

Potentiometric Properties of Polypyrrole Films Doped With Calmagite[†]

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Electrochemically deposited polypyrrole films doped with calmagite, a multivalent complexing ligand, has been studied. The films were deposited on a platinum substrate by using cyclic voltammetry. Calmagite was incorporated in the polymer matrix during polymerisation. Calmagite belongs to the group of metallochromic indicators and forms complexes with calcium, magnesium and copper. By using calmagite as doping ion the sensitivity of the film towards these specific cations is enhanced. This was checked by measuring the potentiometric response of the films. As the complexation between calmagite and the metal ions is pH dependent the proper pH range had to be used to obtain good potentiometric response of the films. EDAX spectroscopy was used to get further information about the complexation.

Badano osadzone elektrochemicznie na platynie i domieszkowane kalmagitem cienkie warstwy polipyrrolu. Kalmagite wbudowywał się w warstwę polimeru w czasie polimeryzacji metodą cyklicznej woltamperometrii. Zaobserwowano wzrost czułości potencjometrycznej otrzymanych warstw polipyrrolu w stosunku do jonów wapnia, magnezu i miedzi, które są kompleksowane przez kalmagite. Dobre zależności

[†] Dedicated to Professor Adam Hulanicki on the occasion of his 70th birthday.

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potencjometryczne otrzymano w ograniczonym przedziale pH. Spektroskopia EDAX pozwoliła na udokumentowanie oddziaływań kalgamitu z jonami metali.

Among the electrodes modified by deposition of conducting polymers much attention has been devoted to polypyrrole (PPy) films. PPy can easily be prepared chemically or electrochemically, both from organic and aqueous solutions [1]. Several factors affect the PPy film properties, *i.e.* polymerisation method (potentiostatic, galvanostatic or potential cycling), monomer concentration, doping ion, supporting electrolyte, and – last but not least – conditioning process [2]. To obtain an ion-sensitive electrode with PPy as the electroactive layer different doping ions can be used. During electropolymerisation of pyrrole the negatively charged doping anions are incorporated in the film to compensate the positively charged polymer backbone. When small and mobile anions are used, the film exhibits anionic sensitivity since an anion-exchange between the film and the solution takes place. When, on the other hand, big, rather immobile anions are used as doping ions, they remain in the film and the electrode shows cationic sensitivity. This type of behaviour has been described in several papers. PPy films sensitive for halides and pseudohalides have been reported [3–5]. Different doping ions were tested (both anionic and cationic), and the redox response has been predicted and observed depending on the nature of the doping ion [6–9]. Non-specific cationic sensitivity was obtained when a bulky multicharged dopants were immobilised in polypyrrole such as naphthalenesulphonates [10,11], indigo carmine [12], methylene blue [13] and hexacyanoferrate(II) [14].

A first deliberate enhancement of the cationic sensitivity, leading to conducting polymer-based ion-selective electrode, has been reported only recently [15]. An improvement in the cationic sensitivity was achieved by use of metal-complexing, multivalent ligands as doping anions during electropolymerisation of PPy and by proper conditioning of the deposited films. Compounds from the group of metallochromic indicators, *i.e.* Eriochrome Black T, Kalces and Tiron have been used as dopants. According to the theoretical interpretation provided by the authors the effect should be observed whenever similar compounds are employed as dopants.

In the present work we report on general potentiometric properties of polypyrrole films doped with calmagite – a metal-complexing multivalent anion of the compound belonging to metallochromic indicators group.

EXPERIMENTAL

Reagents

Pyrrole (Aldrich) was purified by distillation and stored under argon atmosphere at low temperature protected from light.

Calmagite (1-(1-Hydroxy-4-methyl-2-benzolazo)-2-naphthol-4-sulphonic acid), $C_{17}H_{14}N_2O_5S$, (molecular mass: 358.38) has been received from Fluka.

CaO has been purchased from J.T. Baker and all the other chemicals: $CaCl_2 \cdot 2H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $CuCl_2 \cdot 2H_2O$, HCl, NaOH and MgO from Merck. These were all used as received.

Double distilled water was used throughout the work.

Instrumentation

For the electrochemical polymerisation of pyrrole a BAS CW-50 W Voltammetric Analyzer (Bioanalytical Systems Inc.) was used. A conventional three electrode system with a Pt working electrode ($A = 0.07 \text{ cm}^2$), SCE as the reference electrode and a glassy carbon rod as auxiliary electrode was used.

In the potentiometric measurements a Metrohm 654 pH-Meter was used and the potentials were measured vs saturated calomel electrode (SCE). A Metrohm pH electrode was used for pH measurements.

EDAX (energy dispersive analysis of X-rays) spectroscopy experiments were performed with a Leica Cambridge Ltd. Stereoscan 360 Scanning Electron Microscope. In all EDAX experiments the background level was equal to 25 counts at 6 keV.

Procedures

Electrode preparation. Before use the Pt-electrodes were polished with $0.3 \mu\text{m}$ alumina, rinsed with water and cleaned in an ultrasonic bath for about 10 min. The PPy film deposition was performed by cyclic voltammetry from a solution of 0.1 mol l^{-1} pyrrole in saturated calmagite electrolyte. The solutions were always deaerated before polymerisation. The potential was scanned between -0.4 and $+0.8 \text{ V}$ vs SCE at a scan rate of 20 mV s^{-1} . The polymerisation time used was usually 30 min and the polymer films obtained were $5 \mu\text{m}$ thick.

The polymerisation was stopped at -0.4 V and the electrode was kept at this potential for 5 min. In this last step, the polymerisation solution was changed to a monomer-free calmagite electrolyte. After polymerisation the electrodes were rinsed with water and put into a conditioning solution.

Potentiometric measurements. Before the potentiometric response was measured the electrodes were conditioned/soaked in 0.1 mol l^{-1} solutions of appropriate ions. Solutions with Ca^{2+} , Mg^{2+} and Cu^{2+} were used in this study. As the complexation between calmagite and these ions is pH dependent, pH was adjusted in some solutions used for the conditioning process. Usually the electrodes were conditioned for three days before the response was measured. The potentiometric response was carried out in solutions containing the same ions as the conditioning solution, in the concentration range 10^{-5} to $10^{-1} \text{ mol l}^{-1}$. As no constant background was used in the measured solutions, the single-ion activities have been calculated using the Debye-Huckel formalism and convention. The electromotive force (EMF) values were also corrected for the liquid junction potential using the Henderson equation.

The potential was read after 2 and 5 min. The same films were used for a period of one month without significant change of the potentiometric properties. The electrodynamic properties of these films have also been unchanged, which indicate that the films are chemically stable, and do not degrade during ageing.

EDAX measurements. PPy(calmagite) films for EDAX measurements were prepared on Pt sheets in the same way as described. The films were conditioned for minimum three days and rinsed thoroughly with water before the EDAX measurements were performed.

RESULTS AND DISCUSSION

Calmagite belongs to the group of metallochromic indicators and forms complexes with Ca^{2+} , Mg^{2+} and Cu^{2+} . The complexation is pH dependent and the stability of the different complexes varies with pH, as shown in Figure 1. The calculations presented are based on the protonation and stability constants given in the literature [17,18]. From this figure it can be seen that calmagite forms the strongest complex with Cu^{2+} and that the complexation with Ca^{2+} and Mg^{2+} requires pH above 8 to form a

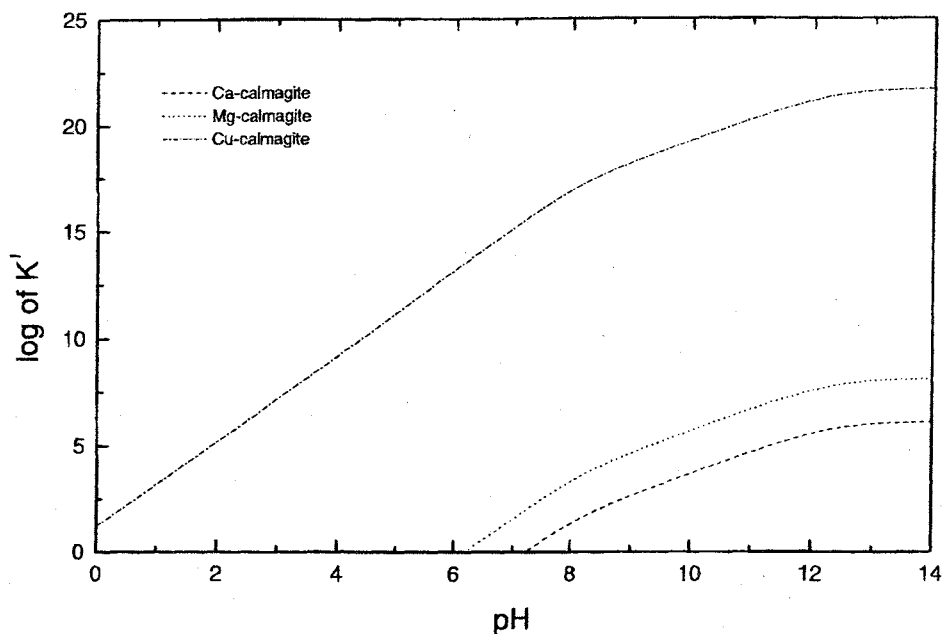


Figure 1. The pH dependence for complexation between calmagite- Ca^{2+} , calmagite- Mg^{2+} and calmagite- Cu^{2+} . Log K' is used as defined by Ringbom and Wänninen [17]

stable complex. According to this, pH of the conditioning solutions was adjusted to a value favourable for complexation.

Potentiometric response

The potentiometric response for each electrode, toward the specific cation, was measured daily during a period of five days. Before the calibration started the electrodes were conditioned for three days in a solution containing the ion of interest. Between the measurements, the electrodes were conditioned in the same solutions. In order to examine the response towards Ca^{2+} , the conditioning and calibration solution was CaCl_2 . The conditioning solution was of 0.1 mol l^{-1} concentration and the calibration was performed in the concentration range from 10^{-5} to $10^{-1} \text{ mol l}^{-1}$. As the complexation calmagite- Ca^{2+} is pH dependent, two different pH values of the conditioning solutions were used, pH 5.2 and pH 10.2. Cationic sensitivity of the films should be expected after soaking in the alkaline solution as was shown before by Migdalski *et al.* [15].

The response curves, potential vs activity of Ca^{2+} , clearly prove that pH is of great importance for the complexation. In Figure 2a the electrode was conditioned in CaCl_2 of pH 5.2 which is below the pH required for predominant complex formation. This resulted in a "close-to-zero" slope of the calibration curves of the films, obviously

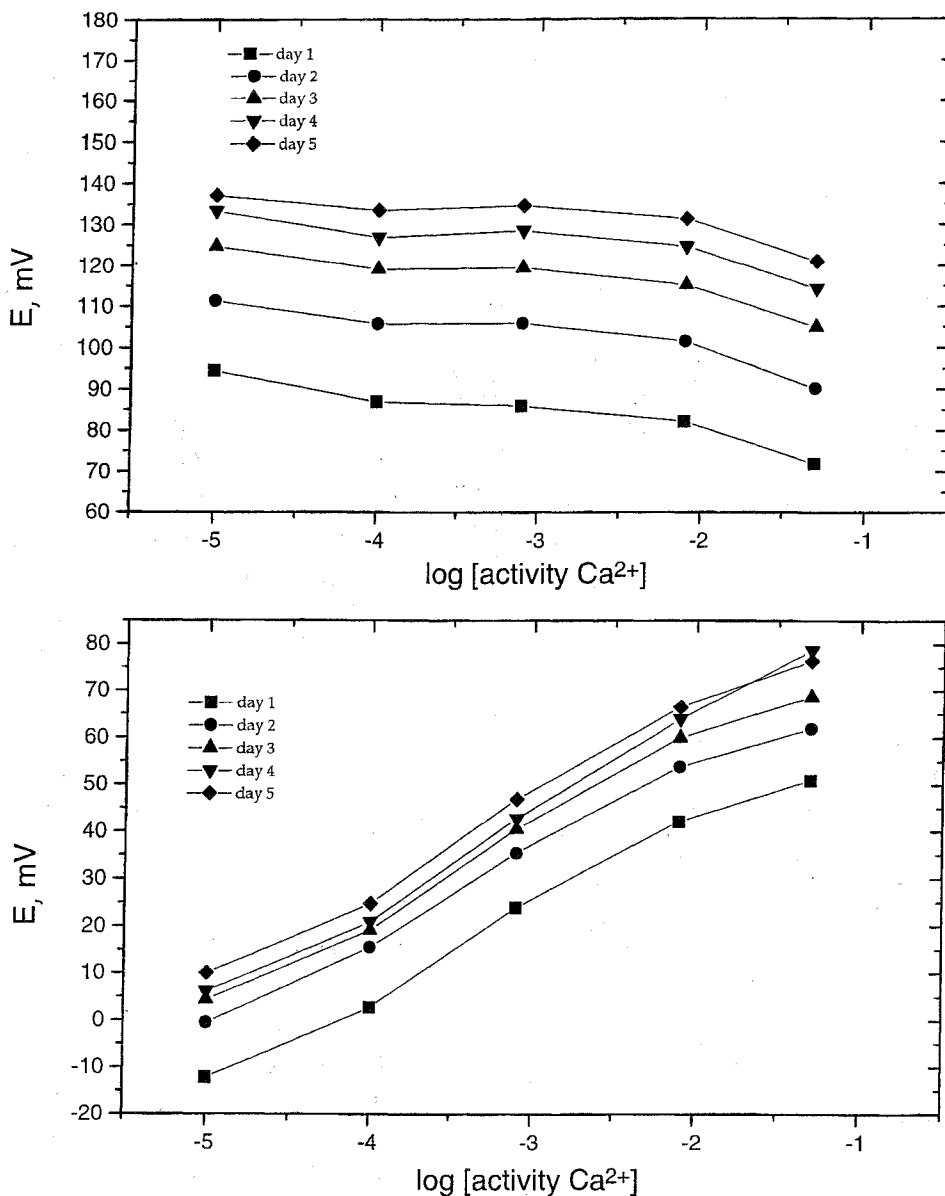


Figure 2. Potentiometric response of a PPy(calmagite) film in CaCl₂. The response was measured daily during five days; the electrode had been conditioned in 0.1 mol l⁻¹ CaCl₂ of pH 5.2 (a) and 10.2 (b) for three days before the response was measured; the electrode was also conditioned between measurements

due to compensating effects of anions and cations in the signal formation process. When the electrode was conditioned in the same solution but with pH adjusted to 10.2 (with CaO) the films gave the response of about 20 mV/dec for Ca²⁺; see Figure 2b. (The

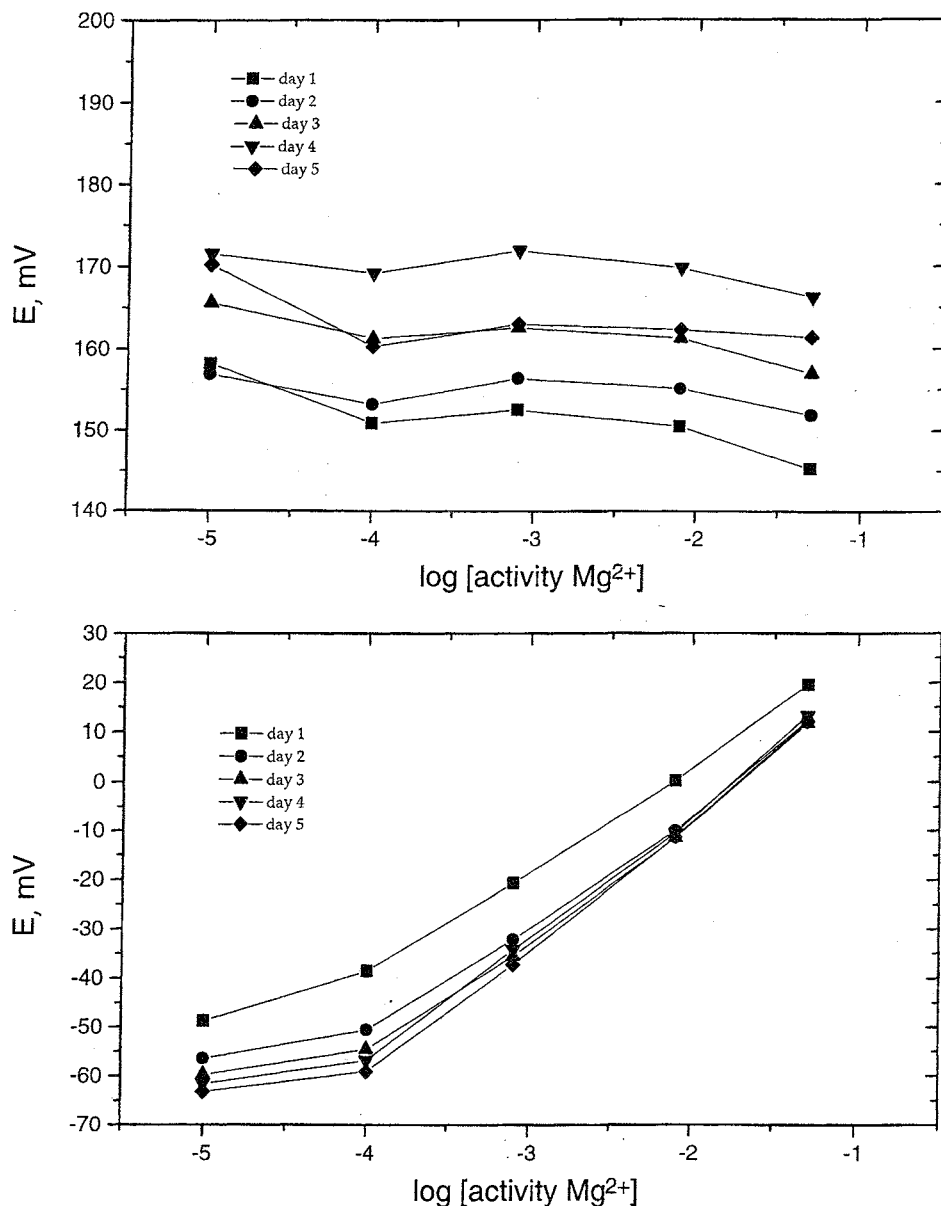


Figure 3. Potentiometric response of a PPy(calmagite) film in $\text{Mg}(\text{NO}_3)_2$. The response was measured daily during five days; the electrode had been conditioned in $0.1 \text{ mol l}^{-1} \text{ Mg}(\text{NO}_3)_2$ of pH 6.5 (a) and 9.5 (b) for three days before the response was measured; the electrode was also conditioned between measurements

theoretical Nernstian response for divalent cations is 29.6 mV/dec). The calibration of PPy(calmagite) electrode was also performed in the solutions containing Mg^{2+} and Cu^{2+} ions.

In Figure 3 the results for conditioning and measuring in $\text{Mg}(\text{NO}_3)_2$ are shown. Here also two different pH values of the conditioning solution were tested. In Figure 3a the electrode was conditioned in $0.1 \text{ mol l}^{-1} \text{ Mg}(\text{NO}_3)_2$ of pH 6.5, and this procedure apparently did not result in cationic sensitivity. When the pH of the conditioning solution was adjusted to 9.5 (with MgO) the calibration curves for the electrode had slopes of an average of 23.6 mV/dec in the whole concentration range, and of 28.6 mV/dec in the concentration range 10^{-1} to $10^{-4} \text{ mol l}^{-1}$. The slopes were calculated similarly as for Ca^{2+} , and they are apparently higher compared with Ca^{2+} . Assuming, as above, a significant influence of cation complexation on the potentiometric sensitivity of the polymer film, the increase of slope may be explained by the fact that calmagite forms a stronger complex with magnesium than with calcium.

The PPy(calmagite) films showed good sensitivity to copper ions as well. Linear potentiometric response, with close to Nernstian slope of the calibration curves (30 mV/dec) in the concentration range from 10^{-1} to $10^{-4} \text{ mol l}^{-1}$, was observed (Fig. 4). This behaviour is predicted by the theory [15], since calmagite forms a strong complex with Cu^{2+} , even in the $0.1 \text{ mol l}^{-1} \text{ CuSO}_4$ conditioning solution where pH was 4.5 (Fig. 1).

The same films were used for calibration against the different ions for a time-period of one month. The electrodes exhibited good stability, *i.e.* standard potential and slope, and performed without "memory-effects".

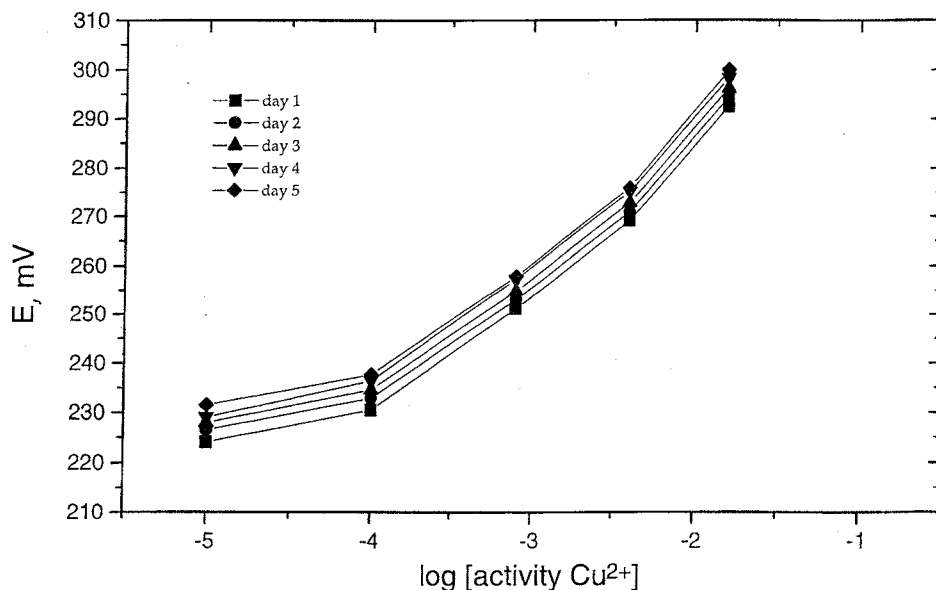


Figure 4. Potentiometric response of a PPy(calmagite) film in CuSO_4 . The response was measured daily during five days; the electrode had been conditioned in $0.1 \text{ mol l}^{-1} \text{ CuSO}_4$ of pH 4.5 (a) for three days before the response was measured; the electrode was also conditioned between measurements

If the films are prepared in a proper way it is possible to use the same films for different ions. It is important here that the films have to be conditioned in the solution containing the appropriate ions and proper pH before calibration is performed. It seems that the conditioning for three days before calibration is sufficient to induce analytically useful sensitivity of the electrodes.

pH response curve

The potential for a PPy(calmagite) film as a function of pH was measured in 10^{-2} mol l⁻¹ CaCl₂. pH was adjusted with HCl and NaOH. From the response curve, shown in Figure 5, it can be seen that the measured potential is independent of pH in the interval 6 to 9. This assures that the obtained potentiometric responses are due to change in concentration/activity of the main ion in this pH range, and possible parasitic processes resulting in mixed potential are suppressed.

Influence of anion

The influence of the anion was checked by measuring the electrode response in the presence of different anions. In these measurements, the polypyrrole films doped with calmagite were used, and similar potentiometric responses were obtained in Mg-nitrate, Mg-chloride and Mg-acetate, which shows that the response is purely cationic. The same results were observed for the films doped with Eriochrome Black T prepared under the same conditions as described for PPy(calmagite) films.

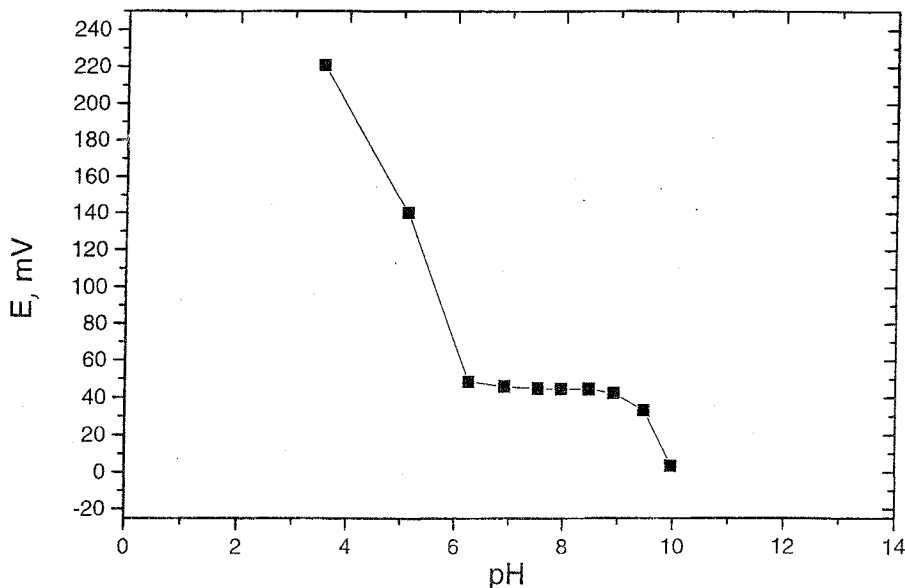


Figure 5. pH response curve of a PPy(calmagite) film in 10^{-2} mol l⁻¹ CaCl₂. pH was adjusted with HCl and NaOH; the electrode had been conditioned in 10^{-1} mol l⁻¹ CaCl₂ of pH 10.8 before the potential was measured

EDAX spectroscopy for PPy(calmagite) films

To prove that the complexation occurs between calmagite incorporated in the polypyrrole matrix, and Ca, Mg and Cu, the films were analysed with EDAX spectroscopy. The films were allowed to condition in 0.1 mol l⁻¹ solutions of CaCl₂, Mg(NO₃)₂ and CuCl₂ for minimum three days before they were analysed. For CaCl₂ and Mg(NO₃)₂ different pH of the conditioning solutions were used and, as the spectra in Figure 6 show, the indicator needs the appropriate pH surrounding to complex

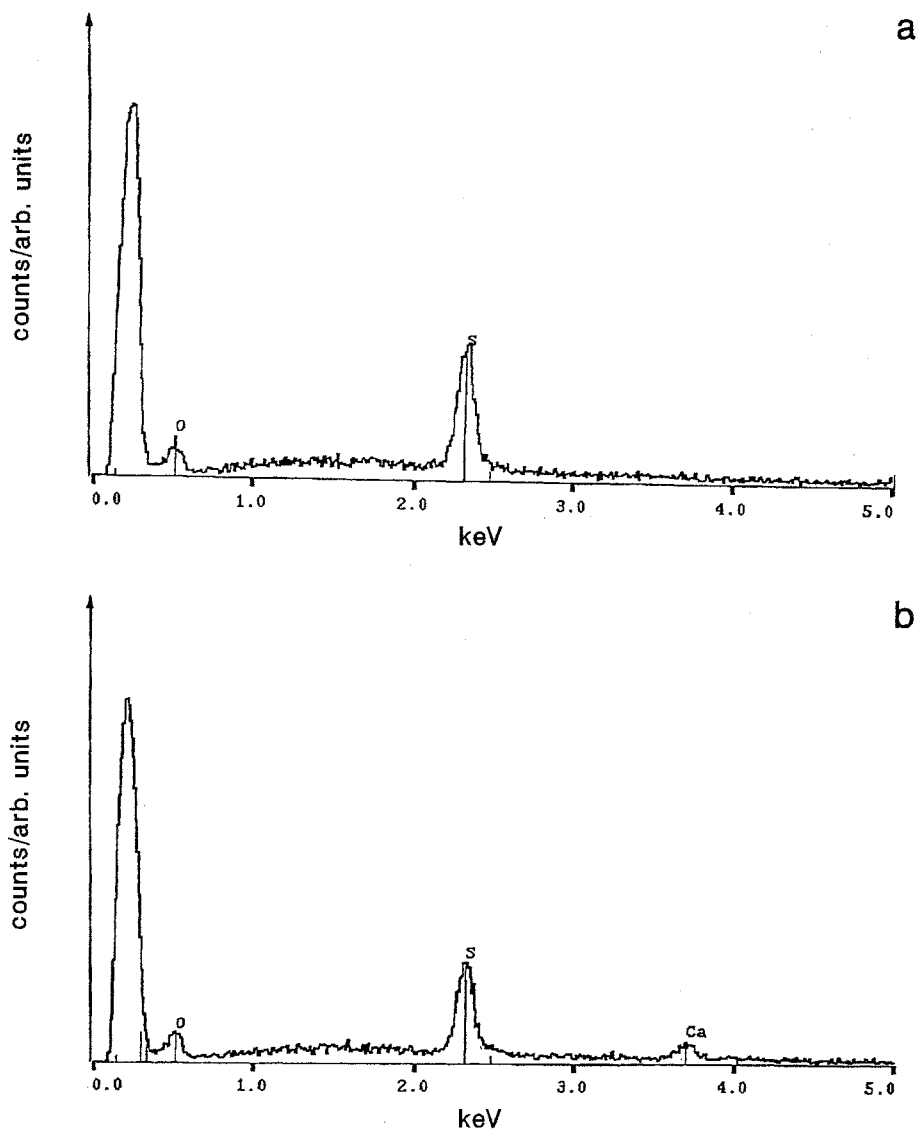


Figure 6.

the metal ion. When the film was conditioned in CaCl_2 of pH 6.4 no Ca^{2+} was complexed by calmagite (Fig. 6a) whereas when pH was 10.2 a peak for Ca^{2+} could be seen in the spectra (Fig. 6b). For the films conditioned with $\text{Mg}(\text{NO}_3)_2$ of pH 5.7 and 9.5 the results were very similar (Fig. 6c and d). Cu^{2+} on the other hand was visible in the spectra when the film was conditioned in pH 4.5 (Fig. 6e). The sulphur peak in all spectra originates from the indicator.

These results verify that the indicator is incorporated in the polypyrrole film and that a complex between the indicator and the specific cations is formed.

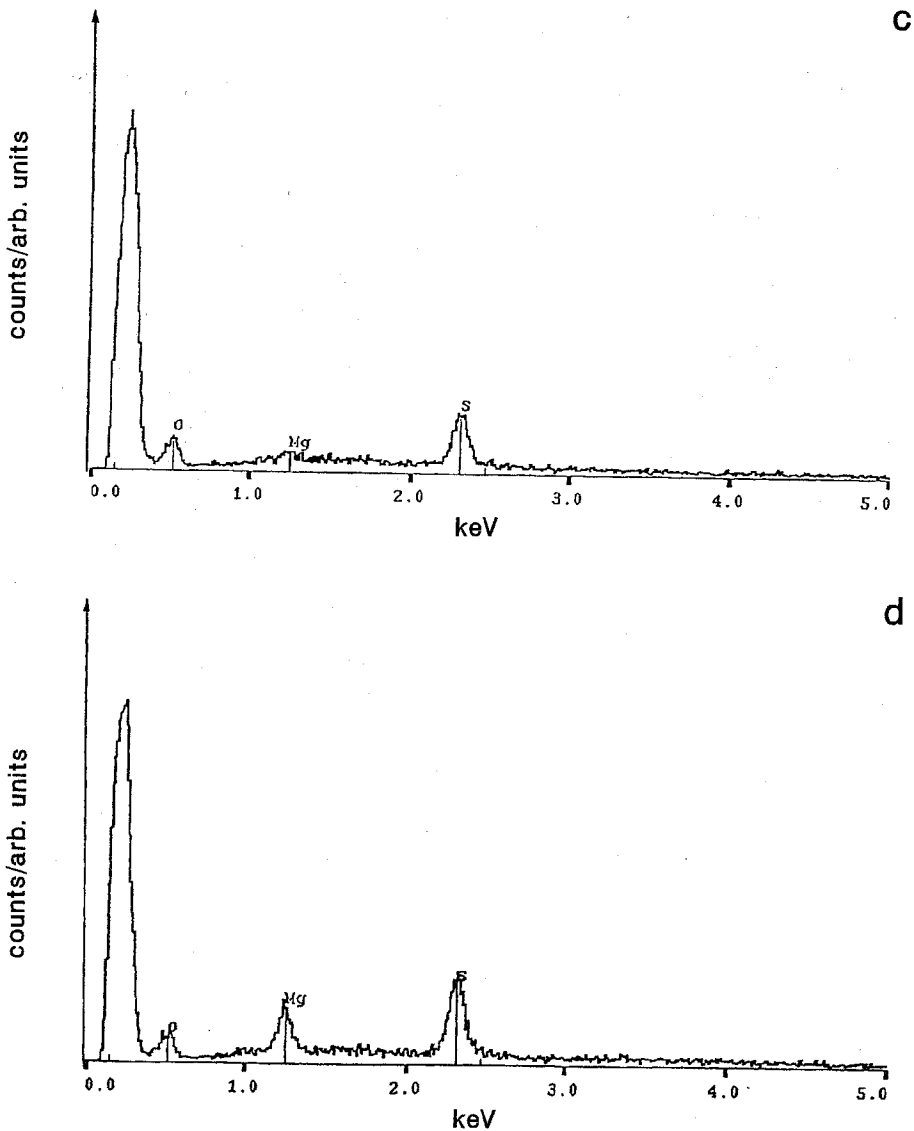


Figure 6.

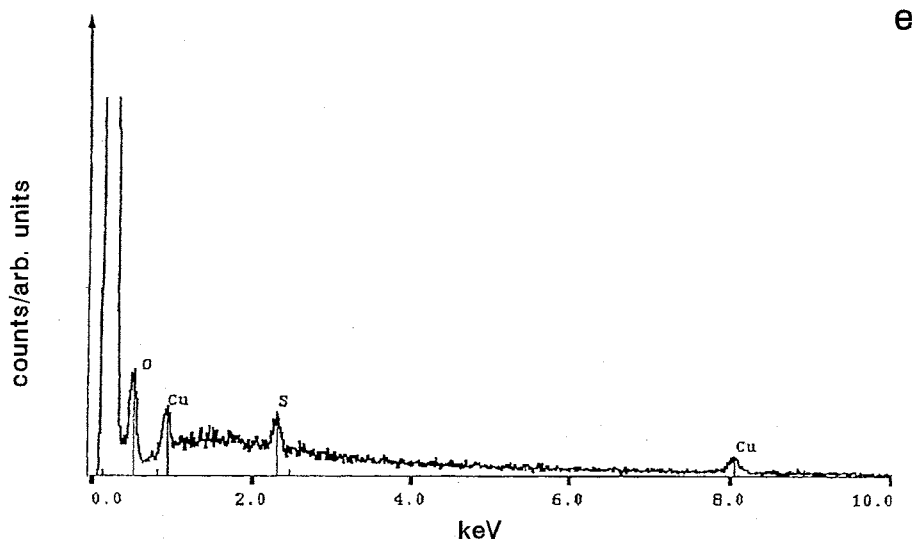


Figure 6. EDAX spectra of PPy(calmagite) films. The films had been conditioned in 0.1 mol l^{-1} solutions of a) CaCl_2 of pH 6.4, b) CaCl_2 of pH 10.2, c) $\text{Mg}(\text{NO}_3)_2$ of pH 5.7, d) $\text{Mg}(\text{NO}_3)_2$ of pH 9.5 and e) CuCl_2 of pH 4.5

CONCLUSIONS

This study shows that polypyrrole films doped with the metallochromic indicator calmagite worked well as potentiometric sensors. For magnesium and copper near Nernstian slopes were obtained. Calmagite was easily incorporated as the doping ion in the polymer film during electropolymerisation and the response of the films was stable and the same films could be used for quite a long period of time. The EDAX results prove the presence of the indicator in the film as well as the complexation between calmagite and the metal ions.

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REFERENCES

1. Evans G.P., *Advances in Electrochemical Science and Engineering*, [Gerischer C. W., Tobias, Eds], VCH New York 1990, p. 1-74.
2. Michalska A., Ivaska A. and Lewenstam A., *Anal. Chem.*, **69**, 4060 (1997).
3. Dong S., Sun Z. and Lu Z., *Analyst*, **113**, 1525 (1988).
4. Lu Z., Sun Z. and Dong S., *Electroanalysis*, **1**, 271 (1989).
5. Cadogan A., Lewenstam A. and Ivaska A., *Talanta*, **39**, 617 (1992).
6. Lewenstam A., Bobacka J. and Ivaska A., *J. Electroanal. Chem.*, **368**, 23 (1994).
7. Bobacka J., Gao Z., Ivaska A. and Lewenstam A., *J. Electroanal. Chem.*, **368**, 33 (1994).
8. Jovanovic V.M., Markicevic L., Stankovic S., Stankovic R. and Jovanovic M.S., *Electroanalysis*, **7**, 574 (1995).
9. Michalska A., Lewenstam A., Ivaska A. and Hulanicki A., *Electroanalysis*, **5**, 261 (1993).
10. Okada T., Hayashi H., Hiratani K., Sugihara H. and Koshizahi N., *Analyst*, **116**, 923 (1991).
11. Okada T., Hiratani K., Sugihara H. and Koshizahi N., *Anal. Chim. Acta*, **266**, 89 (1992).
12. Gao Z., Bobacka J., Lewenstam A. and Ivaska A., *Electrochim. Acta*, **39**, 755 (1994).
13. Gao Z., Bobacka J., Lewenstam A. and Ivaska A., *Synth. Met.*, **62**, 117 (1994).
14. Lewenstam A., Michalska A. and Ivaska A., *Chem. Anat. (Warsaw)*, **40**, 587 (1995).
15. Migdalski J., Blaz T. and Lewenstam A., *Anal. Chim. Acta*, **322**, 141 (1996).
16. Morf W.E., *The Principles of ion-selective electrodes and membrane transport*, Akademiai Kiado, Budapest 1981.
17. Ringbom A. and Wänninen E., reprinted from *Indicators*, [E. Bishop, Ed.], Pergamon Press-Oxford & New York 1973.
18. Hulanicki A., Głab S. and Ackermann G., *Pure and Applied Chem.*, **55**, 1137 (1983).

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