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Schiff Bases Derived from Aminopyridines as Spectrofluorimetric Analytical Reagents

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Fluorescence characteristics of Schiff bases derived from aminopyridines and salicylaldehyde were studied and possibilities of their analytical application were discussed. It is shown that these compounds can be used for spectrofluorimetric monitoring of small pH changes as well as for sensitive metal ion determinations. As an illustration of metal ion determination, a spectrofluorimetric procedure for analysis of Cu^{2+} is presented. Determination of Cu^{2+} was based on the quenching effect of Cu^{2+} on the fluorescence of *N,N'*-bis(salicylidene)-2,3-pyridinediamine in dioxan/water 1/1 (volume fraction of dioxan, $\varphi = 50\%$). Under optimal conditions (pH = 8.9, $\lambda_{ex} = 340$ nm, $\lambda_{em} = 385$ nm, $c_{ligand} = 1.0 \times 10^{-5}$ M), the linearity range of the calibration curve was 30–350 μg L^{-1} Cu^{2+}. The procedure is fast, simple and reproducible. It is characterized by high sensitivity and satisfactory selectivity. An additional advantage of Schiff bases derived from aminopyridines as analytical reagents lies in the simplicity of preparation procedures, enabling improvement of the determination methods not only by optimization of experimental conditions, but also by designing suitable structural characteristics of the reagent.

Key words: aminopyridines, Cu^{2+}, quantum efficiency, salicylaldehyde, Schiff bases, spectrofluorimetric reagent.

INTRODUCTION

Application of many new analytical devices requires the presence of organic reagents as essential components of the measuring system. They are

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used, *e.g.* in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection or enhance selectivity and sensitivity.[1–4]

Among the organic reagents actually used, Schiff bases possess excellent characteristics: structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties.[5,6]

Schiff bases are widely applicable in analytical determinations: using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed (determination of compounds with an amino or a carbonyl group); using complex formation reactions (determination of amines, carbonyl compounds and metal ions); or utilizing the variation in their spectroscopic characteristics following changes in pH and solvent (pH or solvent polarity indicators). Unfortunately, most Schiff bases are chemically unstable and show a tendency to be involved in various equilibria, like tautomeric interconversions, hydrolysis, or formation of ionized species.[5,7–9,18,23] Therefore, successful application of Schiff bases requires a careful study of their characteristics.

The Schiff bases most often applied are condensation products of *o*-hydroxyaromatic aldehydes (*e.g.* salicylaldehyde) with aliphatic and aromatic mono- and diamines (*e.g.* 1,2-ethandiamine, 1,2-benzenediamine, aniline, 2-aminophenol and its derivatives.[6,10–14] Heteroaromatic Schiff bases are seldom used, although some compounds from this group show promising properties.[15–17]

In this work, the spectroscopic characteristics, equilibria and possibilities of analytical applications of a group of new, recently prepared Schiff bases derived from salicylaldehyde and aminopyridines[18–21] are presented (Scheme I).

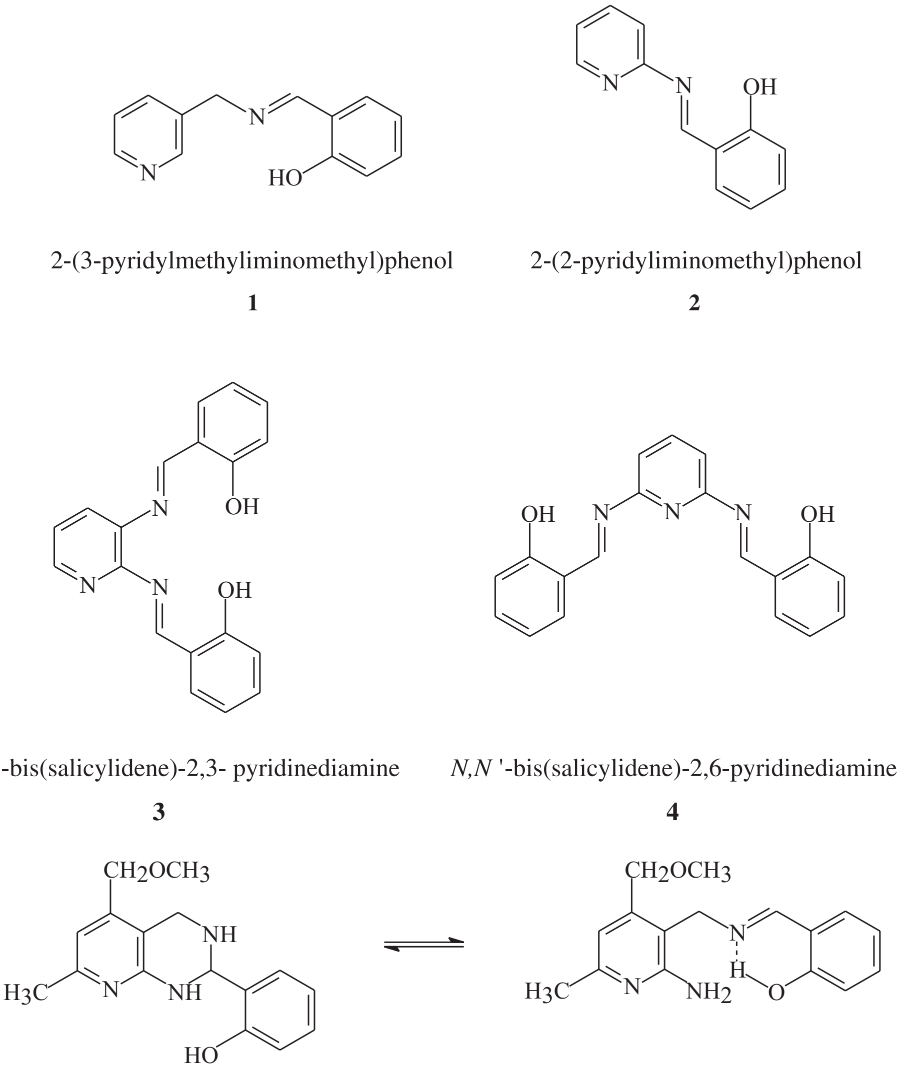
EXPERIMENTAL

Materials

General procedures for the preparation of Schiff bases of aminopyridines had been reported earlier.[18–21] All other chemicals used were of analytical purity grade. All solutions were prepared with solvents of spectroscopic grade (additionally purified when necessary) and doubly deionized water that was free from carbon dioxide. Quenching by oxygen was avoided by bubbling each solution with N_2 for 2 minutes before fluorescence measurement. The pH was adjusted with a universal buffer mixture consisting of acetic, phosphoric and boric acids and their sodium salts.

Apparatus

UV-vis absorption spectral data were obtained on a Varian Cary 3 spectrometer. Fluorescence measurements, correction of spectra and integration of the corrected spectra area were performed on a Perkin-Elmer LS 50 fluorescence spectrometer.



2-(3-pyridylmethyliminomethyl)phenol

1

2-(2-pyridyliminomethyl)phenol

2

N,N'-bis(salicylidene)-2,3- pyridinediamine

3

N,N '-bis(salicylidene)-2,6-pyridinediamine

4

2-(2-amino-4-methoxymethyl-6-methyl-3-pyridylmethyliminomethyl)phenol

5

Scheme I.

For pH measurements, a Radiometer pH/mV meter, pHM 85 with a Radiometer combined glass-calomel electrode GK2401 C was used. Th e pH meter was calibrated with standard aqueous buffer solutions. Factors, U_{H}, of van Uitert and Haas[22] for conversion of pH measured in dioxan/water 1/1 (volume fraction of dioxan, $\varphi = 50\%$) to H^+ concentrations, log m_{H}, amount to $-0.1 < \log U_{\mathrm{H}} < 0.1$ at applied ionic strengths.

NMR spectra were recorded on a Varian XL Gemini 300 spectrometer using tetramethylsilane as the internal standard. IR spectra were taken on a Perkin Elmer 783 spectrometer.

Methods

The procedures for monitoring tautomeric equilibria and determining tautomeric constants were reported in detail earlier.[18,23]

Determination of Quantum Yield

Stock solutions of Schiff bases were prepared in an appropriate organic solvent and those of metal ions in water. The concentrations of Schiff bases and metal ions in working solutions were 1.0×10^{-4} M or 5.0×10^{-5} M for UV-vis absorption measurements, and 1.0×10^{-5} M or 5.0×10^{-6} M for fluorescence measurements.

Absorption and fluorescence spectra were always recorded within the first three minutes following the preparation of solutions, since hydrolysis of Schiff bases may take place in solvents containing water. During measurements, the samples were thermostated at 20 °C.

The excitation source (a xenon lamp) was calibrated using the high absorbance solution method[24] and rhodamin B (1.0×10^{-5} M solution in deionized water) as a quantum counter (λ_{em} = 581 nm). Relative fluorescence quantum efficiencies were calculated by the method of Parker and Rees[25] from the equation

$$Q_\mathrm{s} = Q_\mathrm{r} \cdot \frac{A_\mathrm{r}(\lambda_\mathrm{r})}{A_\mathrm{s}(\lambda_\mathrm{s})} \cdot \frac{I_\mathrm{r}(\lambda_\mathrm{r})}{I_\mathrm{s}(\lambda_\mathrm{s})} \cdot \frac{n_\mathrm{s}^{\,2}}{n_\mathrm{r}^{\,2}} \cdot \frac{D_\mathrm{s}}{D_\mathrm{r}}$$

where, Q – quantum yield;
$A(\lambda)$ – absorbance of the solution at excitation wavelength;
$I(\lambda)$ – relative intensity of the exciting light at wavelength λ;
D – integrated area under the corrected emission spectrum;
n – refractive index;
subscripts r and s refer to the reference material and the examined compound, respectively.

Quinine sulphate solution (1.0 ppm solution in 1.0 M sulphuric acid) was used as a reference standard.

Determination of Cu^{2+}

Into a 10 ml tube containing an appropriate amount of Cu^{2+} (to give a final concentration in the range 30 – 350 μg L^{-1}) in 5.0 ml water buffer solution, pH = 8.9, 1.0 mL of 1×10^{-4} M reagent dissolved in dioxan was added and, finally, the mixture was diluted to 10.0 ml with dioxan. The fluorescence intensity was measured at 385 nm (λ_{ex} = 340 nm).

The effect of various ions on the determination of Cu^{2+} was studied by testing the 10 000 : 1 molar ratio of the interferent ion to the one being determined. If interference occurred, the ratio of the interferent ion to Cu^{2+} was gradually reduced until interference ceased. The tolerance limit was taken to be the concentration of an interfering species which gave variation in fluorescence intensity lower than 5%. Cations were added as chlorides or nitrates and anions as sodium or potassium salts.

RESULTS AND DISCUSSION

Equilibria of Schiff Bases in Solution

Although structurally closely related, the investigated compounds (see Scheme I) exhibited different behaviour in solution. It was proved by NMR, IR and UV-vis measurements that in non-polar solvents (diethylether, cyclohexane, chloroform, dioxan, *etc.*) compounds **1–4** were in the enolimino form with a strong hydrogen bond between the imino nitrogen and the proton of the hydroxylic group.[18–21,23] In polar protic solvents, like methanol and mixtures of methanol and dioxan with water, a tendency towards the interconversion of Schiff bases **1–4** to ketoamine was noted. However, it was significant only in the case of compound **1**; the corresponding tautomeric constant K_t (K_t = [ketoamine] / [enolimine]) amounted to 0.21 in methanol/water 4/1 (volume fraction of methanol, φ = 80%) and 0.25 in dioxan/water 1/1 (volume fraction of dioxan, φ = 50%).[20] In the case of compounds **2**, **3** and **4,** K_t was very low, amounting to 0.02, 0.14 and 0.03, respectively, in methanol/water 4/1.[23]

Compound **5** was a tautomeric mixture of cyclic diamine and enolimine in most solvents.[18] Only cyclic diamine could be isolated in the crude state. After dissolution, interconversion of cyclic diamine to enolimine took place, as shown by NMR and IR spectroscopy. The ratio of both forms in the equilibria depended on solvent polarity, concentration, pH and the temperature. The cyclic structure was preferred in less polar and aprotic solvents (diethylether, chloroform, dioxan, dimethylformamide, *etc.*) in diluted solutions, at neutral and weakly basic pH values as well as at low temperatures.

In methanol, ethanol and in solvents containing water, slow hydrolysis of compounds **1–5** took place, which was particularly noticeable in the case of bis Schiff bases **4** and **5** (*e.g.* in methanolic solution, signals of hydrolysis products became visible in the NMR spectrum after 24 hours).

UV-vis Absorption and Emission Characteristics of Schiff Bases in Various Solvents

The long-wave absorption maxima of the enolimino form of compounds **1–5** were in the region 300–375 nm and were assigned to the $\pi^*\leftarrow\pi$ transition, extending over the entire molecule[26,27] (Table I). In the case of compounds **1–4** in polar protic solvents, an additional absorption band of ketoamine appeared above 400 nm (*e.g.* 403 nm, comp. **1**; 442 nm, comp. **2**; 466 nm, comp. **3**; 452 nm, comp. **4**). The band was missing in the spectrum of compound **5**. In the case of compound **5**, only one band was present in the long-wave region. The intensity of this band ($310\text{ nm} < \lambda_{\max} < 312\text{ nm}$)

TABLE I

Absorption and emission characteristics of compounds **1**–**5** in different solvents

Compound	Solvent	$\frac{\lambda_{abs}}{nm}$	$\frac{\lambda_{ex}}{nm}$	$\frac{\lambda_{em}}{nm}$	$\frac{\varepsilon \times 10^{-4}}{mol^{-1} cm^{-1} L}$	Q
1	Dioxan/H_2O 1/1[a]	316	–	–	0.37	–
	Dimethylformamide	317	–	–	0.42	–
	Methanol[a]	317	–	–	0.42	–
	Dioxan	318	–	–	0.46	–
2	Dioxan/H_2O 1/1[a]	305	304	365	1.08	0.072
	Dimethylformamide	306	309	341	1.30	0.001
	Methanol[a]	304	306	339	1.33	0.001
	Dioxan	305	306	339	1.33	0.001
3	Dioxan/H_2O 1/1[a]	338	338	381	1.78	0.001
	Dimethylformamide	338	412	507	2.03	0.024
	Methanol[a]	339	339	381	2.01	0.001
	Dioxan	339	–	–	2.16	–
4	Dioxan/H_2O 1/1[a]	331	331	387	1.42	0.053
	Dimethylformamide	371	422	507	2.43	0.002
	Methanol[a]	367	367	387	2.45	0.001
	Dioxan	372	–	–	2.48	–
5	Dioxan/H_2O 1/1[b]	312	312	376	0.75	0.295
	Dimethylformamide[b]	311	313	372	0.61	0.435
	Methanol[b]	311	312	372	0.75	0.064
	Dioxan[b]	310	310	364	0.79	0.203

[a] A weak additional absorption maximum of the ketoamino form is observable above 400 nm.
[b] Absorption maximum is due to the absorption of both enolimino and cyclic forms.

changed with the ratio of cyclic diamine and enolimine, revealing that both forms had the same absorption maximum, but different molar absorption coefficients.

Excitation at the absorption maximum of enolimine (cyclic diamine) was followed by emission, the wavelength and intensity of the corresponding band depending strongly on the solvent properties (Table I). Compound **1** was not fluorescent in the investigated solvents at pH < 8. Compounds **2**–**4** were not fluorescent in non-polar and moderately polar solvents, like hexane, diethylether and chloroform, whereas weak emission was observed in polar solvents like methanol, dimethylformamide and dioxan/water mixtures with a volume fraction of water, $\varphi < 50\%$. Further increase in the water content, that is, in the polarity of dioxan/water mixtures resulted in a significant increase in quantum efficiencies of compounds **2–4**. Figure 1 illustrates the dependence of quantum efficiency of compounds **1–5** on the polarity of dioxan/water mixtures containing various volume fractions of water. Since the dioxan/water mixture does not behave like an ideal solvent mixture, polarity is expressed as an empirical polarity parameter.[28] Increase in quantum efficiency of compounds **2–4** was followed by an increase in Stokes shifts over 5 000 cm^{-1}, indicating that a new species, most probably a complex with polar water molecules, was formed in the excited state.[29]

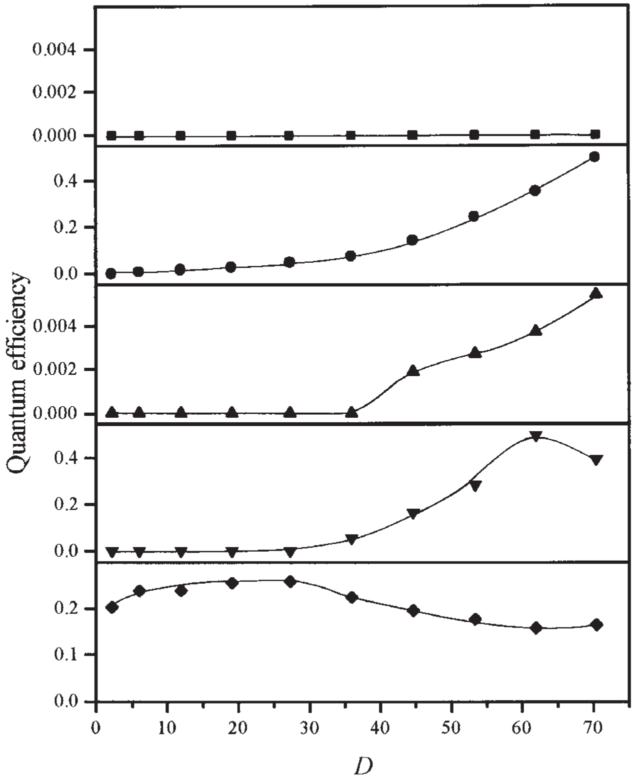


Figure 1. Dependence of quantum efficiency of Schiff bases on the polarity of dioxan/water mixtures. ■ **1**; ● **2**: 302 nm < λ_{ex} < 306 nm, 339 < λ_{em} < 369 nm; ▲ **3**: 338 nm < λ_{ex} < 339 nm, 377 nm < λ_{em} < 410 nm; ▼ **4**: 329 nm < λ_{ex} < 336 nm, 368 nm < λ_{em} < 392 nm; ◆ **5**: 310 nm < λ_{ex} < 312 nm, 367 nm < λ_{em} < 376 nm.

Compound **5** exhibited fluorescence in polar as well as in non-polar solvents (Table I). The strong emission in non-polar and aprotic solvents (dioxan, dimethylformamide) was ascribed to the cyclic form, preferably present in such medium. Cyclic diamine was more rigid than enolimine, giving rise to a decrease in the efficiency of non-radiative decay. The increase in the content of polar protic water in dioxan/water mixtures affected the ratio of tautomeric forms in the equilibrium as well as their emission. Accordingly, the quantum efficiency of compound **5** increased initially with the increase of the water content in the dioxan/water system, reached the maximum value in the mixtures containing 30–40% water ($20 < D < 30$) and then decreased (Figure 1). Addition of more than 40% water ($D > 30$) resulted in the predominance of the less fluorescent enolimine, which was preferred in polar protic media.

One is to note that the increase in quantum efficiency of compounds **2–5** with the increase in the water content in dioxan/water mixtures was reproducible and can therefore have analytical relevance.

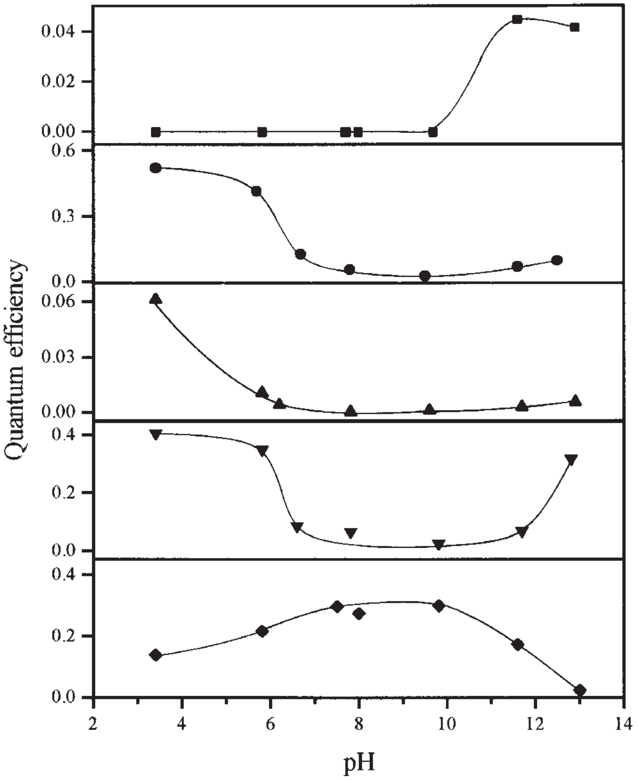


Figure 2. Dependence of quantum efficiency of Schiff bases dissolved in dioxan/water 1/1 on pH. ■ **1**: 391 nm < λ_{ex} < 392 nm, 489 nm < λ_{em} < 495 nm; ● **2**: 291 nm < λ_{ex} < 300 nm, 351 nm < λ_{em} < 368 nm; ▲ **3**: 315 nm < λ_{ex} < 392 nm, 381 nm < λ_{em} < 493 nm; ▼ **4**: 305 nm < λ_{ex} < 336 nm, 353 nm < λ_{em} < 387 nm; ◆ **5**: 308 nm < λ_{ex} < 316 nm, 363 nm < λ_{em} < 380 nm.

Dependence of the Fluorescence of Schiff Bases on pH

Dependence of quantum efficiencies of Schiff bases on pH value was studied in a buffered mixture dioxan/water 1/1. Compound **1** exhibited fluorescence only at pH > 8, when excited at 390 nm, the wavelength corresponding to that of the phenolate anion. The other compounds emitted in the whole pH range, but the values of their quantum efficiencies depended strongly on pH (Figure 2). Quantum efficiencies of compounds **2**–**4** increased significantly at pH < 7, where a pyridinium cation was formed.[23] The effect of the increase in quantum efficiency with the shift of the equilibria from neutral to the protonated form was most striking for compounds **2** and **4**, preferring a planar structure.[19,21] The quantum yield of compound **5** reached the highest value in the range 7 < pH < 10, where cyclic diamine was preferably present. It decreased out of this range, going to more acidic or more basic pH values, where enolimine was preferred.

The sensitivity of Schiff bases **1**–**5** to changes in pH enables their application as fluorimetric pH indicators. The value of the slope of quantum efficiency *versus* pH curve was particularly high for compounds **2** and **4** in the acidic region and for compounds **4** and **5** in the basic region. Such high sensitivity opens attractive possibilities for the application in optical sensors, where small pH changes are monitored over a limited pH range.

Dependence of the Fluorescence of Schiff Bases on the Presence of Metal Ions

The reaction of Schiff bases **1**–**4** with Zn^{2+}, Al^{3+}, Be^{2+} and Mg^{2+} in the dioxan/water system induced small shifts of the excitation and emission maxima (Table II) and an increase in quantum efficiency (Figure 3). Metal

TABLE II

Excitation and emission maxima of compounds **1**–**4** in the presence of Be^{2+}, Mg^{2+}, Al^{3+} and Zn^{2+}

Compound	pH	Metal ion									
		–		Be^{2+}		Mg^{2+}		Al^{3+}		Zn^{2+}	
		$\frac{\lambda_{ex}}{nm}$	$\frac{\lambda_{em}}{nm}$	$\frac{\lambda_{ex}}{nm}$	$\frac{\lambda_{em}}{nm}$	$\frac{\lambda_{ex}}{nm}$	$\frac{\lambda_{em}}{nm}$	$\frac{\lambda_{ex}}{nm}$	$\frac{\lambda_{em}}{nm}$	$\frac{\lambda_{ex}}{nm}$	$\frac{\lambda_{em}}{nm}$
1	7.7	–	–	274	431	–	–	–	–	–	–
2	6.7	295	363	295	363	295	360	303	368	295	360
3	6.2	315	385	313	382	312	380	333	404	325	395
4	6.6	330	387	333	386	311	363	333	386	311	363

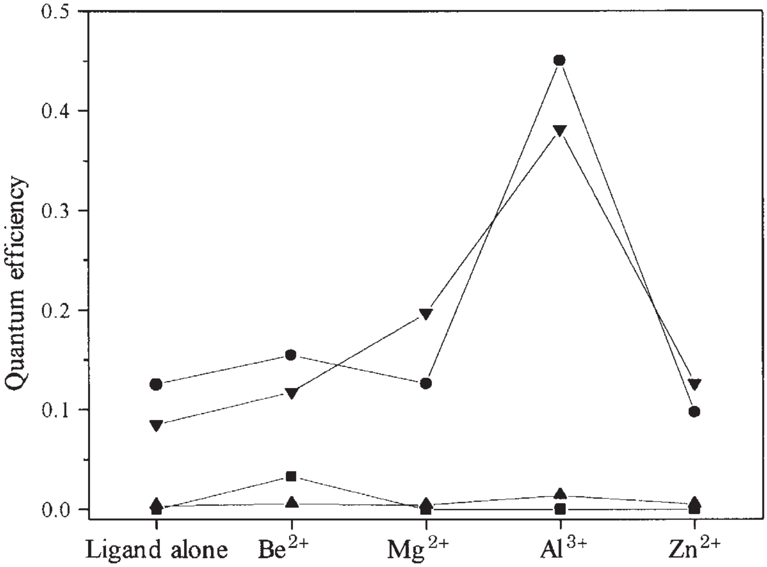


Figure 3. Quantum efficiency of compounds **1**–**4** dissolved in dioxan/water 1/1 in the presence of Be^{2+}, Mg^{2+}, Al^{3+} and Zn^{2+}, [M]/[L] = 1. ■ **1**; ● **2**; ▲ **3**; ▼ **4**. Measuring conditions are described in Table II.

ions did not have much effect on the fluorescence characteristics of compound **5**.

Significant changes in quantum efficiency with respect to ligand alone followed the reactions of complex formation of Al^{3+} with compounds **2** and **4** in neutral and weakly acidic pH media (Figure 3). These complexes were formed within 15–30 minutes and were stable during time. This was an indication that the hydrolysis of Schiff bases was slowed down or was prevented by formation of these complexes. Unfortunately, the emission of Schiff bases **1**–**4** was very sensitive to pH changes just in the pH range where fluorescent complexes were formed and the differences between emission maxima of ligands and complexes were low. Therefore, development of the corresponding analytical procedures is hardly practicable.

However, the reaction of compound **1** with Be^{2+}, proceeding at pH values, where ligand alone did not exhibit any fluorescence, seems to be a promising basis for the determination of beryllium (Figure 3).

The fluorescence of compounds **2**–**4** was quenched by Cu^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+} and Cr^{3+}. The most distinct quenching effect was observed for Cu^{2+} and compound **3** and it was used for developing a copper determination procedure.

Example of Relevant Analytical Use: Determination of Cu^{2+} Using the Quenching Effect

It was shown earlier that the reaction of compound **3** with Cu^{2+} can serve for sensitive spectrophotometric determination of copper after the complex extraction into chloroform.[30] The value of the molar absorption coefficient, ε, of this complex was higher than the values of ε of copper(II) complexes with other Schiff bases applied as spectrophotometric copper reagents.[31,32] It was also higher than ε of the complexes of the best known spectrophotometric copper reagents, such as cuproin,[33] neocuproin,[34] bathocuproin,[35] sodium diethyldithiocarbamate,[36,37] 3-(6-methyl-2-py)-5,6-bis(2- furyl)-as-triazine,[38] phenylthiosemicarbazones,[39] *etc*.

Therefore, the quenching effect of Cu^{2+} on the emission of compound **3** was studied in detail and applied for developing a fluorimetric copper determination procedure. The emission intensity of compound **3** was sufficiently high in the dioxan/water system, which was chosen as appropriate medium. The widest linear range of the decrease in the emission intensity depending on Cu^{2+} concentration was observed in the dioxan/water system 1/1. The pH values above 8 were suitable for complex formation and were found to be optimal for the determination of copper. Although the emission of the reagent in this pH range was not intensive, the effect of fluorescence quenching by Cu^{2+} was stronger than in a more acidic medium. In addition, emission of compound **3** was not very sensitive to pH changes at pH > 8. Figure 4 shows excitation and emission spectra of compound **3** at pH = 8.9 in the presence and absence of Cu^{2+}. Optimal conditions for copper determination in amounts up to 350 μg L^{-1} were found to be dioxan/water mixture 1/1, pH = 8.9, $c(\mathbf{3}) = 1.0 \cdot 10^{-5}$ M, λ_{ex} = 340 nm, λ_{em} = 385 nm. Fluorescence intensity changed with time. Therefore, for rapid analysis, it was necessary to perform the measurement at a precisely defined time, *e.g.* exactly 3 minutes after the preparation of the sample solution. Since after 24 h fluorescence intensity changed no more, time independent measurements were achievable, which, however, had the disadvantage of a time consuming analysis.

Decrease in the fluorescence intensity caused by the presence of Cu^{2+} was linear in the range 30–350 μg L^{-1} Cu^{2+}. The slope, intercept and correlation coefficient of the corresponding calibration curve were –377.4, 229.7 and –0.9995, respectively, whereas the relative standard deviation for seven standard samples (each containing 180 μg L^{-1} of copper) was 2.1%. The sensitivity of the method was 10-fold higher than that of the spectrophotometric method with the same reagent.[30] Determination of Cu^{2+} was selective with regard to Cd^{2+}, Pb^{2+}, V^{4+}, Mg^{2+}, Sr^{2+}, Ba^{2+} and Al^{3+}, present in 1000-fold excess, whereas Zn^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Mn^{2+} and Hg^{2+}, present in equimolar

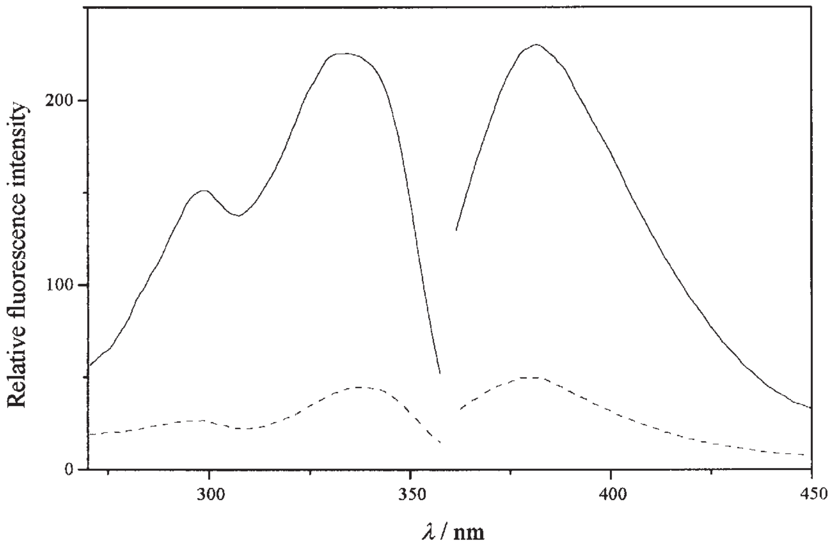


Figure 4. Excitation and emission spectra of compound **3** in dioxan/water 1/1 at pH = = 8.9 (universal buffer mixture) in the presence and absence of copper(II) nitrate. $c(\mathbf{3}) = 1.0 \times 10^{-5}$ M, $c(Cu^{2+}) = 1.0 \times 10^{-5}$ M. ——— compound **3**, – – – – compound **3** and Cu^{2+}.

concentrations, as well as Fe^{2+} and Ca^{2+}, present in 10-fold excess, interfered. Most anions, like CO_3^{2-}, PO_4^{3-}, SCN^-, NO_3^-, ClO_4^-, SO_4^{2-}, CH_3COO^-, BO_4^{3-}, oxalate, tartrate, *etc.*, did not interfere.

Future Prospects

Future efforts will focus on two topics. First, the applicability of Schiff bases derived from aminopyridines for measurements in optical sensors will be evaluated and optimized. Installation of a highly sophisticated measuring cell is in progress.

Second, new Schiff bases showing stronger fluorescence in non-polar organic solvents as well as those forming stable fluorescent complexes in non-polar media will be designed on the basis of the current knowledge about the structural properties and spectroscopic characteristics of the now available Schiff bases. An extraction equilibrium of the reagents or complexes in favour of the organic phase would improve the flexibility of their use in optical sensors and would also enhance selectivity and sensitivity of determinations. The current efforts concern the preparation of condensation products of aminopyridines, diaminopyridines, aminoalkylpyridines and nicotinohydrazides with *o*-vanillin and lipophilized *o*-vanillin derivatives.

CONCLUSION

Schiff bases derived from aminopyridines and salicylaldehyde possess fluorescent characteristics, which enable their wide application in fluorimetry.

The fluorescence of all compounds is strongly pH dependent and can be used for monitoring pH. The effect is striking in the case of 2-(2-pyridyliminomethyl)phenol and *N,N*'-bis(salicylidene)-2,6-pyridinediamine in the acidic medium as well as in the case of 2-(2-amino-4-methoxymethyl-6-methyl-3-pyridylmethyliminomethyl)phenol and *N,N*'-bis(salicylidene)-2,6-pyridinediamine in the basic medium, opening attractive possibilities of application in optical sensors where high pH sensitivity is required over limited pH range.

It was shown that the quenching effect of Cu^{2+} on the fluorescence of *N,N*'-bis(salicylidene)-2,3-pyridinediamine can be used for copper determination. Although not highly selective, the proposed reagent is more sensitive than copper reagents described in the literature. The procedure suggested here is simple and fast.

Based on the correlation of structural properties, spectroscopic characteristics and complex formation capabilities of the condensation products of aminopyridines and salicylaldehyde, attempts to design compounds with higher quantum efficiencies in non-polar organic solvents are in progress.

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SAŽETAK

Schiffove baze aminopiridina kao spektrofluorimetrijski analitički reagensi

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Proučavana je fluorescencija Schiffovih baza izvedenih iz aminopiridina i salicilaldehida i razmotrene mogućnosti njihove analitičke primjene. Pokazano je da se ti spojevi mogu iskoristiti za spektrofluorimetrijsko praćenje malih promjena pH, kao i za osjetljiva određivanja iona metala. Kao ilustracija određivanja iona metala

predložen je spektrofluorimetrijski postupak analize Cu^{2+}. Određivanje Cu^{2+} temelji se na efektu gašenja fluorescencije *N,N'*-bis(saliciliden)-2,3-piridindiamina bakrom(2+) u smjesi dioksan/voda 1/1. Pri optimalnim uvjetima (pH = 8,9, λ_{ex} = 340 nm, λ_{em} = 385 nm, $c_{ligand} = 1,0 \times 10^{-5}$ M), linearno područje kalibracijske krivulje proteže se od 30 do 350 μg L^{-1} Cu^{2+}. Analitički je postupak brz, jednostavan i reproducibilan. Odlikuje se visokom osjetljivošću i zadovoljavajućom selektivnošću. Dodatna je prednost Schiffovih baza izvedenih iz aminopiridina kao analitičkih reagensa jednostavan način priprave, koji omogućava poboljšanje metoda određivanja, ne samo optimalizacijom eksperimentalnih uvjeta, nego i prilagođavanjem strukturnih značajki reagensa.