

Electrochimica Acta 44 (1999) 2543-2548



Thiocyanate-selective PVC membrane electrodes based on Mn(II) complex of N,N'-bis-(4-phenylazosalicylidene) *o*-phenylene diamine as a neutral carrier

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Received 9 June 1998; received in revised form 16 September 1998; accepted 1 October 1998

Abstract

A series of transition metal chelates of N, N'-bis-(4-phenylazosalicylidene) o-phenylene diamine (H₂L) were synthesized and their anion response characteristics were investigated. The results show that the behavior of the electrode is considerably influenced by the properties of the central metals. A novel electrode prepared with the Mn(II) chelate exhibited a linear response towards thiocyanate over the concentration range of $0.1-7.02 \times 10^{-6}$ M in phosphate buffer solutions of pH 5.38 with a slope of -57.3 mV per decade, the electrode anti-Hofmeister selectivity demonstrated behavior; the selectivity sequence observed was: an thiocyanate > todide > todidElectrodes based on the Co(II) chelate demonstrated a preferential response to iodide ion. Electrodes based on the Hg(II) and Ni(II) chelates had weak anion response characteristics. The response mechanism was also investigated by use of impedance and spectroscopic techniques and the influence on the electrode performances by lipophilic charged additives. The electrodes were applied to the determination of thiocyanate in wastewater with satisfactory results. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Potentiometry; Thiocyanate-selective electrodes; N,N'-bis-(4-phenylazosalicylidene) o-phenylene diamine; Neutral carrier; Ionophores

1. Introduction

The conventional anion-selective electrodes based on quaternary ammonium or phosphonium salts always display the so-called Hofmeister selectivity pattern: $ClO_4^- > SCN^- > I^- > NO_3^- > Br^- > NO_2^- > Cl^- > SO_4^{2-}$ [1]. Since the 1980's, research on anti-Hofmeister anion selective membrane electrodes have been more and more interested. Recently, electrodes based on derivatives of vitamin B₁₂ or on transitional metal complexes of porphyrin and phthalocyanine [2–8] have been reported. These electrodes demonstrated potentiometric anion selectivity sequences apparently deviating from the Hofmeister sequence. These deviations result from the unique interactions of the central metals with anions rather than from the hydration free energy and the relative solubility of the individual anions in the solvent mediator. The research on new carriers for the improvement of the potentiometric response characteristics of these electrodes continues to attract widespread interest in order to be applied for the analysis of anions in biological samples. The transitional metal chelates of some Schiff bases were also used as neutral carriers in anion selective membrane electrodes. These

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electrodes always show preferential response to iodide [9-12]. Because of the convenient preparation of these compounds, they are expected to be excellent anion ionophores in ISEs and to accelerate the development of novel anion carriers. In this work, we report the anion response behavior of four transition metal chelates of a new Schiff base, N,N'-bis-(4-phenylazosalicylidene) o-phenylene diamine. The results show that the Mn(II) chelate-based electrodes demonstrate a highly specific response towards thiocyanate. Meantime we underline the importance of lipophilic ionic additives, as well as endogenous ionic impurities on the potentiometric response characteristics and selectivity. It is obvious that anion exchangers are needed for thiocyanate-selective electrodes based on the Mn(II) chelate of H_2L .

2. Experimental

2.1. Reagents and materials

For all experiments, doubly distilled water was used. Dodecyltrioctylammonium iodide (DTOAI) was prepared according to the literature method [13]. Tetrahydrofuran, Dioctyl phthalate (DOP) and chromatographic-grade poly(vinyl chloride) (PVC) were purchased from Shanghai Chemicals (Shanghai, People's Republic of China). The ligand and its chelates of transition metals were synthesized in this laboratory, they were characterized by elemental analysis.

2.2. Apparatus

The PVC membrane electrodes were fabricated from various carriers and assembled according to Thomas et al. [14, 15]. Before use, the electrodes were conditioned in 0.1 M sodium thiocyanate aqueous solution for 24 h. Potentiometric and pH measurements were made with a model PHS-3E digital ion analyzer (Jiangshu Instruments). The cells for millivolt measurements were of the following type:

Hg – Hg₂Cl₂|KCl (satd.)|sample solution||membrane|| 0.01 M KCl|AgCl – Ag.

The impedance of the electrode membrane was recorded with a PAR M386-2 System (EG and G Princeton Applied Research) in KH_2PO_4 -Na₂HPO₄ buffer at pH 5.38. The frequency region used was from 10^5 to 10^{-2} Hz (25°C).

Elemental analysis was made with a Heraeus C-H-N-O-S Rapid elemental analyzer (Germany). UV-VIS absorption spectra were recorded on a Lambda 17 UV-VIS spectrophotometer (Perkin-Elmer Norwalk, CT, USA). Chloroform was employed as solvent.

2.3. Synthesis of N,N'-(4-phenylazosalicylidene) ophenylene diamide (H_2L)

To a solution of 4.43 cm³ of freshly distilled aniline (0.05 mol) in 18 cm³ of concentrated hydrochloride and 20 cm³ of water, was added 4.00 g of sodium nitrite (0.10 mol) in 20 cm³ of water, the reaction was carried out for 1 h below 5°C. The reaction mixture was then added to a solution of 18 g of sodium carbonate (0.17 mol) and 5.24 cm³ of salicylaldehyde in 150 cm³ of water, the reaction temperature was remained within $0-5^{\circ}$ C. The yellow precipitate was filtered off after 1 h and recrystallized from ethanol. The above product (2.26 g, 0.01 mol) refluxed with ethylene diamine (0.30 g, 5.0 mmol) in 50 cm³ of absolute alcohol for 2 h with stirring to give a golden yellow solid which was purified by recrystallization from alcohol. Melting point: 224–226°C.

2.4. Synthesis of the Hg(II), Co(II), Mn(II) and Ni(II) chelates of H_2L

M(II)L were prepared as follows: a solution of $M(OAc)_2$ (5.5 mmol) in absolute ethanol was added into an absolute ethanol solution containing H_2L (5.0 mmol). The reaction mixture was refluxed for 2 h. After cooled to the room temperature and stand overnight, the chelates obtained were filtered, washed with absolute alcohol and dried in vacuum. Melting point: > 350°C (dec.). Tables 1 and 2.

3. Results and discussion

3.1. Response characteristics of the electrodes

The structures of the carriers studied are shown in Fig. 1, and potentiometric response characteristics of the electrodes assembled with the different membranes are shown in Fig. 2. The electrodes assembled with membrane 4 show a linear response towards thiocyanate over the concentration range of $0.1-7.0 \times 10^{-6}$ M in a KH₂PO₄-Na₂HPO₄ buffer solution at pH 5.38 with a slope of -57.3 mV/dec., the electrodes assembled with membrane 1 and 2 exhibit similar response behavior to thiocyanate, the linear response range is $0.1-4.51 \times 10^{-5}$ and $0.1-4.16 \times 10^{-5}$ M, respectively, the slope is -53.8 and -55.6 mV/dec., respectively. The electrodes assembled with membrane 3 display a linear response towards thiocyanate ranging from $0.1-2.81 \times 10^{-4}$ M with a slope of -49.0 mV/ dec., the results show that the potentiometric response characteristics of these electrodes assembled with different membranes are considerably influenced by the component of the membrane phases, the potentiometric response characteristics deteriorate to some

No.	Formula	Yield (%)	Color	Elemental analysis (%) ^a			
				C	Н	N	
1	C ₂₈ H ₂₄ N ₆ O ₂	49	golden yellow	70.43 (70.57)	5.38 (5.08)	17.62 (17.64)	
2	$C_{28}H_{22}HgN_6O_2$	75	orange	50.06 (49.82)	3.41 (3.28)	12.81 (12.45)	
3	$C_{28}H_{22}CoN_6O_2$	80	brown	63.42 (63.04)	4.48 (4.16)	15.37 (15.75)	
4	$C_{28}H_{22}MnN_6O_2$	68	blackish green	63.97 (63.52)	4.32 (4.19)	15.49 (15.87)	
5	$C_{28}H_{22}N_6NiO_2$	74	red	63.37 (63.07)	4.47 (4.16)	15.67 (15.76)	

Table 1 Elemental analysis of the ligand and its transitional metal chelates

^a Calculated values are given in parentheses.

 Table 2

 Composition of membrane phases (wt%) for thiocyanate-selective PVC membrane electrodes

Component	Membrane 1	Membrane 2	Membrane 3	Membrane 4
Carrier (MnL)	3.82	3.82	3.81	3.81
PVC	30.53	15.27	30.44	30.44
PVC-OH	-	15.27	_	_
NaTPB	_	_	0.30	and as
DTOAI	_	_	_	0.30
DOP	65.65	65.45	65.64	65.45

extent as the lipophilic anion additive (e.g. sodium tetraphenylborate) is incorporated into the PVC membrane. On the other hand, the cation additive (e.g. dodecyltrioctylammonium iodide) improves the potentiometric properties of anion-selective electrodes. This is in accordance with the results reported previously that the cationic sites in neutral carrier-based electrodes can stabilize the formation of the negatively charged product (MnL-SCN⁻) in the membrane phase as well as lower the electrical membrane resistance, improve the potentiometric response characteristics of the membrane electrodes [16-19]. The incorporation of hydroxyl PVC into the membrane phase has less influence on the potentiometric properties, but the decrease in stability of potential readings. The standard deviation of potential readings of the electrodes assembled with membrane 4 is 0.78 mV (n = 24) in 0.001 M sodium thiocyanate buffered with KH₂PO₄-Na₂HPO₄ to a pH 5.38 over a period of 4 h. The potential readings for the same electrodes dipped alternatively into

stirred solutions of 1.0×10^{-3} and 1.0×10^{-4} M sodium thiocyanate show a standard deviation of 1.0 mV over 4 h (n = 12). The response time ($t_{90\%}$) is less than 10 s in the linear response range, that implies the reversible anion exchange is rapid, these novel prepared electrodes do not display any hysteresis effects. Detectable loss of performance characteristics has not been found after these electrodes have been used for 2 months. The potentiometric response characteristics are closely correlated to the properties of the central metals. The Co(II) chelate-based electrodes demonstrate preferential response to iodide, while the electrodes based on the chelates of Hg(II) and Ni(II) show quite weak response to anions.

3.2. Effect of pH on response characteristics of the membrane electrodes

The pH dependence of the electrode potential response is shown in Fig. 3. The increasing interference



Fig. 1. The structures of the carriers studied. 1, M is Hg(II), 2, Co(II), 3, Mn(II) and 4, Ni(II).



Fig. 2. Potentiometric response to thiocyanate for the electrodes assembled with various membranes: (\blacksquare) membrane 1, (\bullet) membrane 2, (\blacktriangle) membrane 3 and (\triangledown) membrane 4.

from hydroxide at higher pH (>7) results in a narrower linear response range with a concomitant decrease in the response slope. The effect of pH is negligible at lower pH (4–6.5) and a near-Nernst response towards thiocyanate is observed. The working pH for the determination of thiocyanate is pH 5.38. The effect of pH on the response characteristics can be explained by coordination competition between thiocyanate and hydroxide. This is in accordance with the results of pH effect on potential response in anion-selective electrodes as reported previously [20].

3.3. Selectivity of the electrodes

Possible interferences from a number of monovalent anions were studied. Anion selectivity coefficients,



Fig. 3. Potentiometric response of an electrode assembled with membrane 4 at different pH. (•) pH 4.28, (\blacksquare) pH 5.38, (\blacktriangle) pH 6.24 and (\bigtriangledown) pH 7.50.

log $K_{A,B}^{\text{pol}}$ were determined by the separate solution method according to IUPAC recommendations and were obtained with the respective 0.1 M solutions of sodium salts [21]. The single ion activities were calculated by the extended Debyl-Hückel equation. Generally, the most thiocyanate-selective electrodes based on quaternary ammonium and some Mn(III), Sn(IV) metalloporphyrin species suffered from the interference of strongly lipophilic anions such as perchlorate, salicylate and iodide. Some anion-selective electrodes which have improved selectivity for thiocyanate over the above anions must be developed to be used in actual samples [22–26]. The results shown in Table 3 indicate that the new electrodes based on the Mn(II) chelate of H₂L and cationic sites demonstrate

Table	3
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Selectivity coefficients, log $K_{A,B}^{pot}$ for electrodes assembled with different membrane phases

Anion	Α	В	Membrane 1	Membrane 3	Membrane 4
Thiocyanate	0.0	0.0	0.00	0.00	0.00
Iodide	-0.2	0.2	-1.13	-1.00	-1.34
Salicylate	-0.3	0.8	-1.26	-0.86	-1.44
Benzoate	-	-	-2.03	-1.23	-2.28
Perchlorate	1.6	0.2	-2.19	-1.47	-1.40
Nitrite	_	-	-2.61	-2.02	-3.12
Bromide	-2.4	-1.0	-3.02	-2.42	-4.05
Acetate	-	_	-3.70	-2.80	-4.61
Nitrate	-	-	-3.84	-2.96	-4.59
Chloride	-3.0	-1.3	-4.26	-2.94	-4.84

A and B are quaternary ammonium salt and metalloporphyrin species in Ref. [19].



Fig. 4. UV–VIS absorption spectra of chloroform solutions of Hg(II)L (a) and Hg(II)L treated with 0.1 M NaSCN solution (b).

excellent selectivity towards thiocyanate. A selectivity sequence of anions in the following order is observed: thiocyanate > iodide > salicylate > benzoate > perchlorate > nitrite > bromide > acetate > nitrate > chloride. The most striking feature of these data is the apparent relationship between the selectivity and the charged ionic additives, the addition of mobile anion exchange sites in the electrodes assembled with membrane 4 is shown to be favorable to the potentiometric selectivity. These results can be well explained by the theoritical model for neutral carrier-based electrodes given by M.E. Meyerhoff [16].

3.4. UV-VIS spectra of the chloroform solutions containing the carriers treated with and without 0.1 M NaSCN solution

The preferential response towards thiocyanate is believed to be associated with the coordination of thiocyanate with the central metals of the carriers. In order to investigate the interactions between anions and the central metals. UV–VIS spectra of the chloroform solutions containing the carriers (0.001 M) are



Fig. 5. UV–VIS absorption spectra of chloroform solutions of Mn(II)L (a) and Mn(II)L treated with 0.1 M NaSCN solution (b).

compared with that of the same solutions treated with 0.1 M NaSCN solution for 2 h (see Figs. 4 and 5). Obvious changes are observed in UV–VIS spectra of the chloroform solution containing Mn(II)L after treated with 0.1 M NaSCN solution, it can be due to the unique interactions between the central metal Mn(II) and thiocyanate ion which may result in the anti-Hofmeister behavior of the Mn(II)L-based electrodes. No detectable changes in UV–VIS spectra of the chloroform solution containing Hg(II)L are noted after treated with 0.1 M NaSCN solution for 2 h. It can be due to the weak interactions between the central metal Hg(II) and anions that explains the quite weak potentiometric response characteristics towards anions for the Hg(II)L-based electrodes [9, 11].

4. Analytical applications

The electrodes based on the Mn(II) chelate of H_2L were found to be useful in the potentiometric determination of thiocyanate in wastewater. The samples were treated previously according to the literature

Table 4

Comparison of the results of electrode (n = 3) and HPLC methods for the detection of thiocyanate concentration (mM) in waste-water

Method	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Electrode	0.75	1.11	1.17	1.94	3.20	3.48
HPLC	0.78	1.07	1.15	1.88	3.24	3.51

method [27]. The results obtained by electrode method (n = 3) are in good accordance with the results by HPLC (see Table 4), the relative deviation is less than 3.2%. It indicates that the novel electrodes can be applied for the determination of thiocyanate in actual samples with satisfactory results.

5. Conclusion

The anion selectivity behavior of electrodes based on transitional metal chelates of N,N'-bis-(4-phenylazosalicylidene) o-phenylene diamine is closely related to the properties of the central metals. The Co(II) chelatebased electrodes demonstrate preferential response towards iodide. The Hg(II) and Ni(II) chelate-based electrodes exhibit quite weak anion potentiometric response. The Mn(II) chelate-based electrodes show highly selective response towards thiocyanate. The influence of ionic sites on the behavior of the Mn(II) chelate-based electrode is described. The cation exchanger, sodium tetraphenylborate is harmful to the response characteristics of the electrodes. On the other hand, the anion exchanger, dodecyltrioctylammonium iodide, proved to be a beneficial additive for thiocyanate-selective electrodes. The incorporation of the anion exchanger clearly improves the potential response characteristics, (i.e. the linear response range, the slope and the selectivity). This behavior leads us to presume that the Mn(II) chelate-based electrodes show a highly specifically response towards thiocyanate via a neutral carrier mechanism [16-19].

Acknowledgements

This work was supported by the Chinese National Education Committee for Ph.D. thesis research. Natural Science Foundation of Hunan Province and the Foundation for the Technological Development of Machinery Industry.

References

[1] F. Hofmeister, Arch. Exp. Pathol. Pharmakol. 24 (1888) 247.

- [2] S. Daunert, L.G. Bachas, Anal. Chem. 61 (1989) 499.
- [3] P. Schulthess, D. Ammann, B. Kräutler, C. Caderas, R. Stepinek, W. Simon, Anal. Chem. 57 (1985) 1397.
- [4] R. Stepinek, B. Kräutler, P. Schulthess, B. Lindemann, D. Ammann, W. Simon, Anal. Chim. Acta. 182 (1986) 83.
- [5] D. Gao, J.Z. Li, R.Q. Yu, Anal. Chem. 66 (1994) 2245.
- [6] S. Daunert, S. Wallace, A. Florido, L.G. Bachas, Anal. Chem. 63 (1991) 1676.
- [7] J.Z. Li, X.C. Wu, R. Yuan, H.G. Lin, R.Q. Yu, Analyst 119 (1994) 1363.
- [8] M. Rothmaier, W. Simon, Anal. Chim. Acta. 271 (1993) 135.
- [9] M. Ying, R. Yuan, X.M. Zhang, Y.Q. Song, Z.Q. Li, G.L. Shen, R.Q. Yu, Analyst 122 (1997) 1143.
- [10] Z.Q. Li, R. Yuan, M. Ying, G.L. Shen, R.Q. Yu, Anal. Lett. 30 (1997) 1455.
- [11] R. Yuan, R.Q. Yu, Anal. Chem. 65 (1993) 2572.
- [12] Y.Q. Song, R. Yuan, M. Ying, Z.Q. Li, G.L. Shen, R.Q. Yu, Fresenius J. Anal. Chem. 360 (1998) 47.
- [13] R.Q. Yu, S.S. Huang, Talanta 30 (1983) 427.
- [14] G.J. Moody, R.B. Oke, J.D.R. Thomas, Analyst 95 (1970) 910.
- [15] A. Craggs, G.J. Moody, J.D.R. Thomas, J. Chem. Educ. 51 (1974) 541.
- [16] E. Bakker, E. Malinowska, R.D. Schiller, M.E. Meyerhoff, Talanta 41 (1994) 881.
- [17] R. Eugster, P.M. Gehrig, W.E. Morf, U.E. Spichiger, W. Simon, Anal. Chem. 63 (1991) 2285.
- [18] U. Schaller, E. Bakker, U.E. Spichiger, E. Pretsch, Anal. Chem. 66 (1994) 391.
- [19] P.C. Meier, W.E. Morf, M. Läubli, W. Simon, Anal. Chim. Acta. 156 (1984) 1.
- [20] Z.R. Zhang, R.Q. Yu, Anal. Chim. Acta. 285 (1994) 81.
- [21] IUPAC, Recommendation for nomenclature of ion-selective electrodes, Pure Appl. Chem. 48 (1976) 129.
- [22] M. Huser, W.E. Morf, K. Fluri, K. Seiler, P. Schulthess, W. Simon, Helv. Chim. Acta. 73 (1990) 1481.
- [23] D. Ammann, M. Huser, B. Krautler, B. Rusterholz, P. Schulthess, E. Halder, W. Simon, Helv. Chim. Acta. 69 (1986) 849.
- [24] N.A. Chaniotakis, A.M. Chasser, M.E. Meyerhoff, Anal. Chem. 60 (1988) 185.
- [25] D.V. Brown, N.A. Chaniotakis, I.H. Lee, S.C. Ma, S.B. Park, M.E. Meyerhoff, J.T. Groves, Electroanalysis 1 (1989) 477.
- [26] T.Y. Bart, A.B. Valiotti, I.A. Sikorova, I.V. Shashkina, J. Appl. Chem. USSR 65 (1992) 446.
- [27] T. Korenaga, Mikrochim. Acta. II (1979) 455.