three bands in cyclohexane, whereas two bands can be observed in ethanol within the range of 200–600 nm (Table 1). The first band (A, 230–260 nm) can be assigned to the π–π^* transition of the aromatic ring representing the (1La → 1A) state, whereas the second band (B, near 280 nm) is due to the low energy π–π^* transition corresponding to the ($^1L_b \rightarrow {}^1A$) state.

In ethanol, bands A and B strongly interact in the spectra of all compounds; therefore, the band observed is assigned to an overlap of the absorption due to the two π–π^* transitions of the benzenoid system. The band at longer wavelength, observed at 225–450 nm, is assigned to an intermolecular charge transfer interaction involving the whole molecule.

IR spectra

The IR spectra of compounds **1–4** (Table 2) show a weak band within the range of 3455–3380 cm^{-1} corresponding to ν(OH). The low value reveals that an OH group is involved in an intramolecular H-bonding. The IR spectra also show weak bands

Table 1. Electronic absorption spectra of the azo dyes **1–4** in ethanol and cyclohexane (nm)

	Ethanol				Cyclohexane					
	A		B		A		B		C	
	λ	$\varepsilon \cdot 10^{-3}$	λ	$\varepsilon \cdot 10^{-3}$	λ	$\varepsilon \cdot 10^{-3}$	λ	$\varepsilon \cdot 10^{-3}$	λ	$\varepsilon \cdot 10^{-3}$
1	235	32.5	450	10.5	255	sat.	270	sat.	360	sat.
2	235	24.0	362	34.5	275	sat.	270	sat.	345	sat.
3	237	32.0	350	37.5	225	4.0	265	10.0	350	34.0
4	225	28.5	355	44.5	235	19.0	275	14.0	355	27.8

Table 2. IR spectra of compounds **1**–**4** (cm^{-1})

	δ(CH)	ν(OH)	ν(C=C)	ν(N=N)	δ(OH)
1	710	3455	1620–1590	1450	1330
2	790	3450	1595–1570	1445	1350
3	750	3380	1590–1570	1447	1355
4	760	3440	1620–1595	1448	1350

located at 3060–3010 and 2980–2940 cm^{-1} which are assigned to the aromatic C–H asymmetrical and symmetrical stretching vibrations, respectively. The symmetrical stretching vibration of the N=N group leads to the band located near 1450 cm^{-1}, whereas the stretching vibrations in the range 1600–1530 cm^{-1} are masked by the intense bands due the ring vibrations.

The in-plane deformation of the OH group gives rise to a band appearing in the range of 1355–1330 cm^{-1}, whereas the medium band at 910–890 cm^{-1} is ascribed to the out-of-plane deformation of the isolated H atom of the aromatic system. Also, the spectra of all compounds exhibit two strong bands of 760–750 and 710–690 cm^{-1} which correspond to the out-of-plane deformation of the five adjacent hydrogen atoms of the aniline ring.

^{1}H NMR spectra

The main signals in the ^{1}H NMR spectra of compounds **1**–**4** are given in Table 3. The OH group gives rise to a signal at 9.2 ppm which disappears upon deutration. Its high field shift as compared to that of azo dyes based on salicylaldehyde indicates a weaker H-bond. This can be explained by the delocalizing influence of the phenyl group on the nitrogen atom which lowers the contribution to intramolecular hydrogen bonding, an effect which is absent in azo dyes based on salicylaldehyde [13].

The CH_3 groups of all compounds give a sharp signals at 3.8–3.2 ppm. The aromatic protons of the phenyl and quinoline rings resonate in the range of 7.0–6.8, 7.1–6.9, 7.1–6.9, 6.9–6.5, and 7.2–6.4 ppm respectively. Generally, donor substituents cause a shift to higher field, whereas acceptor substituents result in a downfield shift.

Table 3. ^{1}H NMR spectra of compounds **1**–**4** (δ, ppm)

	OH	aromatic protons	CH_3
1	8.7	6.8–7.0	3.2
2	9.2	6.9–7.1	3.8
3	8.6	6.5–6.9	3.7
4	8.5	6.4–7.2	3.7

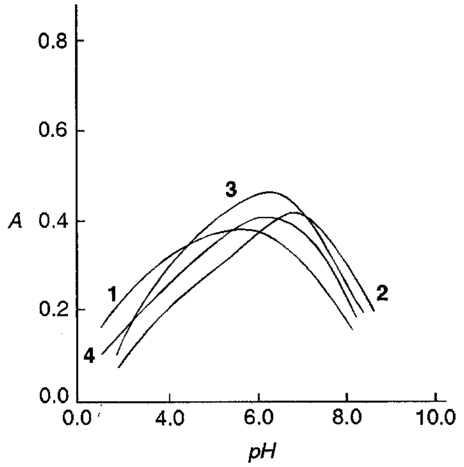


Fig. 1. Effect of *pH* value on the absorbance of 15 μg/ml of silver using $2.4 \times 10^{-4} M$ of reagents **1**–**4**

Analytical studies

An examination of variables influencing complex formation and colour intensity demonstrated that the optimum *pH* values required for compounds **1**–**4** are 7.5, 10, 9, and 8.5, respectively. A representative curve for the effect of different *pH* values on complex formation is shown in Fig. 1.

The sequence of addition "reagent-metal-buffer" was the most suitable one for high absorbance reading. Experiments concerning the effect of solvent ratio have shown that clear solutions are formed at a $\geqslant$25% (v/v) ethanol. Therefore, a content of 30% (v/v) ethanol was chosen for the measurements. The absorption spectra of the complexes in buffer solutions of various *pH* values are characterized by one sharp band with $\lambda_{max} = 430$, 390, 320, and 433 nm for reagents **1**–**4**, respectively.

The colour of the complexes is completely developed after 5 min and remains constant for about 3, 2, 6, and 4 h (reagents **1**–**4**, respectively). The absorbance value suffers from a slight decrease and regains the orginal value by shaking. Raising the temperature to 60 °C has no effect on the formed complexes, whereas at higher temperatures the absorbance starts to decay. Boiling destroys the complexes.

Investigation of the molecular structure of the complexes (molar ratio, continuous variations, straight line and slope ratio methods) reveal the formation of 1:1 complexes with all reagents under investigation. A representative example of the complex formed by Ag^+ and ligand **2** is shown below.

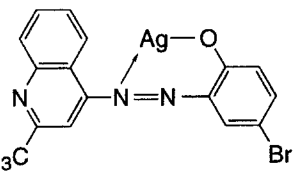


Table 4. Characteristics of complexes of Ag^+ with compounds **1**–**4**

	1	**2**	**3**	**4**
λ_{max} (nm)	430	390	320	433
Optimum *pH*	7.5	10.0	9.0	8.5
Stoichiometry	1:1	1:1	1:1	1:1
Logarithmic stability constant	4.23	5.14	4.51	4.78
Beer's law limiting conce. ($\mu g \cdot ml^{-1}$)	22	26	20	24
Ringbom optimum conc. ($\mu g \cdot ml^{-1}$)	2–20	2.5–23	2.5–170	2–21.5
Molar absorptivity ($l\,mol^{-1} \cdot cm^{-1}$)	2.75×10^3	3.07×10^3	3.3×10^3	2.97×10^3
Sandell sensitivity ($\mu g \cdot cm^2$)	0.039	0.035	0.033	0.036

Table 5. Interfering ions in the determination of silver (15 $\mu g \cdot ml^{-1}$) using reagents **1**–**4**

Ion	Tolerance	ratio	(µg/ml)	
	1	**2**	**3**	**4**
Na^+, K^+, Ba^{2+}, $BO4^{3-}g^{4-}$	5000	5000	6000	5500
Li^+, Ca^{2+}, Sr^{2+}, succinate, Cl^-	4000	4000	5000	4000
Mg^{2+}, Co^{2+}, Ni^{2+}, SO_4^{2-}, NO_3^-	2500	2200	3000	2750
Zn^{2+}, Zr^{4+}, V^{5+}, tratrate, acetate	1000	1200	1800	1500
Pd^{2+}, Pt^{2+}, Y^{3+}, benzoate, ClO_4^-	500	250	300	250
Sc^{3+}, Al^{3+}, In^{3+}, oxalate, CO_3^-	200	250	300	250
Ga^{3+}, Se^{4+}, Ti^{4+}, F^-, I^-	80	100	120	100
Fe^{2+}, Fe^{3+}	20	15	10	12

The logarithmic stability constants of the complexes calculated from data of molar ratio and continuous variation methods applying the *Harvey* and *Manning* equation [14] are listed in Table 4.

The effect of interfering ions was studied individually (Table 5). The criterion applied was a change in absorbance of ±2.5% for 15 $\mu g \cdot ml^{-1}$ of silver.

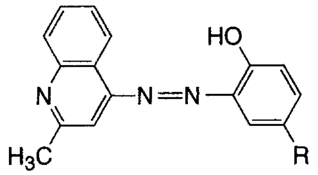
The proposed method was applied to silver determination in a photographic fixing solution after processing a black and white, film (36 exposures) without further pretreatment. Six replicates were analyzed spectrophotometrically using reagents **1**–**4** and by atomic absorption spectroscopy after appropriate dilution (1:200). The silver concentration of the diluted sample was determined to 2.44 mg/l by AAS and to 2.50, 2.54, 2.47, and 2.25 mg/l by the proposed method with a relative error (*Er*) of 2.46, 4.10, 1.23, and 3.28% (*Er* = (Ag found spectroscopically Ag found with AAS)/(Ag found with AAS)).

Experimental

The azo dyes under investigation were prepared by coupling phenol, *p*-chlorophenol, *p*-bromophenol, and *p*-nitrophenol with the diazonium salt of 4-amino-2-methylquinoline as described by *Ospenson*

[11]. The compounds were purified by crystallization from ethanol. Their general structure is given below.

	R
1	H
2	Cl
3	Br
4	NO_2



The reagent solution (2×10^{-3} M) was prepared by dissolving the appropriate amount of substance in 100 ml ethanol. A Perkin Elmer λ3B double beam scanning spectrophotometer was used for recording UV/Vis spectra and for individual absorbance measurements (10 mm quartz cells). The IR spectra were recorded on a perkin Elmer IR spectrophotomer, the ^{1}H NMR spectra were obtained with a Varian EM-390 (90 MHz) spectrometer using $DMSO$-d_6 as solvent. The *pH* value of the solutions was checked using an Orion Research Model 601 A Digital lonalyzer.

All reagents used were of analytical grade. A standard solution of Ag(I) was prepared by dissolving 0.1698 g of silver nitrate in 10 ml bidistilled water. Further dilutions were made accordingly. *Thiel* buffer solutions of different *pH* values (2–12) were prepared as recommended [12].

An aliquot of the stock soluting containing 25–650 μg of Ag^+, 12.5 ml of buffer solution, 4 ml of 2×10^{-3} M reagent solution, and 3.5 ml of absolute ethanol was transferred to a 25 ml measuring flask and completed to the mark with water. After mixing, the absorbance was measured at 430, 320, and 433 nm using reagents **1–4** respectively, against a reagent blank prepared in the same manner. The amount of Ag^+ in the sample solution was then deduced from standard calibration curves.

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Received June 11, 1996. Accepted (revised) September 16, 1996