The Analyst
FULL PAPER

Ionophores based on 1,3-dithiole-2-thione-4,5-dithiolate (DMIT) as potentiometric silver sensors

Martin R. Bryce,[a] Brian Johnston,[a] Ritu Kataky*[a] and Klara Toth[b]

[a] Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE.
E-mail: Ritu.Kataky@durham.ac.uk
[b] Technical University of Budapest, Institute of General and Analytical Chemistry, H-1111
Szent Gellert tér 4, Budapest, Hungary

Received 17th February 2000, Accepted 22nd March 2000
Published on the Web 17th April 2000

A range of acyclic compounds based on 1,3-dithiole-2-thione-4,5-dithiolate (DMIT), functionalised with a silver binding chain and an alkyl chain, were synthesised and assessed as silver ionophores suitable for incorporation into potentiometric ion-selective electrodes as sensors for silver ions in photographic emulsions. The new ionophores were compared with a commercially available ionophore and a 14-crown-4-based ionophore. The membrane compositions were optimised for silver ion selectivity over a range of ions of relevance in the photographic process. 4-(Butylsulfanyl)-5-(phenylmethylthioethylsulfanyl)-1,3-dithiole-2-one was shown to be the most suitable ionophore in plasticised membrane electrodes, with a Nernstian response in the range 10^{-1}–10^{-6} mol dm^{-3} and selectivity coefficients of the order of log $K^{\mathrm{POT}}_{\mathrm{Ag/M}} \leq -4.0$.

Introduction

Several ionophores for silver have been synthesised and used in ion-selective electrodes. Thia-crown ethers, such as those membrane electrodes prepared by Lai and Shih[1] using a range of diether crown ethers, were among the first compounds to be incorporated into PVC membrane electrodes. Amongst the ionophores tested, 1,4-dithia-15-crown-5 showed the best sensitivity (40 mV dec^{-1}) with good selectivity coefficients over alkali, alkaline-earth and transition metals, log $K^{\mathrm{POT}}_{\mathrm{Ag/M}} > -3.5$ (by the fixed interference method, FIM), although mercury was still a strong interferent. Similar selectivity values towards alkali, alkaline-earth and transition metals were achieved by Oue *et al*[2,3] also using thia- and dithia-crowns. Siswartha *et al.*[4] synthesised a range of 14-crown-4 compounds and analysed the performance of the corresponding membrane ion-selective electrodes. They investigated the variation of ring size, number, degree of oxidation of sulfur atoms and the steric bulk of substituents in cyclic as well as acyclic thioether molecules. The best silver ionophore was **1m** (Fig. 1), with selectivity coefficients of the order of log $K^{\mathrm{POT}}_{\mathrm{Ag/M}} = -4$ and -5 (by the separate solution method, SSM) for the alkali/alkaline-earth metal ions and heavy metal ions, respectively. This was attributed to the presence of the bulky pinane substituent, which prevented the formation of stable complexes with other interfering ions, rather than this structure having an optimum binding geometry for the silver ion.

Macrocyclic polythia ethers [**1n(a)**, **1n(b)** and **1n(c)**] have been used by Casabó *et al.*[5] incorporating aromatic rings as macrocyclic components. These were tested as membrane electrodes and showed an excellent Nernstian response, in the range 10^{-7}–10^{-2} mol dm^{-3}, as well as good selectivity towards a wide range of cations, including values for mercury which ranged between log $K^{\mathrm{POT}}_{\mathrm{Ag/M}}$ (SSM) = -2.1 to -2.6. The authors could not explain this high selectivity, but they reasoned that it could be attributed to 'electronic factors or mobility problems inside the membrane'.

O'Connor *et al.*[6] synthesised a range of calixarenes, incorporating nitrogen and sulfur atoms to make them suitable for silver binding. These calixarenes exhibited acceptable silver responses: the best, bearing $CH_2CO_2C_2H_2SCH_3$ groups, displaying almost Nernstian response (50 mV dec^{-1}) with a detection limit of the order of 10^{-4} mol dm^{-3}. Further work was carried out on the incorporation of this ionophore into both membrane and membrane-coated glassy carbon electrodes. From selectivity coefficient determinations, Na^+ and Hg^{2+} were the main interferents with log $K^{\mathrm{POT}}_{\mathrm{Ag/M}}$ (SSM) values of 0 and +2.0, respectively. The best selectivities were over the heavy metal ions, such as Pb^{2+} and Cd^{2+}, which were of the order of log $K^{\mathrm{POT}}_{\mathrm{Ag/M}}$ (SSM) = -3.0. The high interference from the alkali metal ions is probably due to the presence of the hard oxygen atoms in the ester group. In a later publication by the same group, the effect of the conformation of the calixarene on silver binding was investigated.[7] A calixarene with practically the same chemical structure, but in a partial cone conformation, showed superior selectivity compared with a full cone conformation. This was accounted for by the increase in the size of the cavity, which disfavours binding by the smaller interfering cations. Work on calixarenes was extended by Malinowska *et al.*[8] with calix[4]arenes functionalised with $C_2H_4SCH_3$ groups incorporated into PVC membranes. These electrodes showed good responses to silver over a wide range of concentrations in the presence of alkali, alkaline-earth and transition metals and, for mercury, showed a high selectivity: log $K^{\mathrm{POT}}_{\mathrm{Ag/M}}$ (FIM) = -2.5. When comparing the values for the two calix[4]arenes, one bearing two $C_2H_4SCH_3$ groups, the other bearing four, it was found that the number of sulfur donor atoms in the receptor molecule did not significantly influence the selective complexation of silver ions.

Recently there has been a move towards the use of acyclic sulfides in the design of silver ionophores. Wróblewski and Brzózka[9] noted that the selectivities of thia-crown ethers were similar in spite of the different numbers and positions of the sulfur atoms in the rings, an observation which prompted them to investigate acyclic thioethers [**1o**: **(a)**, **(b)**, **(c)**, **1p**: **(a)**, **(b)**, (*c*)]. Sulfides, **1o(a)** and **1o(b)** showed a Nernstian response, whilst the third **1o(c)** deviated at higher concentrations. This deviation was thought to be indicative of this molecule forming an extremely strong complex with silver. The second group of sulfides **[1p (a)–(c)]** contained one oxygen atom, which had the effect of reducing the selectivity over other transition metal ions, but enhanced that of silver over mercury.

DOI: 10.1039/b001342k

The potential of simple thioethers to act as sensor molecules was also explored by Casabó and coworkers[10,11] who, after a systematic search of the literature, hypothesised that ‘the macrocyclic nature of the cavity size of thioether ligands was not the main basis for a good selectivity for Ag^+, but rather simply the existence of the thioether group in the sensor molecule’. To confirm their hypothesis they took simple sulfides, *viz*. EtSEt, PhSEt and PhSPh, and incorporated these into PVC membrane electrodes. They obtained Nernstian responses for all three electrodes and found very little difference in their response parameters, thus showing the absence of an influence of the nature of the moieties attached to sulfur. Selectivity studies were also reported for a range of metal ions. Excellent selectivity coefficients, with values around $K^{\mathrm{POT}}_{\mathrm{Ag/M}}$ (FIM) = −5, were reported. However, the selectivity towards mercury was $K^{\mathrm{POT}}_{\mathrm{Ag/M}}$ (FIM) = −1.8.[4] This relatively high interference was attributed to the simplicity of the molecule.

Silver-selective electrodes have also been reported with other classes of ionophores. Among these is a pyridinophane (**1q**), which is an interesting silver ionophore as it does not contain any sulfur atoms.[12] A series of podands containing nitrogen and sulfur atoms has recently been reported.[13–15] Results from this work presented an exception to the ‘simple existence of a sulfur atom’ hypothesis of Casabó as the nature of the podand had a significant effect on the response of the membrane electrode. The podands **1r(a)** and **1r(b)** gave negligible slopes compared to **1r(c)** and **1r(d)** which displayed near Nernstian slopes.

Experimental

Materials

Ionophores **1c–1j**;[16] and **1l**[17] were synthesised in this laboratory. The procedures for **1f** and **1j** detailed below are representative of all the members of this series. Ionophore **1k** was obtained from Fluka (Sigma-Aldrich Co. Ltd., Poole, Dorset, UK). The membrane components, PVC (high molecular weight), potassium tetrakis(4-chlorophenyl)borate (KTpClPB), 2-nitrophenyl octyl ether (oNPOE) and bis(2-ethylhexyl)sebacate (DOS) were also obtained from Fluka. Silver nitrate was obtained from Sigma-Aldrich. Salts of analytical grade were obtained from BDH (Merck, Poole, Dorset, UK). All standard

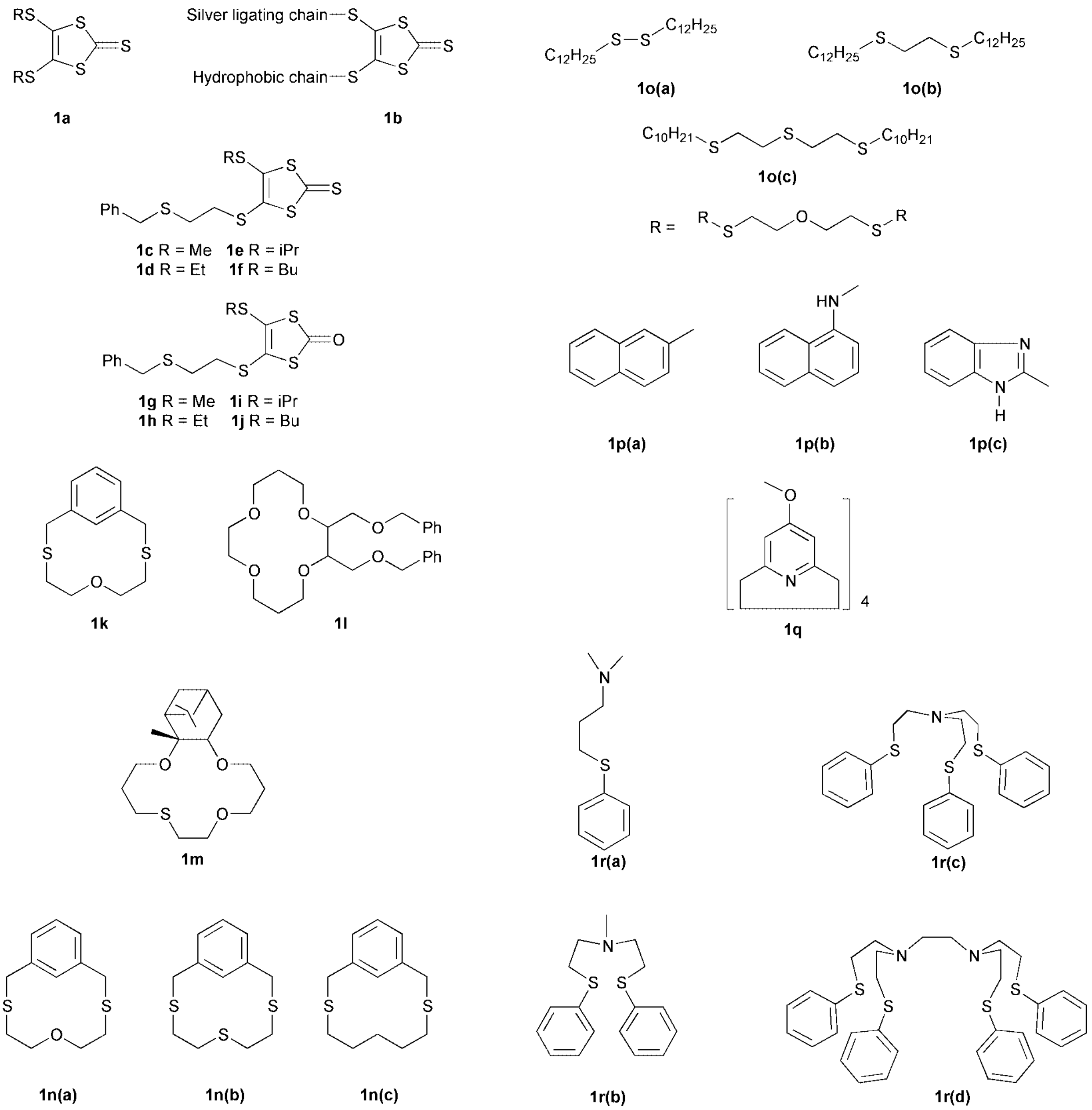

Fig. 1 Structures of ionophores discussed.

solutions were prepared in deionised water. Tetrahydrofuran (THF) was of spectroscopic grade distilled from sodium benzophenone ketyl.

Synthesis

4-(Butylsulfanyl)-5-(2′-cyanoethylsulfanyl)-1,3-dithiole-2-thione. To a solution of 4,5-bis(cyanoethylsulfanyl)-1,3-dithiole-2-thione[18] (1.0 g, 3.28 mmol) in chloroform (50 cm^3) at 20 °C was added a solution of caesium hydroxide (0.61 g, 3.28 mmol) in ethanol (5 cm^3), and the mixture was stirred for 1.5 h. n-Butyl iodide (0.60 g, 3.28 mmol) was added and the mixture was stirred for 12 h. The solvent was removed *in vacuo* and the crude product was purified by column chromatography [silica gel; eluent, chloroform–hexane (1 : 1 v/v)] to afford the product as an orange solid (1.01 g, 50%), mp 60–61 °C. High-resolution mass spectrometry (HRMS) found 306.9650; $C_{10}H_{13}NS_5$ requires 306.9652; δ_H (200 MHz, CDCl3) 3.06 (2 H, t, *J* 6 Hz), 2.92 (2 H, t, *J* 8 Hz), 1.73–1.56 (2 H, m), 1.54–1.32 (2 H, m), 0.91 (3 H, t, *J* 7 Hz); δ_C ($CDCl_3$) 210.3, 143.2, 128.5, 117.1, 36.3, 31.9, 31.6, 21.7, 18.8, 13.5.

4-(Butylsulfanyl)-5-(phenylmethylthioethylsulfanyl)-1,3-dithiole-2-thione (1f). To a solution of the above compound (1.79 mmol) in chloroform (50 cm^3) at 20 °C was added caesium hydroxide (0.30 g, 1.79 mmol) in methanol (5 cm^3), and the mixture was stirred for 1.5 h. Benzyl-2-iodoethylsulfide[19] (2.69 mmol) was added and the mixture was stirred at 20 °C for 12 h. The solvent was removed *in vacuo* and the product purified by column chromatography [silica gel; eluent, chloroform–hexane (1 : 1 v/v)] to afford **1f** as a burgundy oil (0.68 g, 95%). HRMS found 403.9996; $C_{16}H_{20}S_6$ requires 403.9991. δ_H (200 MHz, $CDCl_3$) 7.37–7.24 (5 H, m), 3.74 (2 H, s), 2.87–2.81 (4 H, m), 2.70–2.61 (2 H, m) 1.69–1.52 (2 H, m), 1.48–1.34 (2 H, m), 0.93 (3 H, t, *J* 7 Hz); δ_C ($CDCl_3$) 211.1, 137.5, 137.3, 136.7, 128.8, 128.7, 127.4, 41.7, 36.3, 36.25, 30.8, 23.2.

4-(Butylsulfanyl)-5-(phenylmethylthioethylsulfanyl)-1,3-dithiole-2-one (1j). To a solution of **1f** (0.25 mmol) in chloroform–acetic acid (3 : 1 v/v, 20 cm^3) was added mercuric acetate (0.63 mmol) at 20 °C and the mixture was stirred for 16 h. The precipitate was removed by filtration with celite, and washed with chloroform. The organic layer was refluxed with activated charcoal, washed with sodium bicarbonate, dried ($MgSO_4$) and evaporated *in vacuo* to yield **1j** as a colourless oil (69 mg, 72%). Found C, 49.3; H, 5.2; $C_{16}H_{20}OS_5$ requires C, 49.5; H, 5.2. *m*/*z* 388 (M^+). δ_H (200 MHz, $CDCl_3$) 7.37–7.24 (5 H, m), 3.74 (2 H, s), 2.95–2.79 (4 H, m), 2.70–2.61 (2 H, m), 1.69-1.55 (2 H, m), 1.48–1.34 (2 H, m), 0.93 (3 H, t, *J* 7 Hz); δ_C ($CDCl_3$) 189.7, 137.7, 132.2, 128.8, 128.7, 127.3, 124.3, 36.3, 36.2, 36.15, 30.8, 21.6, 13.5.

Electrodes

Membranes were cast by a controlled evaporation method according to published procedures.[20] Typically, the following compositions were used: 1.2 wt.% ionophore, 0–70 mol.% (of ionophore) KTpClPB, 64–67 wt.% plasticiser (oNPOE or DOS) and 33 wt.% PVC. The components were dissolved in 5 cm^3 of freshly distilled THF and were agitated overnight on a mechanical shaker. The resulting syrup was poured into a glass mould and the THF solvent allowed to evaporate off slowly at room temperature over a period of 24–48 h. A semi-transparent flexible film resulted, from which a disc of 9 mm in diameter was cut using a cork borer and positioned in the electrode. The electrodes were assembled in Philips electrode bodies IS (561) (Philips Analytical, Eindhoven, The Netherlands) with 10^{-3} mol dm^{-3} $AgNO_3$ as inner fill solution. The electrodes were conditioned in a solution of 10^{-3} mol dm^{-3} $AgNO_3$ for 24 h.

The reference electrode was an Orion double junction reference electrode with a silver/silver chloride inner filling solution and a 0.1 mol dm^{-3} potassium nitrate salt bridge.

Techniques employed

Initially, to assess the most suitable ionophore from **1c**–**1j**, calibrations were performed in batches of six in dip-tests, followed by the SSM for determining selectivity coefficients.[21] A membrane composition without a lipophilic anion was selected to optimise the binding contribution of the molecule, to eliminate any contribution towards silver binding with a soft tetraphenylborate anion. Comparisons were made with a 'blank' electrode excluding the ionophore. The membrane composition was optimised by systematically varying the lipophilic anion and plasticiser content. Following evaluation of the ionophores, the best was selected and assessed more thoroughly using the constant dilution technique and FIM, as described elsewhere.[22] All measurements were made at 298 K.

Results and discussion

Separate solution studies

Comparison of the thione (1c–1f) *versus* the ketone (1g–1j) derivatives. Compounds **1c**, **1d**, **1e** and **1f** (Fig. 1) exhibited sub-Nernstian behaviour with electrode slopes between 15–30 mV dec^{-1} (Table 1). The potentials of these electrodes showed considerable scatter (up to ±20 mV), and a decrease in potential on increasing the silver concentration from 10^{-2} to 10^{-1} mol dm^{-3}. These electrode characteristics suggest that all of these electrodes are binding silver irreversibly. This behaviour is not affected by the change in ionophore lipophilicity (*i.e.* on going from R = methyl to R = butyl group). The results of the

Table 1 Electrode compositions and Nernstian responses using separate solution method (T = 294 K)

Electrode[a]	Compound	PVC/ wt.%	oNPOE/ DOS/ wt.%	Ionophore/ wt.%	KTpClPB/ mol.%	Electrode slopes (SSM)/ mV/dec^{-1} at 21 °C
Thione 1	**1c**	31.8	67	1.2	—	< 30
Thione 2	**1d**	31.8	67	1.2	—	< 30
Thione 3	**1e**	31.8	67	1.2	—	< 30
Thione 4	**1f**	31.8	67	1.2	—	< 30
Ketone 1	**1g**	31.8	67	1.2	—	35
Ketone 2	**1h**	31.8	67	1.2	—	35
Ketone 3	**1i**	31.8	67	1.2	—	38
Ketone 4	**1j**	31.8	67	1.2	—	45
1N	—	33	67.00	0	0	33
2N	—	33	66.43	0	30	50
3N	—	33	65.93	0	70	45
4N	**1j**	33	65.80	1.23	0	51
5N	**1j**	33	66.34	1.23	30	55
6N	**1j**	33	64.73	1.23	70	54
7N	**1k**	33	65.80	1.23	0	21
8N	**1k**	33	65.06	1.23	30	27
9N	**1k**	33	64.07	1.23	70	50
1D	—	33	67.00	0	0	33
2D	—	33	66.54	0	30	45
3D	**1j**	33	65.80	1.23	0	52
4D	**1j**	33	65.34	1.23	30	54
5D	**1k**	33	65.80	1.23	0	35
6D	**1k**	33	65.06	1.23	30	20
10N	**1l**	33	66.34	1.23	30	—

[a] N = oNPOE, D = DOS.

calibration of the thiones (electrodes Thione 1–4, Table 1) indicate that a site other than the side-chains, probably the thione group, is binding silver strongly. This thione is easily converted to a ketone using mercuric acetate[17] to form the analogous compounds **1g–1j**. This series of ketones was used to make a new set of membranes, using the same composition as that employed for compounds **1c–1f**.

Although the calibration plots of these electrodes exhibited sub-Nernstian behaviour (35 mV dec^{-1} for **1g** and **1h**, 38 mV dec^{-1} for **1i** and 45 mV dec^{-1} for **1j**; electrodes Ketone 1–4, Table 1), they were linear to micromolar levels of concentration with less than ±1.0 mV scatter. Moreover, there was a clear change in electrode response upon increasing the lipophilicity of the molecule, as the slope of the response increased from 35 mV dec^{-1} for the methyl group to 45 mV dec^{-1} for the butyl group. These results contrast with those of the thione analogues, where no difference in response was observed upon changing the lipophilicity. This result suggests: (i) the main mode of silver binding is at the intended side-chain binding site; and (ii) the extent of this binding may be controlled by varying the functionality in the side-chain. The selectivities of the electrodes prepared using the ketone analogues (**1g–1j**, Fig. 2) indicate an improvement in selectivity with increasing lipophilicity, the exception being the isopropyl analogue, **1i**.

The preceding studies revealed that **1j** was the most appropriate ionophore. Subsequently, **1j** was chosen for optimising membrane compositions by varying the percentages of plasticiser and lipophilic anion. Electrode responses were compared to 'blank' membrane electrodes, which did not contain the ionophore, and with a commercially available silver ionophore, **1k**. A series of membranes was prepared with either the more polar plasticiser oNPOE (relative permittivity, ε = 23.06) or DOS (ε = 3.88) (Table 1). Selectivities were measured by the SRM [Figs. 3(a) and 3(b)].

Comparisons of electrodes with 1j using oNPOE as plasticiser. The response of the oNPOE electrodes (1N and 4N) without the lipophilic anion, showed acceptable scatter in potential values (±2 mV) and were linear to approximately 10^{-5} mol dm^{-3}. As expected the 'blank' electrode, without ionophore, showed sub-Nernstian behaviour. The fact that this electrode showed any linear response suggests the presence of anionic sites in the membrane originating from impurities in the PVC. In contrast, electrode 7N showed substantial scatter, sub-Nernstian slopes and a tailing off in potentials at concentrations higher than 10^{-4} mol dm^{-3}. This behaviour is indicative of an ionophore that may be binding Ag^+ irreversibly.

The inclusion of 30 mol.% of lipophilic anion additive significantly improved the response of the 'blank' membrane electrode 2N (from 33 to 50 mV dec^{-1} for 1N and 2N, respectively). The response of electrode 5N also improved from 51 to 55 mV dec^{-1} for 4N and 5N, respectively. In comparison, the potentials for 8N (with **1k**) showed more scatter and more pronounced tailing off in linearity at higher concentrations. These combined observations indicate that the lipophilic additive binds the Ag^+ ion; the effect is most pronounced in the 'blank' electrode 2N. The additional binding contribution of the additive is not as pronounced in the electrode 5N as the ionophore **1j** already binds silver ion. The increased scatter and more pronounced tailing off at higher concentrations, demonstrated by electrode 8N, is further evidence of the irreversible binding of the Ag^+ ion by ionophore **1k** being made more pronounced by the inclusion of 30 mol.% of lipophilic additive.

Increasing the concentration of the additive to 70 mol.% had a pronounced effect on the electrodes, in particular the electrode 9N, which contained the Fluka ionophore **1k**. The degree of scatter (±2–5 mV) between different potential readings was considerably reduced and the electrode slope, although sub-Nernstian, at 50 mV dec^{-1} was much improved. These observations suggest that it is the additive which is the more significant component in the reversible binding of the silver ion, rather than the ionophore **1k**, which probably binds irreversibly. The increased percentage of additive had the opposite effect on the responses of the 'blank' electrode (3N) and the electrode containing the ionophore **1j**, (6N).

The lipophilic additive also had a pronounced effect on the selectivity coefficients of the oNPOE-based membrane electrodes [Fig. 3(a)]. Comparing the 'blank' electrodes 1N and 2N, the 30 mol.% additive in electrode 2N resulted in an increase of almost two orders of magnitude in the selectivities, compared to electrode 1N. A further increase to 70 mol.% in electrode 3N caused a decrease in selectivity across the range of cations. The highest selectivities observed were those over the smaller cations Na^+ and Mg^{2+} and the worst selectivity over Hg^{2+}. This is in agreement with the fact that the soft polarisable tetraphenylborate anion of the additive prefers soft cations, such as silver and mercury, to the hard cations, such as sodium and magnesium.

A similar trend was observed for the electrodes 4N, 5N and 6N where the optimum percentage of additive appeared to be 30 mol.%. The order of selectivity in the range of cations was

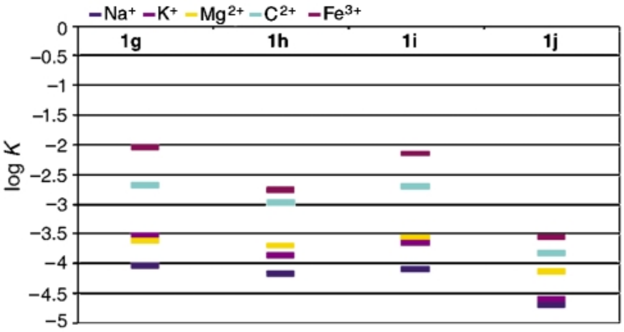

Fig. 2 Selectivity coefficients of electrodes using thione and ketone derivatives of 1,3-dithiole-2-thione-4,5-dithiolate (DMIT) as ionophores without the inclusion of the lipophilic anion additive using the separate solution method (T = 294 K).

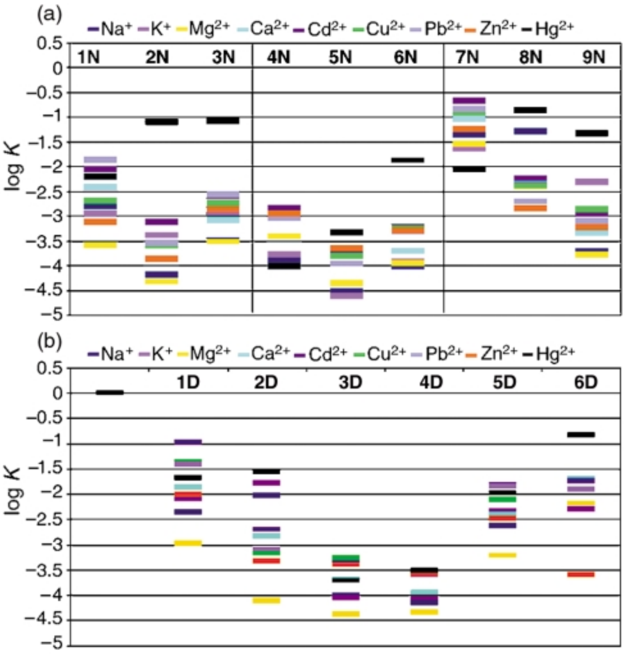

Fig. 3 (*a*) Selectivity coefficients of electrodes 1N–9N using the separate solution method (T = 294 K). (*b*) Selectivity coefficients of electrodes 1D–9D using the separate solution method in 0.1 mol dm^{-3} metal nitrate solutions (T = 294 K).

Table 2 Calibrations and selectivity coefficients of electrodes 5N and 10N using the constant dilution method ($T = 298$ K)

		Calibration	Na^+	K^+	Mg^{2+}	Ca^{2+}	Fe^{3+}
5N	Slope/mV dec^{-1}	62 ± 4	66 ± 7	61 ± 3	60 ± 2	57 ± 2	65 ± 3
	LOD ($-\log C$)	4.6 ± 0.4	4.5 ± 0.3	4.6 ± 0.2	3.7 ± 0.2	3.6 ± 0.1	4.2 ± 0.1
	$-\log K_{ij}^{POT}$	—	3.5 ± 0.3	3.6 ± 0.2	3.2 ± 0.2	3.2 ± 0.1	3.8 ± 0.1
10N	Slope/mV dec^{-1}	62 ± 5	46 ± 5	61 ± 4	60 ± 1	60 ± 7	—
	LOD ($\log C$)	5.0 ± 0.4	2.3 ± 0.2	2.7 ± 0.0	2.7 ± 0.1	1.3 ± 0.1	—
	$-\log K_{ij}^{POT}$		1.2 ± 0.2	1.7 ± 0.0	3.2 ± 0.1	1.8 ± 0.1	—

similar, with the highest selectivity observed over the smaller cations Na^+, Mg^{2+} and K^+. A notable exception was electrode 4N, with no lipophilic anion additive, which gave the best selectivity over Hg^{2+} with a value of $\log K_{Ag/M}^{POT} = -4.0$, which is the highest of the values reported in the literature.[15,23]

The Fluka silver ionophore **1k** displayed a completely different behaviour upon addition of additive. A noticeable difference was the optimal selectivity observed for electrode 9N, with 70 mol.% additive. This implies that the additive plays a more active role in apportioning the selectivity compared with the ionophore. Interestingly, the electrodes 7N and 8N reveal opposite selectivity patterns to those observed for electrodes 1N–6N. This could be due to binding by the hard oxygen atom of ionophore **1k**, which prefers the small hard cations.

Comparisons of electrodes with DOS as plasticiser. Changing the plasticiser reduces the relative permittivity of the membrane from $\varepsilon = 23.06$ for oNPOE to $\varepsilon = 3.88$ for DOS.[24] This appeared to have a pronounced effect on the responses of all the electrodes. A decrease in scatter of the electrode 5D was observed, suggesting that the lower relative permittivity had acted to reduce the binding affinity of the ionophore **1k** for Ag^+. The linear range of all the electrodes was extended to higher concentrations; all electrodes displayed good linear fits in the concentration range $-\log[Ag] = 1–5$, compared to the linear region of the oNPOE-plasticised electrodes, *i.e.* $-\log[Ag] = 2–5$. This behaviour can be explained by a lowering of the silver ion binding affinity of the membrane, which allows a Nernstian response at higher concentrations. The slopes of electrodes 1D and 3D were almost identical to those of the corresponding oNPOE-plasticised electrodes. However, the slope of 5D (34 mV dec^{-1}) had improved considerably from the equivalent oNPOE-plasticised electrode 8N (21 mV dec $^{-1}$).

The effect of the lipophilic anion additive on the DOS-plasticised membrane electrodes was quite significant. The most notable change was with electrode 6D**,** which showed considerable scatter, presumably due to an increase in binding of the membrane on inclusion of the additive. This was a surprising result, as the corresponding DOS-plasticised membrane without additive (5D) showed very little scatter; this observation suggests that the ionophore **1k** only binds reversibly in a membrane of low relative permittivity, such as a DOS-plasticised membrane with no additive, and that the presence of the additive increases this relative permittivity out of the working range of the membrane.

The selectivities across the range of electrodes were very similar, with the same trends evident for the DOS-plasticised membranes as those observed for the oNPOE-plasticised membranes [Fig. 3(b)]. The selectivity coefficient for electrode 4D (**1j** with DOS) was very similar to that of the corresponding oNPOE-plasticised membrane 5N, apart from a slightly better selectivity for Hg^{2+}. On comparing the selectivity of membranes with and without the lipophilic anion, the improvement in selectivity was not as pronounced as in the oNPOE-plasticised membranes, showing a shift of approximately half an order of magnitude in silver selectivity compared to an order of magnitude in oNPOE membranes.

In conclusion, any unexpected behaviour of the commercially available ionophore (**1k**), when incorporated into plasticised liquid membrane electrodes, compared with literature values is probably attributable to the fact that the characteristics quoted for **1k** were for membranes coated on solid supports with conductive polymer composites.[25]

Calibration and selectivity results using constant dilution

The optimised electrode with the best performance (5N) was further characterised using the FIM. The results were compared to those obtained with compound **1l** (electrode 10N, Table 1) which was used in previous work for sensing silver ions.[1] Selectivity coefficient measurements were restricted to ions of importance in emulsions used in photography.

The values obtained for the electrode calibrations for the two electrodes were comparable (Table 2). Marginally super-Nernstian slopes were observed, which are typical of this technique owing to a hysteresis effect. Selectivity coefficient studies showed that the selectivities over the monovalent cations (Na^+ and K^+) and Ca^{2+}, for electrode 5N, were better than those of electrode 10N. The selectivities over Mg^{2+} were in good agreement. Oveall, 5N shows very good selectivity for silver and is significantly better than 10N as a silver sensor.

Conclusion

The new silver ionophore **1j** was found to be an excellent ionophore, amongst a series of 1,3-dithiole-2-thione-4,5-dithiolate (DMIT)-based thiones and ketones, for the detection of silver ions in photographic emulsion media. The binding of silver was shown to depend on the lipophilicity of the molecule, compound **1j** functionalised with a butyl group displaying the best results. On comparing this electrode with one prepared using a commercial ionophore (**1k**) and an ionophore used in previous work for Kodak (**1l, 1j**) displayed a superior response. Changing the plasticiser had only a slight effect on the electrode selectivity and the optimum lipophilic additive concentration was 30 mol.% of the ionophore. A subsequent paper will discuss the application of the electrode in photographic emulsions.

Acknowledgements

We thank Kodak Limited and EPSRC for funding this work.

References

1 M. Lai and J. Shih, *Analyst*, 1986, **111**, 165.

2 M. Oue, K. Akama, K. Kimura, M. Taneka and T. Shono, *Anal. Sci.*, 1989, **5**, 165.

3 M. Oue, K. Akama, K. Kimura, M. Taneka and T. Shono, *J. Chem. Soc., Dalton Trans.*, 1989, 891.

4 D. Siswanta, K. Nagatsuka, H. Yamada, K. Kumakura, H. Hisamoto, Y. Shichi, K. Toshima and K. Suzuki, *Anal. Chem.*, 1996, **68**, 4166.

5 J. Casabó, L. Mestres, L. Escriche, F. Texidor and C. Pérez-Jiménez, *J. Chem. Soc., Dalton Trans.*, 1991, 1969.

6 K. O'Connor, G. Svehla, S. Harris and M. McKervey, *Talanta*, 1992, **39**, 1549.
7 K. O'Connor, W. Henderson, E. O'Neil, D. W. M. Arrigan, S. Harris, M. McKervey and G. Svehla, *Euroanalysis*, 1997, **9**, 311.
8 Z. Malinowska, Z. Brzózka, K. Kasiura, R. J. M. Egberinek and D. Reindoudt, *Anal. Chim. Acta*, 1994, **298**, 245.
9 W. Wróblewski and Z. Brzózka, *Sens. Actuators, B*, 1995, **24**, 183.
10 J. Casabó, T. Flor, M. I. Romero, F. Teixidor and C. Pérez-Jiménez, *Anal. Chim. Acta*, 1994, **294**, 207.
11 F. Teixidor, M. A. Flores, L. Esriche, C. Viñas and J. Casabó, *J. Chem. Soc., Chem. Commun.*, 1994, 963.
12 W. Hasse, B. Ahlers, J. Reinbold, K. Cammann, G. Brodesser and F. Vögtle, *Sens. Actuators, B*, 1994, **18**, 380.
13 S. S. Lee, M. K. Ahn and S. B. Park, *Analyst*, 1998, **123**, 383.
14 S. Chung, W. Kim, S. B. Park, I. Yoon, S. S. Lee and D. D. Sung, *J. Chem. Soc., Chem. Commun.*, 1997, 965.
15 S. Chung, W. Kim, S. B. Park, D. Y. Kim and S. S. Lee, *Talanta*, 1997, **44**, 1291.
16 B. Johnston, PhD Thesis, University of Durham, 1998.
17 D. M. Singh, PhD Thesis, University of Newcastle upon Tyne, 1994.
18 N. Svenstrup and J. Becher, *Synthesis*, 1995, 215. For an improved synthesis of bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiol)zincate used in this preparation see: C. Wang, A. S. Batsanov, M. R. Bryce and J. A. K. Howard, *Synthesis*, 1998, 1615.
19 U. Scöllkopf and R. Lonsky, *Synthesis*, 1983, 675.
20 A. Craggs, G. J. Moody and J. D. R. Thomas, *J. Chem. Educ.*, 1974, **51**, 542.
21 *IUPAC Recommendations*, Commission on Electroanalytical Chemistry, IOPAC, 1994, p. 2528.
22 R. Kataky, P. G. Nicholson., D. Parker and A. K. Covington, *Analyst*, 1991, **116**, 135.
23 D. Siswanta, K. Nagatsuka, H. Yamada, K. Kumakura, H. Hisamoto, Y. Shichi, K. Toshima and K. Suzuki, *Anal. Chem.*, 1996, **68**, 4166.
24 R. D. Armstrong and G. Horvai, *Electrochim. Acta*, 1990, **35**, 1.
25 S. Alegret and E. Martinez-Fabergas, *Biosensors*, 1989, **4**, 287.