Spectroelectrochemical characterization of polyselenide ions in *N*,*N*-dimethylacetamide

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Polyselenide ions formed by the reduction of variable amounts of electrodeposited selenium on a gold grid cathode have been studied in *N*,*N*-dimethylacetamide by voltammetry coupled with UV-visible absorption spectrophotometry. Grey selenium reduces in three successive steps to the stable ions $Se_8{}^{2-}$ (λ_{max} = 648, 453, 398 and 260 nm), $Se_6{}^{2-}$ (λ_{max} = 598, 440 and 260 nm) and $Se_4{}^{2-}$ (λ_{max} = 550, 417, 307 and 260 nm). Temperature and concentration effects gave no evidence to suggest the dissociation of $Se_x{}^{2-}$ species, in particular $Se_6{}^{2-} \rightarrow Se_3{}^{\cdot -}$.

Although numerous polyselenide salts ($Se_x{}^{2-}$, $x = 2$–10) have been structurally characterized in the solid state,[1] the nature of the stable $Se_x{}^{2-}$ species in aprotic solvents remains controversial. The formation of $Se_2{}^{2-}$ ions was reported from the reduction of selenium, either *via* chemical reagents [$Li(C_2H_5)_3BH$,[2] N_2H_4,[3] Li[4]] in THF and DMF, or by exhaustive electrolysis on mercury, platinum and graphite electrodes[5] in THF, DMF and acetonitrile. However, from ^{77}Se NMR studies in DMF[1] and UV-visible spectroscopy in liquid ammonia,[6] $Se_2{}^{2-}$ was believed to greatly disproportionate into $Se_3{}^{2-}$ and Se^{2-} ions, whereas $Se_x{}^{2-}$ species were characterized in DMF ($x = 3$–6)[1] and NH_3 (x = 3, 4, 6).[6] In both cases, no evidence was found for anions with $x > 6$. There is now general agreement concerning the nature of stabilized polysulfide ions $S_x{}^{2-}$ (x = 3, 4, 6, 8) in dipolar aprotic media,[7] with an equilibrium between $S_6{}^{2-}$ and the blue radical anion $S_3{}^{\cdot -}$. In spite of assumptions on the existence of $Se_3{}^{\cdot -}$ ions[8–10] the dissociation of $Se_6{}^{2-}$ was experimentally questioned,[1,6,11] or regarded as occurring only to a low extent.[10]

In order to gain information on the stability of polyselenide ions, we report here on their spectroelectrochemical properties after generation by electroreduction of elemental selenium on a gold electrode in *N*,*N*-dimethylacetamide (DMA).

Results and discussion

Prior to this work, to overcome the insolubility of selenium, a mixture of Se–graphite was fused upon a Pt net,[12] or Se pearls were enclosed in a graphite cloth[5d] and the electrodes thus obtained were cathodically polarized. The formation of $Se_2{}^{2-}$ was assumed from the yield of RSe_2R as major products when electrolyses were performed in the presence of RX substrates in DMF, THF or CH_3CN.[5d,13] In DMA, $Se_x{}^{2-}$ ions ($\bar{x} \approx 6$) were at first generated by the reaction between selenium and hydrazine with sodium methanolate as the base according to the procedure of Eggert *et al.*:[14]

$$12\ Se + 4\ MeO^- + N_2H_4 \rightarrow 2\ Se_6{}^{2-} + 4\ MeOH + N_2 \quad (1)$$

In this work, a series of six weighed amounts of Se (17.6–64.8 mg) were deposited on a large gold grid electrode by electro-oxidation of polyselenide ions (see Experimental). Fig. 1 shows the cyclic voltammogram that was obtained on a gold disc electrode coated with Se in the same way. The reduction of solid selenium (sharp peak A, $E_p^c = -0.49$ V) is followed by three cathodic waves such as $E_p^c(B) = -0.62$ V, $E_p^c(C) = -0.88$ V and $E_p^c(D) = -1.28$ V; the latter is associated with the anodic peak E ($E_p^a \approx -1.0$ V) whereas the reverse processes for peaks C, B and A give indistinguishable oxidation currents ($E_p^a \approx -0.33$ V), leading to the deposition (F) of solid Se on the disc. The polyselenide solutions ($v = 40$ cm^3) stemming from steps A, B and C were studied by UV-visible spectrophotometry coupled with voltammetry at a rotating gold disc electrode (RDE); the changes in the spectra and voltammograms are illustrated in Figs. 2–4, relating to the electroreduction of selenium (w = 31.4 mg, ~0.4 mmol Se) coating the large electrode. When electrolysis was at first performed at −0.40 V (n Faraday mol^{-1} Se) the three cathodic waves B, C and D increased [Fig. 2, curve 1, $E_{1/2}(B) = -0.55$ V, $E_{1/2}(C) = -0.83$ V] with passivation for the latter [$E_{1/2}(D) \approx -1.2$ V], and three visible absorption bands increased at the same time (Fig. 3, curves 1–3, λ_{max} = 648, 453 and 398 nm). The limiting currents of the waves B and C, which were small and roughly reproducible in comparison with those of sulfur species,[7a] remained in a ratio i_C/i_B close to 1.85 and satisfied the Levich equation when the rotation rate of the electrode was varied between 400 and 5000 rpm at 20 °C. The i_B and absorbance values reached a maximum after the consumption of 0.25–0.26 Faraday mol^{-1} Se. For $0 < n \leqslant 0.25$ the spectra had the same shapes (constant ratio between maximal absorbances) whatever the initial Se mass to be reduced. We therefore propose eqn. (2) for the first reduction step A of sele-

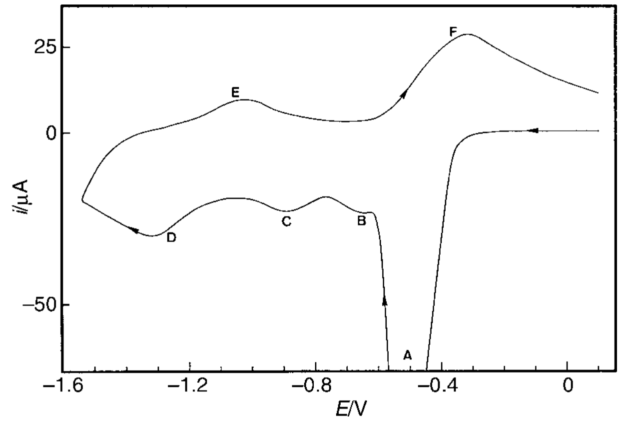

Fig. 1 Cyclic voltammogram at a Se-coated gold disc electrode (second scan). Scan rate 100 mV s^{-1}.

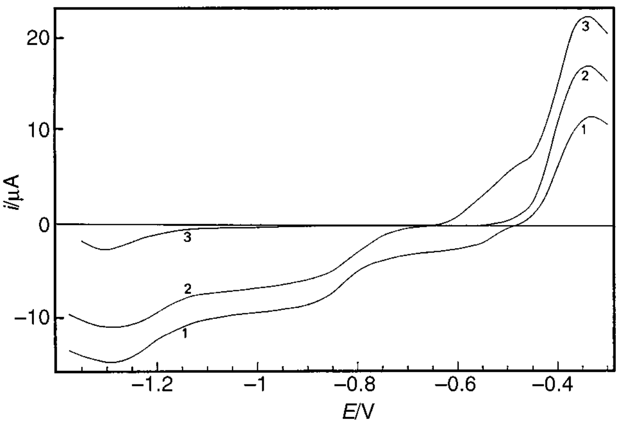

Fig. 2 Voltammograms of Se_x^{2-} solutions at a rotating gold disc electrode after electrolysis at n Faraday mol^{-1} Se: $n = 0.26$ (1); 0.36 (2); 0.55_5 (3). $w(Se) = 31.4$ mg. Scan rate = 10 mV s^{-1}.

nium:

$$8\ Se + 2\ e^- \rightarrow Se_8^{2-} \quad (2)$$

Dark brown Se_8^{2-} ions give specific absorbances at 648, 453, 398 and 260 nm, and oxidize into Se ($E_p^a \approx -0.34$ V). Continuing the electrolysis on the plateau of wave B ($E = -0.70$ V), A_{648} and A_{453} shifted towards lower wavelengths (Fig. 3) through two isosbestic points ($\lambda_{is} = 553$ and 396 nm); i_B linearly decreased as a function of the flowing charge, Se_8^{2-} ions being totally reduced after ≈0.68–0.70 Faraday mol^{-1} Se_8^{2-} while the limiting current i_C remained constant (Fig. 2, curves 1,2). These results are in agreement with the reduction of Se_8^{2-} ions (step B) into Se_6^{2-} species:

$$3\ Se_8^{2-} + 2\ e^- \rightarrow 4\ Se_6^{2-} \quad (3)$$

Dark green Se_6^{2-} ions display maximal absorbances at 598, 440 and 260 nm, and shoulders at 400 and 300 nm (Fig. 4, curve 1). Further electrolysis at $E = -1.0$ V entailed the linear decrease of i_C with charge, up to 1.04–1.07 Faraday mol^{-1} Se_6^{2-} depending on initial Se; this is in accordance with the formation of Se_4^{2-} ions [step C, eqn. (4)], the oxidation (4b) of which is detected on the voltammograms [Fig. 2, curve 3, $E_{1/2}^a = -0.54$ V].

$$2\ Se_6^{2-} + 2\ e^- \underset{b}{\overset{f}{\rightleftharpoons}} 3\ Se_4^{2-} \quad (4)$$

The spectra simultaneously evolved to maximal absorbances of brown Se_4^{2-} ions at 550 (shoulder), 417, 307 and 260 nm (Fig. 4, curve 9) through two isosbestic points ($\lambda_{is} = 362$ and 287 nm). The electroreduction of Se_4^{2-} ions (step D) at $E = -1.3$ V entailed the decrease in their maximal absorbances and the loss of the isosbestic points. However, due to passivation at the gold electrode surface, this occurred to a very small extent (⩽5%), thus precluding the coulometric identification of the products.

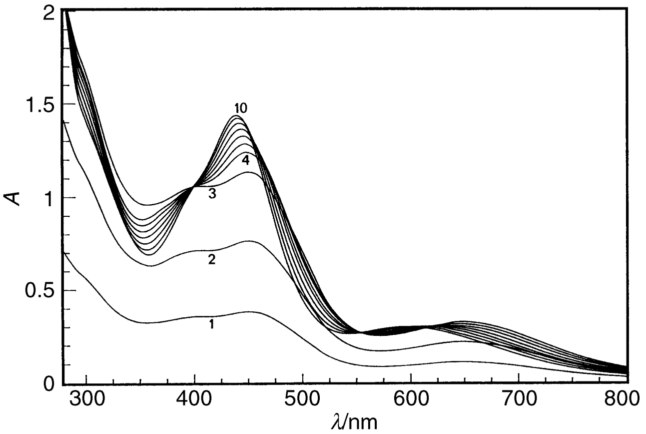

Fig. 3 Changes in UV-vis spectra in the course of electrolysis of electrodeposited selenium on a gold cathode ($w = 31.4$ mg, $v_{sol} = 40$ cm^3) as a function of n Faraday mol^{-1} Se. $n = 0.085$ (1); 0.17 (2); 0.26 (3); 0.28_5–0.36 for (4)–(10). Thickness of the cell = 0.1 cm; scan rate = 1000 nm min^{-1}.

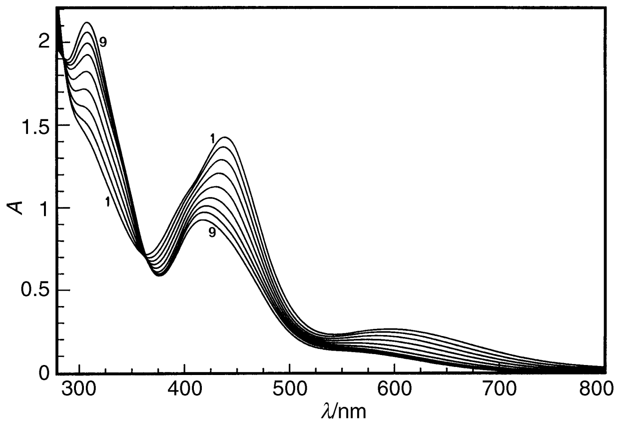

Fig. 4 Continuation of Fig. 3 with the same conditions. $n = 0.36$ (1); 0.39–0.55_5 for (2)–(9).

The constant value $i_C/i_B = 1.85$, which was observed in the course of Se_8^{2-} generation, agrees with the two successive electronic exchanges of reduction steps B and C [eqns. (3) and (4)]. Conversely, the electrochemical oxidations of Se_4^{2-} ions at $E = -0.5$ V [eqn. (4b)] and of Se_6^{2-} ions [$E = -0.4$ V, backward eqn. (3)] led to Se_6^{2-} and Se_8^{2-} ions, respectively, through the same isosbestic points as shown in the forward processes, with concomitant growths of i_C, then $i_B + i_C$. Se_x^{2-} solutions remained stable in the presence of traces of water: the spectra were unchanged by the addition of $[H_2O] = 2.7 \times 10^{-2}$ mol dm^{-3} (20 μL) to solutions (40 cm^3) with $[Se_4^{2-}] = 2.25 \times 10^{-3}$ mol dm^{-3} or $[Se_6^{2-}] = 1.50 \times 10^{-3}$ mol dm^{-3}.

In dipolar aprotic media (DMF, DMSO, HMPA, DMA, acetonitrile) the same anionic polysulfide chains S_8^{2-} ($\lambda_{max} = 515$ nm), S_6^{2-} ($\lambda_{max} = 465$ nm) and S_4^{2-} ($\lambda_{max} = 430$ nm) as polyselenide ones, result from the reduction of cyclic S_8 molecules in solution.[7] The electrolysis of sulfur leads in a first step to S_6^{2-} ions through the disproportionation of S_8^{2-} ions:

$$4\ S_8^{2-} \rightleftharpoons 4\ S_6^{2-} + S_8 \quad (5)$$

The blue colour of the resulting solution is due to the great dissociation [eqn. (6)] of S_6^{2-} into the radical anion $S_3^{\cdot-}$ ($\lambda_{max} = 617$ nm), which was characterized by ESR[15] and Raman[16] measurements. This equilibrium $S_6^{2-}/S_3^{\cdot-}$ is strongly temperature and concentration dependent: the dissociation is reversed upon concentrating or cooling $S^{-1/3}$ solutions.[10,15c]

$$S_6^{2-} \rightleftharpoons 2\ S_3^{\cdot-} \quad (6)$$

The second step ends with the equilibrium:

$$3\ S_4^{2-} \rightleftharpoons 2\ S_3^{2-} + 2\ S_3^{\cdot-} \quad (7)$$

The spectra (800 nm > λ > 250 nm) of the Se_x^{2-} solutions ($x = 8, 6, 4$) here obtained did not vary as a function of temperature (data for $w = 32.4$ mg electrolyzed Se, 60 °C ⩾ T ⩾ 0 °C), except in a minor way (uniform $\Delta A < 5\%$) attributable to density changes of the solvent. Furthermore, the maximal visible absorbances of these anions obeyed Beer's law within the concentration range investigated, as shown in Fig. 5. The existence of $Se_3^{\cdot-}$ in solution could not be assumed from magnetic[11] and ^{77}Se NMR[1,17] investigations, whereas dissociations of dianions were shown by visible absorption and Raman spectroscopy to decrease in the order $S_6^{2-} \gg Se_6^{2-} > Te_5^{2-}$.[10] The recent Raman spectroscopic

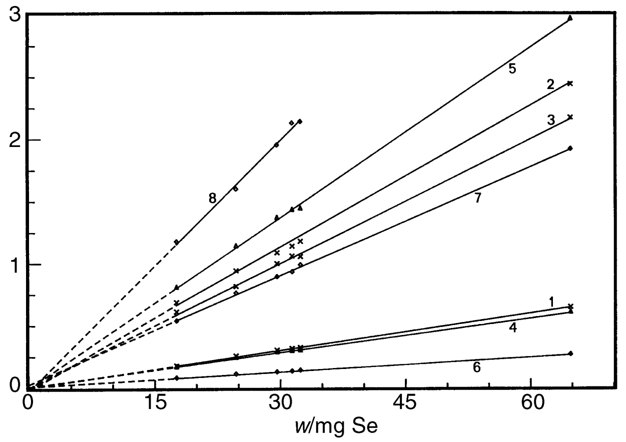

Fig. 5 Maximal absorbances of polyselenide ions: Se_8^{2-} at 648 (1), 453 (2) and 398 (3) nm; Se_6^{2-} at 598 (4) and 440 (5) nm; Se_4^{2-} at 550 (6), 417 (7) and 307 (8) nm as a function of the electrolyzed weight of selenium.

identification of $Se_2^{\bullet -}$ at a very low concentration in Se_4^{2-} aqueous solutions was ascribed to a photolytic process in the electrolyte.[18] Our experimental results on the stability of polyselenide ions *vs.* temperature and concentration agree also with negligible or minor dissociation equilibria for Se_x^{2-} ions, contrary to S_x^{2-} [eqns. (5)–(7)]. The spectrophotometric characteristics of Se_8^{2-}, Se_6^{2-} and Se_4^{2-} species, which were deduced from $A = f(\lambda)$ recordings and the plots in Fig. 5 are listed in Table 1. As the polyselenide ions Se_x^{2-} become larger ($x = 4, 6, 8$) the visible bands shift to higher wavelengths.

Se powder was stoichiometrically added to a solution of Se_4^{2-} ions, $[Se_4^{2-}]_0 = 2.45 \times 10^{-3}$ mol dm^{-3} [15.5 mg Se, eqn. (8)]; the spectra evolved within 45 min. due to the dissolution of reacting Se, to that expected for Se_6^{2-} ions ($\lambda_{is} = 355$ nm), with calculated values of A_{598} and A_{440} meeting the experimental ones ($\pm 4\%$):

$$Se_4^{2-} + 2\,Se \rightarrow Se_6^{2-} \qquad (8)$$

Se_8^{2-} species were obtained in the same way from $[Se_6^{2-}]_0 = 1.49 \times 10^{-3}$ mol dm^{-3} and Se (10 mg, 2 h) according to:

$$Se_6^{2-} + 2\,Se \rightarrow Se_8^{2-} \qquad (9)$$

It is worth noting that UV-vis spectra of Se_6^{2-} (Fig. 4, curve 1) and of Se_4^{2-} (Fig. 4, curve 9) have strictly the same shapes as those that were obtained in liquid ammonia,[6] Se_6^{2-}: $\lambda_{max} = 581$, 436 and 266 nm, $\lambda_{sh} = 382$ and 306 nm; Se_4^{2-}: $\lambda_{max} = 553$, 416 and 304 nm, $\lambda_{sh} = 345$ nm. Similar absorption bands were also reported in acetone for Se_6^{2-} ions:[10] $\lambda_{max} = 625$ and 440 nm, $\lambda_{sh} = 385$ nm. In ammonia solutions[6] all sodium polyselenides were prepared by stoichiometric weights of sodium and selenium. The spectrophotometric investigations indicated that Na_2Se, Na_2Se_3, Na_2Se_4 and Na_2Se_6 are stable species; Na_2Se_5 was found to be a mixture of Na_2Se_4 and Na_2Se_6 whereas Na_2Se_2 disproportionated into Na_2Se and Na_2Se_3. The continuous electronic injections to selenium that we carried out in DMA entail the formation of the same Se_6^{2-} and Se_4^{2-} ions; the nature of the more reducing species (Se_3^{2-}?) cannot be evidenced on gold material. In NH_3, Se_6^{2-} like S_6^{2-},[19] are the least reduced polychalcogenides. In other aprotic solvents the first step of the electrochemical reduction of sulfur to S_8^{2-} ions is regarded as the opening of the ring S_8.[7,20] In a similar way Se_8^{2-} ions, here reported for the first time, could be the result of the opening of crown-shaped Se_8 rings in the solid state.[21]

Table 1 Spectrophotometric characteristics of polyselenide ions Se_x^{2-}($x = 8, 6, 4$) in *N*,*N*-dimethylacetamide

	λ_{max}/nm	ε_{max} [a]
Se_8^{2-}	648	2500
	453	9600
	398	8500
	260	26000[b]
Se_6^{2-}	598	1750
	440	8700
	260	20000[b]
Se_4^{2-}	550	500
	417	3700
	307	8500
	260	10500[b]

[a] ε_{max}/dm^3 mol^{-1} cm^{-1} $\pm 4\%$. [b] ε_i $\pm 10\%$.

The present results on the generation and the spectrophotometric characterization of Se_x^{2-} species ($x = 4, 6, 8$) are currently being applied to the study of the nucleophilic reactivity of Se_6^{2-} and Se_4^{2-} ions towards alkyl halides.

Experimental

Materials and equipment

N,*N*-Dimethylacetamide, selenium (99.999%, 100 mesh), 1 mol dm^{-3} hydrazine in THF and sodium methoxide (28 wt.% in methanol) were purchased from Aldrich. The purification of DMA and its storage after addition of tetraethylammonium perchlorate (Fluka, 0.1 mol dm^{-3}) as supporting electrolyte have been reported elsewhere.[7a] The thermostatted (20.0 ± 0.5 °C) flow-through cell (usable volume = 50 cm^3) was the same as previously described.[7a] Voltammetric curves at a rotating gold disc electrode (diameter 2 mm, 1000 rev. min^{-1}) and electrolyses were performed by using a EGG-PAR 273 A potentiostat. In both cases the counter electrode was a gold foil in a separated compartment [n° 4 glass frit, 5 cm^3 of 0.1 mol dm^{-3} $N(Et)_4ClO_4$]. All potentials are referenced to the $Ag/AgCl_{(s)}$, KCl saturated in DMA/0.1 mol dm^{-3} $N(Et)_4ClO_4$ electrode. UV-vis spectra were registered on a Kontron Uvikon 930 spectrophotometer (pathlength of the cell = 0.1 cm). All experiments were carried out under a dry nitrogen atmosphere.

Electrodeposition of Se on a gold electrode

Five solid deposits of selenium on a large gold grid electrode (Se, $w = 17.6$, 24.7, 29.6, 31.4 and 32.4 mg) were obtained from initial Se_x^{2-}($\bar{x} = 6$) solutions whose chemical preparation [eqn. (1)] was previously reported.[14] As a typical example sodium methoxide (55 µL, 0.26 mmol) was first added under a nitrogen atmosphere in a vessel containing the gold electrode in dry DMA (40 cm^3), followed by hydrazine (75 µL, 0.075 mmol), and finally powdered selenium (62 mg, 0.78 mmol). After the fast evolution of nitrogen, the mixture was stirred at room temperature for 10 min. The assumed Se_6^{2-} dark solution was then oxidized at controlled potentials ranging between −0.2 and +0.1 V (initial intensity, $i = 65$ mA) up to 21 coulombs consumed (theoritical value = 25 C) leading to a weighed quantity of selenium on the electrode, $w = 17.6$ mg. Two electrodes connected together were used in order to reach the largest Se amount ($w = 64.8$ mg). The coated gold cathodes were cleaned with acetone and dried before transfer into the flow-through cell.

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