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Novel triiodide ion-selective polymeric membrane electrodes based on some transition metal–Schiff base complexes

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Abstract

We studied Mn(II) and copper(II) complexes of Schiff bases (with different spacers between the two nitrogens in bis-*N*,*O*-bidentate Schiff base) as ionophores in polymeric membranes of anion selective electrodes. The potentiometric selectivity of the ion selective electrodes (ISEs) based on metalloSchiff bases was significantly dependent on both the nature of the central atom and the spacer between two nitrogens in imine groups. The electrode based on a *N*,*N*′-1,2-propylene-bis-(5-methyl salicylidene iminato) copper(II) complex, **A1**, exhibited a near Nernstian response of 61.4 mV decade^{-1} to I_3^- ions over the activity range 4.0×10^{-5} to 0.7×10^{-1} mol l^{-1} with a limit of detection 1.0×10^{-5} mol l^{-1}. The response time of the electrode was short (<15 s) and the membrane could be used for 2 months without any significant divergence in response. The potentiometric selectivity coefficients were evaluated and displayed the anti-Hofmeister behavior. The electrode based on **A1** revealed comparatively good selectivity with respect to lipophilic anions such as, iodide (I^-), thiocyanate (SCN^-) and perchlorate (ClO_4^-) was used as an indicator electrode in direct and indirect potentiometric titration in real samples.

Keywords: Triiodide selective electrode; Schiff base complexes; Liquid membrane; Lipophilic anions; Selectivity; Potentiometry

1. Introduction

In comparison with cation selective electrodes, only a small number of anion selective electrodes is known and their selectivities are often much worse than those of the cation selective electrodes. Potentiometric sensors for rather lipophilic anions such as perchlorate (ClO_4^-), thiocyanate (SCN^-) and iodide (I^-) or triiodide (I_3^-) are most often based on anion exchangers. The selectivity pattern of these electrodes is governed by the Hofmeister series [1] which is determined by the difference in the free transfer energy of anions into the membrane by ion pairing and solvating processes. However, if the membrane contains an ionophore in addition to the anion exchanger molecules, which are able to bind specific anions, the membrane may become selective to those anions. In this case, they show the anti-Hofmeister selectivity pattern. In last few years, electrodes using PVC membranes incorporating complexes of metals with phthalocyanine, porphyrine and salophen derivatives have been reported for anions [2–13]. Despite the need for the determination of triiodide in indirect evaluation of concentration of some important oxidizing substances; there have been limited reports on the applicability of triiodide ISEs. To the best of our knowledge, there are only nine reports available for triiodide ion selective electrodes (ISEs) [14–23]. The first triiodide ISE based on manganese (III) tetraphenyl porphyrine was reported in 1993 [14]. Afterwards, some of the proposed triiodide electrodes were prepared based on classical ion exchangers [17,18]. We recently reported highly selective liquid membrane electrodes based on charge transfer complexes for triiodide ions as well as others [19,20]. There is only one report on using the Schiff base complex in construction of triiodide ion selective electrode [21].

We became very interested in the subject when the recent paper on a manganese Schiff base complex [22] as ionophore was published, **A2**, showing selectivity to thiocyanate but no comment was made on the triiodide selectivity. Our interest in triiodide ISE persuaded us to further investigate the potential

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ability of this metal–Schiff base complex and to probe other new structures as ionophores in construction of triiodide ISEs. Therefore, some new Schiff base complexes of Mn(II) and Cu(II) were synthesized in preparation of ion selective membranes. The response characteristics of the proposed electrodes and the effect of type of spacer between two amine groups in bis-*N*,*O*-bidentate Schiff base complexes of Mn(II) and Cu(II) ions on the selectivity of the electrodes through **A2**–**A11** were studied. This work could be a comparative study among the Schiff base complexes used and their ability to respond to triiodide ions. Interestingly, the electrodes based on these ionophores responding weakly respond to thiocyanate but exhibit a good selectivity toward triiodide ion.

2. Experimental

2.1. Reagents and materials

All reagents were of the highest grade commercially available and were used without further purification. High molecular weight PVC powder, [bis-(2-ethylhexyl) phthalate] (DOP), sebacic acid dibutyl ester (DBS), *n*-butyl phthalate (DBP), 1-nitro-2-octyloxybenzene (*o*-NPOE) and potassium-*tetra*-*p*-chloro phenyl borate (K*p*ClPB) were obtained from Fluka. Benzyl acetate (BA) and anion salts were obtained from Merck. Dodecyl trioctyl ammonium iodide (DTOAI) was prepared according to the literature method [23]. Standard solutions and buffers were prepared freshly with deionized water.

2.2. Synthesis of Schiff base complex

A new Schiff base *N*,*N*′-1,2-propylene-bis-(5-methyl salicylidene imine) and its related copper complex, **A1**, were synthesized from *p*-cresol in accordance with the previously reported procedures [24,25]. A Schiff base *N*,*N*′-1,2-ethylene-bis-(5-phenylazo salicylidene imine) and its related metal complexes, **A2**–**A5**, were prepared in accordance to the literature [26]. New Schiff bases *N*,*N*′-1,2-pyridine-bis-(5-phenylazo salicylidene imine), *N*,*N*′-1,2-phenylene-bis-(5-phenylazo salicylidene imine), and *N*,*N*′-1,2-propylene-bis-(5-phenylazo salicylidene imine) and their related Mn(II) and Cu(II) complexes, **A6**–**A11**, were prepared in accordance with previous procedures [26,27]. The structures of the synthesized Schiff bases were characterized by IR and ^{1}H NMR spectroscopy and Mass spectrometry: (**A1**: brown-crystal, mp = 378–380 °C, IR (KBr, cm^{-1}) 3050 (w), 2900 (m), 1640 (s), 1575 (s), 1250 (s), 780 (m); ^{1}H NMR/CD_3SOCD_3/δ (ppm): 1.8 (s, 6H), 2.7–3.2 (m, 6H), 6.2–7.4 (s, 6H), 8.1 (s, 2H); UV ($\lambda_{max} = 360$ nm); (**A2**–**A5**: yellow powder, mp = 228 °C; IR (KBr, cm^{-1}) 3030 (w), 1630 (s), 1585 (m), ^{1}H NMR/$CDCl_3$/δ (ppm):2.86 (s, 4H, $2CH_2$), 7.0–8.2 (m, 16H), 8.6 (s, 2H, CH=N), 13.8 (s,2H); ^{13}C NMR/$CDCl_3$—DMSO-d^6/δ (ppm): 59.20, 118.10, 118.15, 122.42, 122.45, 122.65, 127.70, 127.70, 129.02, 129.20, 130.44, 164.64, 166.437; MS, *m*/*z* (%) [(239 ($phN_2C_6H_3(OH)CH{=}NCH_2$, 76), 196 ($phN_2C_6H_3O_9$, 100), 77 (ph, 4.8)]; UV ($\lambda_{max} = 345$ nm); (**A6**, **A7**: red crystals, mp = 224 °C, IR (KBr, cm^{-1}) 3030 (w), 2950 (w), 1610 (s), 1585 (s); ^{1}H NMR/$CDCl_3$/δ (ppm): 7.0–7.9 (m, 2OH), 8.2 (s, 2H, CH=N), 13.8 (s, 2H, 2OH); ^{13}C NMR/$CDCl_3$/δ (ppm):118.57, 122.34, 122.55, 122.77, 126.03, 127.80, 128.97, 129.16, 129.34, 130.69, 131.06, 152.59, 163.74, 196.56; MS, *m*/*z* (%) [(225($phN_2C_6H_3(OH)CH{=}N$, 12.9), 105 (phN_2, 7.0), 91 (phN, 11.8), 77 (ph, 32.9)]; UV($\lambda_{max} = 348$ nm); (**A8**, **A9**: red crystals, mp = 215 °C, IR (KBr, cm^{-1}) 3030 (w), 1610 (s), 1580 (s); ^{1}H NMR/$CDCl_3$/δ (ppm): 7.0–8.0 (m, 2OH), 8.5 (s, 1H, CH=N), 13.8 (s, 2H, 2OH); ^{13}C NMR/$CDCl_3$/δ (ppm): 20.28, 64.69, 65.35, 118.03, 118.04, 118.09, 118.16, 122.35, 122.55, 126.94, 126,99, 129.00, 129.04, 145.25, 145.31, 152.60, 152.63, 164.27, 164.38, 164.39, 164.40, 166.26, 166.28; UV ($\lambda_{max} = 342$ nm); MS, *m*/*z* (%) [(224 ($phN_2C_6H_3(OH)CH{=}N$, 4), 301 (M^+-$PhN_2C_6H_3(OH)CH{=}N$, 12.2), 105 (phN_2, 6.5), 77 (ph, 100)]; **A10**, **A11**: yellow crystals, mp = 143 °C, IR (KBr, cm^{-1}) 3090 (w), 2930 (w), 1630 (s), 1570 (s); ^{1}H NMR/$CDCl_3$/δ (ppm): 1.45 (*d*, 3H), 3.8 (m, 2H), 3.9 (m, 1H), 7.0–7.9 (m, 16H), 8.4 (s, 1H, CH=N), 8.5 (s, 1H, CH=N), 13.8 (s, 2H, 2OH); ^{13}C NMR/$CDCl_3$/δ (ppm): 20.28, 64.69, 65.35, 118.03, 118.03, 118.04, 118.09, 118.15, 118.16, 122.35, 122.55, 126.94, 126,99, 129.00, 129.04, 130.44, 145.25, 145.31, 152.60, 152.63, 164.27, 164.38, 164.39, 164.40, 166.26, 166.28; MS, *m*/*z* (%); [691(M^+, 90), 225 (($PhNCC_6H_3(OH)CH{=}NH$, 20); 197 ($phN{=}NC_6H_3OH$, 100)]; UV ($\lambda_{max} = 344$ nm).

2.3. Preparation of membrane electrodes

A triiodide selective membrane was prepared by dissolving the mixture of appropriate amounts of ionophore, DOP, DTOAI and PVC in 5 ml THF. The solution was left for the solvent to evaporate slowly and an oily mixture was obtained. A Pyrex tube (3 mm o.d.) was dipped into the mixture for about 30 s. Then the tube was pulled out and kept at room temperature for about 2 h, so that a membrane for about 0.3 mm thickness was formed at the end of the tube. The tube was then filled with an internal solution of 1×10^{-3} mol l^{-1} potassium triiodide and preconditioned for 24 h. Finally, the membrane was soaked in a 1×10^{-3} mol l^{-1} potassium triiodide solution for 2 h before use.

2.4. Emf measurements

Potentiometric evaluation of the electrodes was carried out by using the following cell:

Hg | Hg_2Cl_2 |KCl (sat'd) | sample solution | PVC membrane | KCl (sat'd)| Hg_2Cl_2 | Hg

Potential differences between the ISE and the double junction calomel electrode were measured with a digital mV meter WTW (Weinheim, Germany) at room temperature. Activity coefficients of ions in aqueous solutions were calculated according to the modified Debye–Hückel equation [28].

3. Results and discussion

3.1. Optimization of the membrane

Schiff base ligands can coordinate the transition metals in equatorial axes, so leaving the two axial sites for anions such