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Interactions of stilbazolium merocyanine with transition metal ions

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Abstract

The visible absorption spectra of merocyanine 1-(12-hydroxydodecyl)-4-[(3-hydroxy-4-oxocyclohexa-2,5-dienylidene)-ethylidene]-1,4-dihydropyridine in the presence of Cu^{2+}, Co^{2+} and Fe^{3+} ions has been investigated. The metal ions impacted a long wave absorption band of merocyanine with a characteristic wavelength. Both the intensity of the maximum and its position are related to changes in the metal ion concentration. This observed behaviour was dependent on the pH of the solution. Since concentrations of metal ions below 10^{-6} M l^{-1} can be detected, we concluded that the investigated dye demonstrated a high sensitivity for the presence of metal ions. © 2001 Elsevier Science ltd. All rights reserved.

Keywords: Stilbazolium merocyanine; Transition metal ions; Absorption; Complexes

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1. Introduction

The electronic spectra of the stilbazolium betaine type of merocyanines are strongly sensitive to the pH [1–3], polarity of microenvironment [4,5] and the local electric field [6,7] which makes them interesting synthetic dyes. Previous investigations have shown that these compounds incorporate readily into lipid membranes [8,9], human and mouse tumours, leukemia cells and viruses [10,11].

1-Hexadecyl-4-[(4-oxocyclohexa-2,5-dienylidene)-ethylidene]-1,4-dihydropyridine has been used to investigate the hydrogen ion concentration in the vicinity of the surfactant head groups in micelles [9]. In the other study 1-decyl and 1-dodecyl derivatives of this dye have been applied as a photon–driven facilitated proton transport across planar lipid membrane [2].

A strong influence of alkyl substituents on the spectral properties and the orientation of the merocyanines embedded into the polyvinyl alcohol [12,13], nematic liquid crystal [6,7] and bilayer vesicles [3,8] were shown in previous studies. Alkyl substituents were also introduced into the quinonoid ring of merocyanines [4,6–8,10–15]. The electron-withdrawing or electron-donating groups have exhibited influences on the solvatochromic behaviour of these compounds [4]. Merocyanines with different substituents have also shown various efficiencies of incorporation into different types of human peripheral blood leukocytes [14].

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Di-*tert*-butyl substituted dyes showed the cytotoxic effect on human adenocarcinoma cells and human lymphoblasts [10,11], while the other compounds without the bulky substituents were only able to incorporate into cells [10,11,14]. This behaviour indicates that the merocyanines can be used as biological membrane probes.

In this study we introduced a hydroxyl group into the immediate vicinity of the carbonyl group of the quinonoid ring of merocyanine (Fig. 1). We expected that this modification would make the detection of low concentrations of transition metal ions possible. We used Cu^{2+}, Co^{2+} and Fe^{3+} ions to demonstrate changes in UV–Vis spectra of the merocyanine.

2. Materials and methods

2.1. Chemicals

1-(12-Hydroxydodecyl)-4-[(3-hydroxy-4-oxocyclohexa-2,5-dienylidene)-ethylidene]-1,4-dihydropyridine was used as the dye (as shown Fig. 1). It was synthesized as described earlier [16]. Melting point, IR and ^1H NMR spectra of merocyanine were shown previously [15].

Salts of transition metals: $Cu(CH_3COO)_2$, $CoCl_2{*}6H_2O$ and $FeCl_3$ which were purchased from Fluka Chemie AG and were used without further purification. The pH of all solutions was controlled.

2.2. Spectra

Absorption spectra were recorded on a Perkin-Elmer Lambda 20 UV–Vis spectrophotometer. All samples were dissolved in methanol (p.a.). The final concentrations of merocyanine in measured solutions were 10^{-4} and 10^{-5} M l^{-1}. The final concentrations of transition metal ions in the samples were changed as follow: 10^{-3}, 5×10^{-4}, 1×10^{-4}, 5×10^{-5}, 1×10^{-5}, 5×10^{-6}, 1×10^{-6} M l^{-1}.

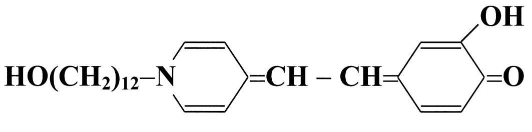

Fig. 1. Structure of the synthesized merocyanine.

3. Results

Fig. 1 shows the structure of the compound studied in this work. The dye was dissolved in anhydrous methanol. Solutions of various merocyanine–ion mixtures were prepared by adding appropriate amounts of methanol solutions of Cu^{2+}, Co^{2+} and Fe^{3+} ions.

Fig. 2 shows the spectra of merocyanine and merocyanine in mixtures with the transition metal ions. Big changes are observed in the long wavelength part of an absorption spectrum. The presence of Cu^{2+} ions is generating absorption maximum at approximately 510 nm, Co^{2+} at approximately 554 nm and Fe^{3+} at approximately 497 nm. The appearance of these new absorption bands allows identifying the transition metal ions applied. Both

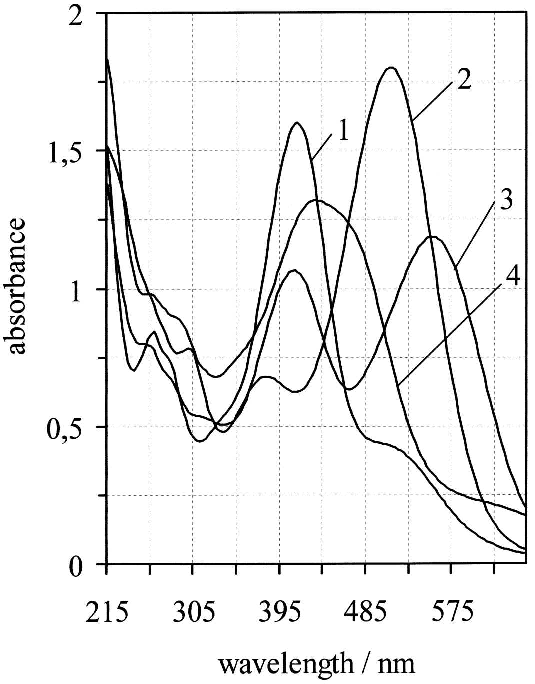

Fig. 2. Absorption spectra of methanol solutions: (1) merocyanine (conc. 10^{-4} M l^{-1}); (2) mixture of merocyanine (10^{-4} M l^{-1}) and Cu^{2+} (10^{-4} M l^{-1}); (3) mixture of merocyanine (10^{-4} M l^{-1}) and Co^{2+} (10^{-4} M l^{-1}); (4) mixture of merocyanine (10^{-4} M l^{-1}) and Fe^{3+} (5×10^{-4} M l^{-1}).

the apparent changes in the intensity and the localization (λ_{max}) of maximum absorption band were observed.

Fig. 3 shows the changes in the absorbance (Fig. 3a) and λ_{max} position (Fig. 3b) of the long wavelength absorption band as a function of metal ion concentrations with constant concentration of the merocyanine of 10^{-4} M l^{-1}. When the concentrations of Cu^{2+} and Co^{2+} ions were gradually increased to the concentration of merocyanine, an increase in the intensity of the long wavelength absorption band was observed (Fig. 3a, curves 1 and 2). However, an increase of the absorption intensity of the ion concentration was observed for Fe^{3+} (Fig. 3a, curve 3) only up to 5×10^{-5} M l^{-1}. A decrease of the long wavelength absorbance, was observed with higher metal ion concentrations in a case when salts of metal ions cause decrease of pH of solutions (Table 1). As shown on Fig. 3b different transition metal ions induced different solvatochromic effects. The Cu^{2+} ions at the concentrations range from 10^{-6} to 10^{-5} M l^{-1} caused a bathochromic shift of the spectrum while at higher concentrations a hypsochromic shift was observed (Fig. 3b, curve 1). The observed results may be related to competitive interactions with the solvent.

For Co^{2+} ions the highest bathochromic shift in the absorption band was observed at concentrations ranging from 5×10^{-6} to 5×10^{-5} M l^{-1} (Fig. 3b, curve2).

For Fe^{3+} ions only the hipsochromic shift was observed at the full range of concentrations employed (Fig. 3b, curve 3). The changes in the absorption intensity (Fig. 4a) and λ_{max} (Fig. 4b) of the long wavelength absorption band when the dye concentration was reduced to 10^{-5} M l^{-1} are shown in Fig 4.

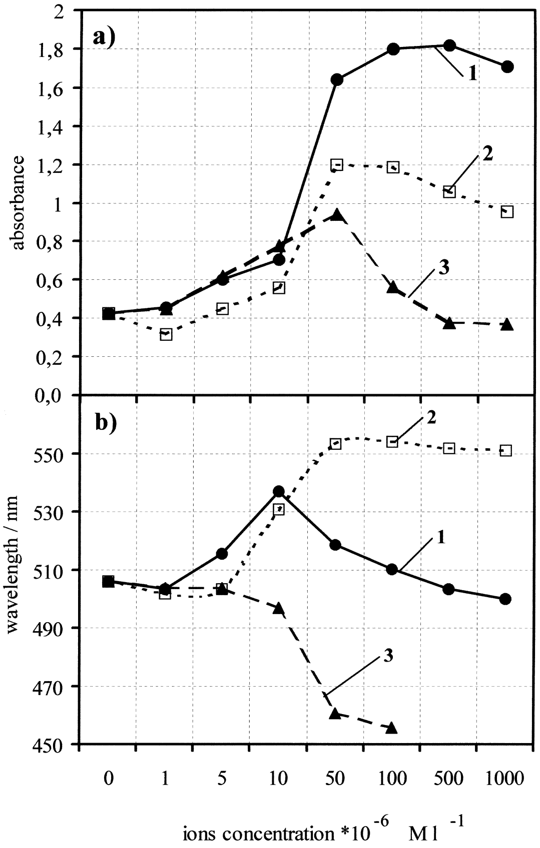

Fig. 3. Effect of the ion concentration changes on the long wavelength absorption band of the merocyanine. The dye concentration 10^{-4} M l^{-1}. (a) Merocyanine absorption dependence on concentration of transition metal ions; (1) merocyanine–Cu^{2+} for $\lambda=510$ nm; (2) merocyanine–Co^{2+} for $\lambda=554$ nm; (3) merocyanine–Fe^{3+} for $\lambda=497$ nm. (b) Merocyanine absorption band shift depending on concentration of transition metal ions; (1) merocyanine–Cu^{2+}; (2) merocyanine–Co^{2+}; (3) merocyanine–Fe^{3+}.

4. Discussion

The merocyanine investigated in this study appears to be a promising compound for medical application based on two observations: (1) it can detect Cu^{2+}, Co^{2+} and Fe^{3+} ions, (2) it showed high incorporation into cell membranes [15]. As shown in this paper the appropriate design of a molecular structure enables construction of compounds that respond with significant changes in the visible absorption spectra to the presence of a low concentration of transition metal ions.

Table 1
The changes of merocyanine–ion solution pH

Merocyanine concentrations (M l^{-1})		10^{-4}	10^{-5}
pH of solution for ion concentrations 0–10^{-3} (M l^{-1})	$Cu(CH_3COO)_2$	7.43–7.12	8.06–7.24
	$CoCl_2*2H_2O$	7.44–7.28	8.73–7.37
	$FeCl_3$	7.42–1.73	8.50–1.62

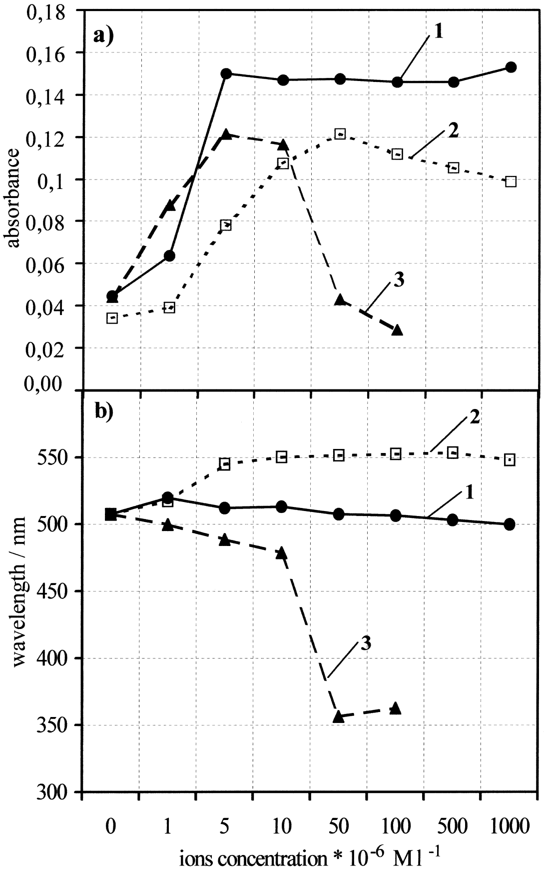

Fig. 4. Effect of the ion concentration changes on the long wavelength absorption band of the merocyanine. The dye concentration 10^{-5} M l^{-1}. (a) Merocyanine absorption dependence on concentration of transition metal ions; (1) merocyanine–Cu^{2+} for $\lambda = 510$ nm; (2) merocyanine–Co^{2+} for $\lambda = 554$ nm; (3) merocyanine–Fe^{3+} for $\lambda = 497$ nm. (b) Merocyanine absorption band shift depending on concentration of transition metal ions. (1) merocyanine–Cu^{2+}; (2) merocyanine–Co^{2+}; (3) merocyanine–Fe^{3+}.

With the formation of merocyanine–ion complexes the investigated dye has demonstrated the sensitivity to ion/merocyanine concentrations ranging from 0.01 to 1. The decrease in intensity and the hipsochromic shift of the long absorption band for larger ion concentrations than the merocyanine concentration may be obtained by the superposition of two effects: (1) the solvatochromism of merocyanines [4] and (2) the protonation of dyes occurring in lower pH of solutions [2,13,17]. An increase in solvent polarity causes a strong solvatochromism of all stilbazolium merocyanines. The low pH of solution creates a protonated form of dye, which shows a characteristic absorption band at approximately 400 nm. The results are presented in Table 1.

Merocyanine–Cu^{2+} and merocyanine–Co^{2+} complexes have demonstrated a slight hypsochromic shift of the long wave absorption bands, accompanied by small changes in the pH of the solution indicating domination of solvatochromism. In the case of merocyanine–Cu^{2+} complexes two different paramagnetic species are observed in electron paramagnetic resonance (EPR) for the samples prepared in the conditions both at room temperature as well as at 77 K too [17]. In contrast Co^{2+} and Fe^{3+} complexes with the merocyanine are not paramagnetic and EPR signals are not observed neither at room temperature or at 77 K. However, the extreme shift of the absorption to shorter wavelengths for merocyanine–Fe^{3+} complex has correlated with the large decrease of the pH mixture. A similar effect, as for Fe^{3+} ions, for Cu^{2+} ions ($CuCl_2$) was observed previously [17]. Probably a strong hypsochromic shift for Fe^{3+} ions was due to protonation of merocyanine.

5. Conclusions

1. Merocyanine with hydroxyl group in the quinoid ring in the vicinity of the carbonyl group is an excellent indicator of Cu^{3+}, Co^{2+} and Fe^{3+} ions presence.
2. Interaction with different ions creates an additional absorption band with a characteristic wavelength for each one.
3. Change of metal ion concentration is reflected both in intensity of the maximum and its position.
4. It seems that synthesized merocyanine can be used as an effective biosensor in the controlled pH of the environment.

Acknowledgements

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