

Realization and properties of a silver-diethyldithiocarbamate electrode

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Received 19 November 1982

Accepted for publication 24 May 1983

Study has been made of the function of a metal-complex electrode of the silver—Ag(I) diethyldithiocarbamate—diethyldithiocarbamate anion type. It was found that it might be conveniently used as an indicating electrode in the potentiometric investigation of dithiocarbamate ion concentration. Formal potential values were assessed and the slope of graphic dependence of potential on the logarithm of relative concentration was determined for the silver and silver—diethyldithiocarbamate electrodes, respectively, in dimethyl sulfoxide, methanol as well as in water (ionic strength of NaClO₄ solution being 0.1 mol dm⁻³). Ag(Et₂dtc) complexing has been confirmed by potentiometric and voltammetric measurements. Values of its stability constant in the stated media as well as the value of its solubility product in water have also been determined.

Изучено действие металлкомплексного электрода типа серебро—диэтилдитиокарбаминат серебра—диэтилдитиокарбаминатный анион. Подтверждена возможность его применения в виде индикационного электрода для потенциометрического определения концентрации дитиокарбаминатного иона. Для серебрянного и серебро-диэтилдитиокарбаминатного электродов определены формальный потенциал и склон графической зависимости потенциала от логарифма относительной концентрации в диметилсульфоксиде, метаноле и в воде (ионная сила раствора NaClO₄ 0,1 моль дм⁻³). Потенциометрически и вольтамперометрически подтверждено образование комплекса Ag(Et₂dtc). Определены его константы устойчивости в указанных растворителях и произведение растворимости в воде.

The possibility of potentiometric study of complex-formation equilibria is augmented by the use of the electrodes of the second type in which poorly soluble

compounds are substituted by slightly dissociated complexes. Such electrodes are called "metal-complex" and are indicated by symbols $M|ML_n^{(z-nb)^+}, L^{b-}$. The general condition for their use is electrochemical reversibility, i.e. sufficiently fast potential stabilization, its time invariability, linear graphic potential dependence on the logarithm of the relative complex-formation agent concentration of a slope numerically equal to $2.303RT/zF$, and a reversible polarization curve [1].

There are but few known electrodes that are reversible with respect to ions the equilibria of which are under study. Of the most widely used are the silver electrodes. Conditions for determining complex-formation agent concentration (of an anion or a neutral molecule) using such an electrode are given in paper [2].

In paper [3] a silver-complex electrode is reported to have been used to investigate a dithiocarbamate anion (further indicated as R_2dtc^-). In this case, however, the authors considered an $Ag(R_2dtc)_2$ complex which is not quite characteristic of $Ag(I)$ [4]. The present paper deals with the determination of the role and characteristics of a silver—diethyldithiocarbamate electrode in three different media (dimethyl sulfoxide, methanol, water) with the aim of verifying its utilization in the study of complex-formation equilibria.

Experimental

Chemicals and solvents

Silver nitrate — $AgNO_3$, anal. grade (Lachema, Brno). Sodium diethyldithiocarbamate — $Na(Et_2dtc) \cdot 3H_2O$, anal. grade (Merck). Newly prepared Et_2dtc^- solutions were used and their concentration was determined by potentiometric titration of Cd^{2+} and Zn^{2+} solutions, standardized with Complexone III [5]. Silver diethyldithiocarbamate — $Ag(Et_2dtc)$ — was prepared by precipitating Ag^+ by an equimolar amount of Et_2dtc^- .

Sodium perchlorate — $NaClO_4 \cdot H_2O$, anal. grade (Lachema, Brno). In nonaqueous media it was used after commercially available reagents had been dehydrated. The ionic strength of all solutions was maintained constant with $0.1 \text{ mol dm}^{-3} NaClO_4$.

Dimethyl sulfoxide — $(CH_3)_2SO$ and methanol — CH_3OH , anal. grade (Lachema, Brno). The grade of both solvents was checked voltammetrically and, in view of a possible content of complex-formation materials, also through the "titration" of an Ag^+ solution ($c = 1 \times 10^{-5} \text{ mol dm}^{-3}$) by a solvent containing $NaClO_4$ (as its only admixture). During this titration there was but a very slight decrease in potential, caused by the dilution of the solution.

For the preparation of aqueous solutions twice-distilled water was used.

Instrumentation

Potentiometric measurements were made by means of a potentiometer, Model OP-205 (Radelkis, Budapest). The indicating electrode used was a silver electrode of cylindrical

shape ($d = 6$ mm) of the OH-944 type (Radelkis, Budapest). Before use it was mechanically polished with chalk, then after rinsing, it was dipped for 15 min in concentrated ammonia and again washed with distilled water and the appropriate solvent. The reference electrode consisted of a calomel electrode in an aqueous LiCl solution ($c = 4$ mol dm⁻³) and of a salt bridge filled with NaClO₄ solution ($c = 0.1$ mol dm⁻³) in the appropriate solvent. Its potential, compared with that of a saturated calomel electrode, was -15 mV. All potentials mentioned in this paper are referred to this electrode.

Solutions were maintained at a constant temperature of (25.0 ± 0.1) °C by means of a VEB Prüfgerate-Wert (GDR) thermostat, Type 3230. Measurements were made in a cell fitted with a tempering jacket.

Voltammetric measurements were made with a three-electrode polarograph, Model OH-102 (Radelkis, Budapest). The working electrode used was a platinum disc microelectrode. The reference electrode consisted of a calomel electrode, constituted as for potentiometric measurements. The auxiliary electrode was a large-surface platinum electrode.

Inert gas, employed in voltammetric measurements, was incandescent lamp nitrogen, dehydrated by calcium chloride and saturated by the vapours of the used solvent.

Results and discussion

Function of the electrode and determination of its characteristics

The working of the electrode was verified by measuring the dependence of its potential on the Ag⁺ concentration and on that of Et₂dtc⁻

Theoretical relation, expressing the dependence of a silver electrode potential on the logarithm of Ag⁺ ion relative concentration is given by the following equation

$$E = E'_{\text{Ag}} + \frac{2.303RT}{F} \log [\text{Ag}^+]_r \quad (1)$$

where E'_{Ag} is formal electrode potential. It has been experimentally confirmed that for the values of [Ag⁺] between 5×10^{-5} and 1×10^{-2} mol dm⁻³ this dependence is linear and its characteristics for separate media are given in Table 1. The Ag electrode potential was getting stabilized in nonaqueous solutions more slowly (ca. 2 min) than in water.

From eqn (1), using the relation for the $\beta_{\text{AgL}_n^{(z-bn)+}}$ complex-formation constant, we get the following general equation for the silver-complex electrode

$$E = E'_{\text{AgL}_n^{(z-bn)+}} - n \frac{2.303RT}{F} \log [\text{L}^{b-}]_r \quad (2)$$

where for the formal potential E'_{AgL} we have

$$E'_{\text{AgL}_n^{(z-bn)+}} = E'_{\text{Ag}} + \frac{2.303RT}{F} \log \frac{[\text{AgL}_n^{(z-bn)+}]_r}{\beta} \quad (3)$$

Table 1

Potentiometric characteristics of silver and silver-diethyldithiocarbamate electrodes, potential (V) vs. water calomel electrode with LiCl solution ($c = 4 \text{ mol dm}^{-3}$), ionic strength $I(\text{NaClO}_4) = 0.1 \text{ mol dm}^{-3}$, $t = 25^\circ \text{C}$

Medium	$E_{\text{Ag}} \text{ vs. } \log [\text{Ag}^+]_r$		$E_{\text{Ag}(\text{Et}_2\text{dtc})} \text{ vs. } \log [\text{Et}_2\text{dtc}^-]_r$		$\log \beta_{\text{Ag}(\text{Et}_2\text{dtc})}$	
	E'_{Ag}	Slope	$E'_{\text{Ag}(\text{Et}_2\text{dtc})}$	Slope	Calculation a	Calculation b
Dimethyl sulfoxide	0.39	0.064	-0.73	-0.065	12.5	12.2
Water	0.52	0.059	-0.63	-0.065	12.7*	12.9*
Methanol	0.69	0.067	-0.55	-0.067	13.5	11.2

* Hypothetical value, complex is insoluble in water (solubility product $K_s = 2.0 \times 10^{-19}$; see the text).

In our case we have been trying to verify the behaviour of an electrode, realized from a commercially available silver electrode in an AgNO_3 solution ($c = 1 \times 10^{-5} \text{ mol dm}^{-3}$), titrated by an Et_2dtc^- solution ($c = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$). Graphically obtained potential dependences on the logarithm of relative Et_2dtc^- concentration (Fig. 1) are linear and are characterized by the values of the slope and of the formal potential, given in Table 1. The slope value indicates the presence of the silver complex with one Et_2dtc^- ligand (assuming that the number of exchanged electrons $z = 1$). This inference will be proved further. The silver-complex electrode potential gets stabilized more slowly than that of a silver electrode (ca. 3 min). No formation of insoluble complexes has been observed.

The silver electrode, thus constituted, is reversible with respect to Ag^+ ions (slope 0.059) in an aqueous medium. Lower reversibility noted in dimethyl sulfoxide and methanol as well as in the presence of the Et_2dtc^- complexing agent may be due to media effects. The shift of E'_{Ag} and $E'_{\text{Ag}(\text{Et}_2\text{dtc})}$ values in separate media towards positive potentials is evidently connected with the measure of the solvation ability of solvents in relation to Ag^+ cation. Values of stability constant of the $\text{Ag}(\text{Et}_2\text{dtc})$ complex (Table 1) were calculated:

a) from the $E'_{\text{Ag}(\text{Et}_2\text{dtc})}$ formal potential according to eqn (3), using experimentally obtained values of E'_{Ag} and of the slope (Table 1) and taking into account that $[\text{Ag}(\text{Et}_2\text{dtc})] = c_{\text{Ag}^+} = 1 \times 10^{-5} \text{ mol dm}^{-3}$, which, with a high excess of Et_2dtc^- with regard to Ag^+ , certainly holds as it follows from constant values of $E'_{\text{Ag}(\text{Et}_2\text{dtc})}$ given by the linearity of graphs in Fig. 1;

b) from the potential difference of the silver electrode in Ag^+ solution ($c = 1 \times 10^{-5} \text{ mol dm}^{-3}$) (electrode I, E_{Ag}) and that of the silver electrode in Ag^+

solution ($c = 1 \times 10^{-5}$ mol dm $^{-3}$) in the presence of Et_2dtc^- (silver-complex electrode II, $E_{\text{Ag}(\text{Et}_2\text{dtc})}$), as a function of Et_2dtc^- concentration in the course of titration

$$E_{\text{Ag}} - E_{\text{Ag}(\text{Et}_2\text{dtc})} = \frac{2.303RT}{F} \log \frac{[\text{Ag}^+]_{\text{I},r}}{[\text{Ag}^+]_{\text{II},r}} \quad (4)$$

where

$$[\text{Ag}^+]_{\text{II},r} = \frac{[\text{Ag}(\text{Et}_2\text{dtc})]_r}{\beta \cdot [\text{Et}_2\text{dtc}^-]_r} \quad (5)$$

If $[\text{Et}_2\text{dtc}^-] \gg c_{\text{Ag}^+}$, then $[\text{Ag}(\text{Et}_2\text{dtc})] = c_{\text{Ag}^+} = [\text{Ag}^+]_{\text{I}}$

$$E_{\text{Ag}} - E_{\text{Ag}(\text{Et}_2\text{dtc})} = \frac{2.303RT}{F} \log \beta + \frac{2.303RT}{F} \log [\text{Et}_2\text{dtc}^-]_r \quad (6)$$

Since the condition $[\text{Et}_2\text{dtc}^-] \gg c_{\text{Ag}^+}$ has been fulfilled, we have for $[\text{Et}_2\text{dtc}^-]$ in calculating b) considered total Et_2dtc^- concentration for each titration point.

The value of E_{Ag} , needed for calculating β under b), was in addition to being experimentally obtained in the Ag^+ solution ($c = 1 \times 10^{-5}$ mol dm $^{-3}$) also determined by the method of extrapolation of E_{Ag} vs. $\log [\text{Ag}^+]_{\text{r}}$ dependences to the value of $[\text{Ag}^+]_{\text{r}} = 1 \times 10^{-5}$ mol dm $^{-3}$. While in dimethyl sulfoxide and water respective values of E_{Ag^+} agreed (± 0.01 V), in methanol they differed (experimentally $E_{\text{Ag}} = 0.20$ V, determined by extrapolation $E_{\text{Ag}} = 0.35$ V). E_{Ag} value of 0.20 V was for $[\text{Ag}^+]_{\text{r}} = 1 \times 10^{-5}$ mol dm $^{-3}$ also confirmed by investigating E_{Ag^+} vs. $\log [\text{Ag}^+]_{\text{r}}$ dependences for $[\text{Ag}^+]_{\text{r}} = 10^{-6}$ — 10^{-5} mol dm $^{-3}$. This difference points to the difficulty of extrapolating E_{Ag} vs. $\log [\text{Ag}^+]_{\text{r}}$ dependences in methanolic medium. The value of E'_{Ag} and that of $\log \beta = 13.5$, calculated from it, for methanol (calculation a ; Table 1) may exhibit, therefore, some error. The value of $\log \beta = 11.2$ (calculation b ; Table 1) is derived from experimentally obtained quantity $E_{\text{Ag}} = 0.20$ V for Ag^+ solution ($c = 1 \times 10^{-5}$ mol dm $^{-3}$). If in calculation b) extrapolated value of $E_{\text{Ag}} = 0.35$ V is used (obtained from the same E_{Ag} vs. $\log [\text{Ag}^+]_{\text{r}}$ dependence as E'_{Ag}), then $\log \beta$ was found to be 13.4, which is in agreement with the result of calculation a).

$\text{Ag}(\text{Et}_2\text{dtc})$ complex in higher concentrations is insoluble in water (Ag^+ solution titration, $c = 1 \times 10^{-3}$ mol dm $^{-3}$, by Et_2dtc^- ; see below). Its stability constant is under these conditions hypothetical and the electrode under study is an electrode of the second type with the scheme $\text{Ag}|\text{Ag}(\text{Et}_2\text{dtc}) (\text{s}), \text{Et}_2\text{dtc}^-$, the formal potential of which includes solubility product K_s of the complex

$$E'_{\text{Ag}(\text{Et}_2\text{dtc})} = E'_{\text{Ag}} + \frac{RT}{F} \ln K_s \quad (7)$$

The value of $K_s = 2.0 \times 10^{-18}$ was obtained from the data in Table 1.

Number of coordinated ligands in diethyldithiocarbamate silver complex

Titration of the Ag^+ solution by an Et_2dtc^- solution, as well as those of the Et_2dtc^- solution by an Ag^+ solution, were performed and potentiometrically and voltammetrically evaluated.

a) Potentiometric study

In the course of Ag^+ solution titration ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$) in water there is a jump in potential on the potentiometric titration curve at an Et_2dtc^- consumption corresponding to a metal—ligand mole ratio of 1:1 and, therefore, to $\text{Ag}(\text{Et}_2\text{dtc})$ formation. The complex is insoluble in an aqueous medium. Similarly, in methanolic solutions there is also a sharp drop of potential at an Et_2dtc^- consumption corresponding to a metal—ligand mole ratio of 1:1 and to the formation of $\text{Ag}(\text{Et}_2\text{dtc})$ (Fig. 2, curve 1). The complex is only partially soluble in methanolic solutions.

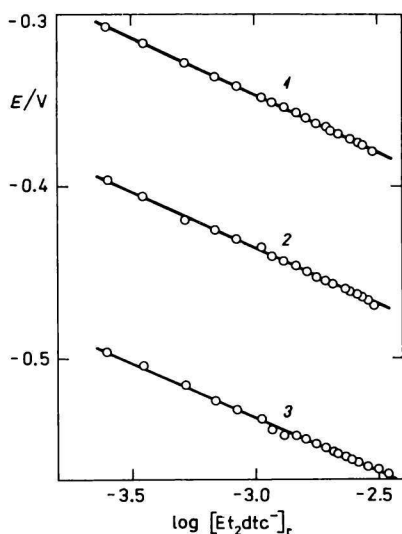


Fig. 1. Dependence of silver-diethyldithiocarbamate electrode potential on logarithm of Et_2dtc^- relative concentration, Ag^+ solution ($c = 1 \times 10^{-5} \text{ mol dm}^{-3}$); ionic strength $I(\text{NaClO}_4) = 0.1 \text{ mol dm}^{-3}$; $t = 25^\circ\text{C}$; medium: 1. methanol, 2. water, 3. dimethyl sulfoxide. Linear dependence calculated by the least-square method.

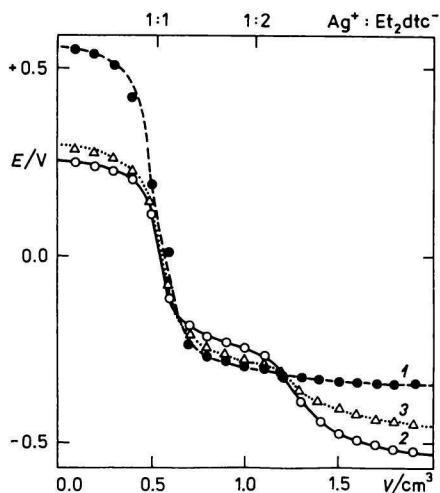


Fig. 2. Potentiometric curves of Ag^+ solution titration ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$) by Et_2dtc^- solution ($c = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$) in methanol (curve 1), dimethyl sulfoxide (curve 2), and in methanol—dimethyl sulfoxide 1:1 mixture (curve 3); ionic strength $I(\text{NaClO}_4) = 0.1 \text{ mol dm}^{-3}$; $t = 25^\circ\text{C}$; potential (V) vs. 4 M-CE.

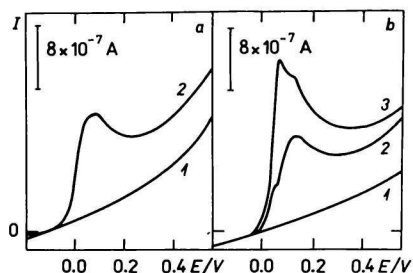
In dimethyl sulfoxide, however, two jumps in potential were observed on the potentiometric titration curve. The first appeared at an Et_2dtc^- consumption corresponding to a metal—ligand mole ratio of 1 : 1, the second, more pronounced, at an Et_2dtc^- consumption, higher by about 20 % than double that corresponding to the mole ratio of 1 : 1 (Fig. 2, curve 2). Dithiocarbamate silver complex in this solvent is soluble. Similar results were obtained through Et_2dtc^- solution titration ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$) by an Ag^+ solution ($c = 5 \times 10^{-3} \text{ mol dm}^{-3}$) as well as through Ag^+ solution titration ($c = 1 \times 10^{-4} \text{ mol dm}^{-3}$) by an Et_2dtc^- solution ($c = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$).

This behaviour discrepancy in methanol, water, and dimethyl sulfoxide was further examined through potentiometric titration in dimethyl sulfoxide and methanol mixtures using solvents of various volume ratios. Here, too, in the course of Ag^+ solution titration ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$) a second jump in potential could be observed (Fig. 2, curve 3) but not until dimethyl sulfoxide and methanol were in their volume ratio of 1 : 1 when the second potential jump grew with the increase of the fraction of dimethyl sulfoxide in the mixture.

b) Voltammetric study

This is based on the free diethyldithiocarbamate anion electroactivity, shown by an anodic oxidation peak which, at the platinum stationary electrode, was observed at the potential $E = +0.09 \text{ V}$ in methanol and $E = +0.13 \text{ V}$ in dimethyl sulfoxide. In the Ag^+ solution titration ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$) by an Et_2dtc^- solution ($c = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$) in methanol, an Et_2dtc^- anodic oxidation peak was registered after the Et_2dtc^- consumption, giving a metal—ligand mole ratio of 1 : 1, had been passed. The peak grew with further additions of Et_2dtc^- . The course of titration is illustrated in Fig. 3a. In the dimethyl sulfoxide medium an Et_2dtc^- anodic oxidation peak also appeared when the Et_2dtc^- consumption corresponding to a metal—ligand mole ratio of 1 : 1 had been passed and then kept on growing with further additions. At an Et_2dtc^- consumption lower than that corresponding to the mole ratio of 1 : 2 there appeared a prepeak of the anodic peak ($\Delta E_p = 0.05 \text{ V}$)

Fig. 3. Voltammogram of Et_2dtc^- anodic oxidation in the course of Ag^+ solution titration ($c = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$) by Et_2dtc^- solution ($c = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$); platinum stationary microelectrode; scan rate 0.1 V s^{-1} ; ionic strength $I(\text{NaClO}_4) = 0.1 \text{ mol dm}^{-3}$; $t = 25^\circ \text{C}$; potential (V) vs. 4 M-CE. Medium: a) methanol, b) dimethyl sulfoxide. Et_2dtc^- consumption corresponding to metal—ligand ratios 1 : 1 (curve 1, identical with the record of base electrolyte), 1 : 2 (curve 2), and 1 : 3 (curve 3).



which, with further additions of Et_2dte^- , exceeded the original anodic oxidation peak. The course of titration is shown in Fig. 3b.

We have also made a voltammetric monitoring of an $\text{Ag}(\text{Et}_2\text{dte})$ solution titration ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$) by an Et_2dte^- solution ($c = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$) in dimethyl sulfoxide. $\text{Ag}(\text{I})$ diethyldithiocarbamate is not electroactive in the potential region investigated. After the first addition of Et_2dte^- there appeared an anodic peak at the prepeak potential of the above-described Ag^+ solution titration which grew with further Et_2dte^- additions.

On the strength of the above arguments and also considering slope values of the metal-complex electrode potential graphic dependence on the logarithm of the ligand relative concentration we are of the opinion that the indicator Ag^+ ion forms an $\text{Ag}(\text{Et}_2\text{dte})$ complex.

The potentiometric behaviour of the system investigated in dimethyl sulfoxide described above can also explain further specific interaction between Ag^+ and Et_2dte^- .

The study confirms the view that a silver-diethyldithiocarbamate electrode can be used as an indicating potentiometric electrode. This electrode enables to make quantitative study of formation equilibria of complexes involving Et_2dte^- , which will be the subject of another publication.

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Translated by J. Dravecký