

Formation and stability of diethyldithiocarbamate complexes

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The formation of diethyldithiocarbamate complexes with Mn(III), Fe(III), Co(III), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), and Bi(III) central atoms has been potentiometrically studied using a silver-complex electrode. Stability constants of complexes were determined in dimethyl sulfoxide and methanol as well as solubility products of Cu(II), Zn(II), and Cd(II) diethyldithiocarbamates in water.

Потенциометрически с помощью серебро-комплексного электрода изучено образование диэтилдитиокарбаминатных комплексов с центральными атомами Mn(III), Fe(III), Co(III), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II) и Bi(III). Определены константы устойчивости комплексов в диметилсульфоксиде и метаноле и произведения растворимости диэтилдитиокарбаминатов Cu(II), Zn(II) и Cd(II) в воде.

From the viewpoint of coordination, analytical as well as industrial chemistry it is highly important to understand the formation and stability of dithiocarbamate complexes and to know the exact experimental methods of their investigation. In the past, inferences were often made only on the relative stability of dithiocarbamates on the basis of differences in solubility in aqueous solutions or on that of the reciprocal metal displacement capacity at extraction. Absolute stability evaluation of dithiocarbamate complexes is based on competitive reactions of two metals and one ligand or of two ligands and one metal, as for example in [1—5]; processes based on extraction yielded the so-called two-phase stability constants [2—5]. The formation of dithiocarbamate complexes of some metals and ligand derivatives was further studied spectrophotometrically [6—8] and potentiometrically [9]. Stability constants so obtained were markedly lower in value than those determined by the mentioned competitive reaction technique.

In view of the contradictory statements found in literature the present paper deals with the formation and stability of diethyldithiocarbamates in three different media, studied by a sensitive potentiometric method using a silver-complex indicating electrode [10]. Redox changes were voltammetrically monitored.

Experimental

Chemicals and instrumentation

Crystalline nitrates of separate metals as well as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were used and all were of anal. grade (Lachema, Brno). Concentration of metal ions was complexometrically determined by standard techniques [11]. Sodium diethyldithiocarbamate, cupral $\text{Et}_2\text{dtcNa} \cdot 3\text{H}_2\text{O}$, was an anal. grade Merck preparation and its solutions were standardized by titration as described in paper [9]. Iron(III) and cobalt(III) diethyldithiocarbamates were prepared according to the procedure given in [12].

The purity of solvents — distilled dimethyl sulfoxide, anal. grade methanol (Lachema, Brno), and redistilled water — was verified by the procedure described in [10]. All the solvents were adjusted to a constant ionic strength ($I = 0.1 \text{ mol dm}^{-3}$) using NaClO_4 , dehydrated for nonaqueous media.

Potentiometric measurements were made with a potentiometer, Model OP-205 (Radelkis, Budapest) and voltammetric measurements with an OH-102 type polarograph (Radelkis, Budapest). The potentiometric measuring cell consisted of a silver-diethyldithiocarbamate indicating electrode [10], constituted from a commercially obtained silver electrode of OH-944 type (Radelkis, Budapest) dipped into an AgNO_3 solution ($c = 1 \times 10^{-5} \text{ mol dm}^{-3}$) titrated by an Et_2dtc^- solution ($c = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$), and of a calomel electrode in an aqueous LiCl solution ($c = 4 \text{ mol dm}^{-3}$) with a salt bridge containing NaClO_4 ($c = 0.1 \text{ mol dm}^{-3}$) in the appropriate solvent.

Voltammetric measurements were made with a carbon indicating electrode of cylindrical shape, $d = 6 \text{ mm}$ (Elektrokarbon, Topoľčany), coated with paraffin wax. The auxiliary electrode used was a large-surface platinum electrode and the reference electrode was constituted as for potentiometric measurements. Measurements were made at a constant temperature of $(25.0 \pm 0.1)^\circ\text{C}$.

Other equipment used was the same as that described in paper [10].

Evaluation of potentiometric measurements

The value of $[\text{Et}_2\text{dtc}^-]$ equilibrium concentration at separate titration points was determined according to [10] from the difference in silver-complex electrode potential of the cell containing the indicator Ag(I) ion, where $[\text{Et}_2\text{dtc}^-] = c(\text{Et}_2\text{dtc}^-)$ and that of the cell containing Ag(I) and the ion of the studied metal M ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$), using the following equation

$$\ln [\text{Et}_2\text{dtc}^-]_r = \ln c_r(\text{Et}_2\text{dtc}^-) + \frac{\Delta E}{R} \frac{F}{T} \quad (1)$$

where index r denotes relative concentration and $c(\text{Et}_2\text{dtc}^-)$ is the total Et_2dtc^- concentration. From $[\text{Et}_2\text{dtc}^-]$ values it was possible to calculate the average number of ligands coordinated with metal M atom in the separate titration points [13]

$$\bar{n} = \frac{c(\text{Et}_2\text{dtc}^-) - [\text{Et}_2\text{dtc}^-]}{c(M)} = \frac{\sum_{i=1}^n i \beta_i [\text{Et}_2\text{dtc}^-]^i}{1 + \sum_{i=1}^n \beta_i [\text{Et}_2\text{dtc}^-]^i} \quad (2)$$

Stability β_i total constants were calculated from eqn (2), transformed by the Rossoti—Rossoti method [13] into

$$\sum_{i=0}^{j-1} \frac{\bar{n} - i}{j - \bar{n}} \beta_i [\text{Et}_2\text{dtc}^-]^{i-j} = \beta_j + \sum_{i=j+1}^n \frac{i - \bar{n}}{j - \bar{n}} \beta_i [\text{Et}_2\text{dtc}^-]^{i-j} \quad (3)$$

The solubility product was calculated as described in paper [14] using the equation

$$E = E'(\text{Ag}(\text{Et}_2\text{dtc})) - \frac{R}{z} \frac{T}{F} \ln K_s + \frac{R}{z} \frac{T}{F} \ln [M]_r \quad (4)$$

where $E'(\text{Ag}(\text{Et}_2\text{dtc}))$ is the formal silver-diethyldithiocarbamate electrode potential in aqueous solution [10]. Equilibrium concentration $[M]$ was calculated from $c(M)$ and $c(\text{Et}_2\text{dtc}^-)$ values. Compucorp 610 (USA) and M 4030-1 (USSR) computers were used in making these calculations.

Results

Titration of $\text{Mn}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Hg}(\text{II})$, $\text{Pb}(\text{II})$, and $\text{Bi}(\text{III})$ ions were carried out in dimethyl sulfoxide. Resulting complexes proved to be soluble, the potential stabilization lasting 3 to 4 min. In the case of $\text{Hg}(\text{II})$ titration, the potential of the indicating electrode, dipped in an $\text{Ag}(\text{I})$ and $\text{Hg}(\text{II})$ solution without Et_2dtc^- , was by 220 mV higher than the normally registered $\text{Ag}(\text{I})$ and M system potential — though even the latter used to be by 20 to 50 mV higher when compared with the potential of the indicating electrode of the cell with the indicator $\text{Ag}(\text{I})$ ion alone. The case of $\text{Hg}(\text{II})$ is closely connected with the existence of further redox equilibrium and so it could be evaluated only from the mole ratio of $n(\text{Hg}(\text{II})) : n(\text{Et}_2\text{dtc}^-)$ value in the equivalent point, which was 1 : 2. The calculation of the Hg -complex stability constant would be otherwise distorted.

Fig. 1 shows the dependence of the average number of ligands \bar{n} on the logarithm of ligand equilibrium concentration, i.e. the formation curves of complexes in dimethyl sulfoxide.

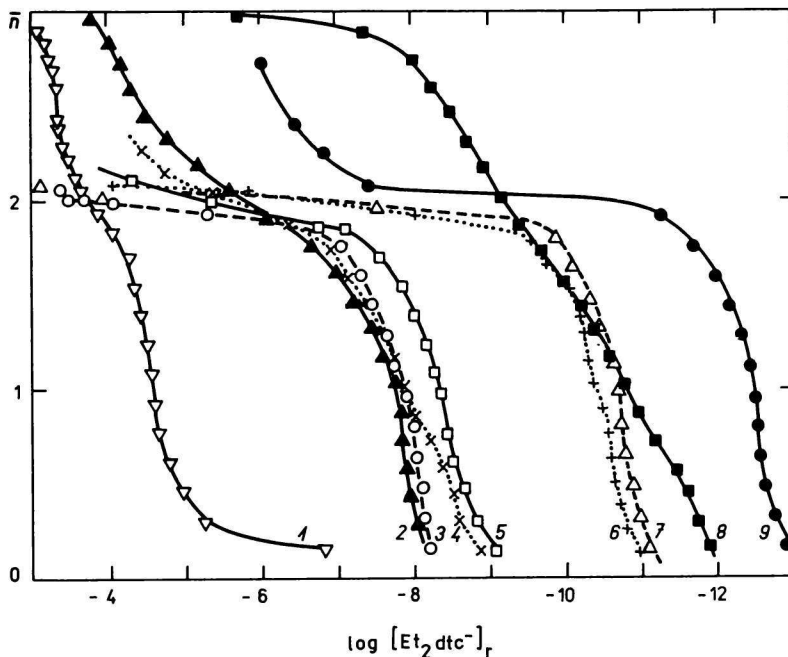


Fig. 1. Formation curves of complexes in the course of M^{2+} ion solution titration ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $V = 10 \text{ cm}^3$) by Et_2dtc^- solution ($c = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$). M: 1. Mn; 2. Fe; 3. Zn; 4. Pb; 5. Cd; 6. Co; 7. Ni; 8. Bi; 9. Cu. Dimethyl sulfoxide, ionic strength 0.1 mol dm^{-3} , 25°C .

Titration of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) ions were carried out in methanol. Mn(II), Fe(II), and Bi(III) salts did not prove soluble and so were not studied. Potential stabilization time in methanol was the same as that in dimethyl sulfoxide. Formation curves of complexes are given in Fig. 2.

The formation of iron and cobalt complexes was also studied voltammetrically. Products formed with air access were investigated and their properties compared with the voltammetric behaviour of synthetically prepared $\text{Fe}(\text{Et}_2\text{dtc})_3$ and $\text{Co}(\text{Et}_2\text{dtc})_3$ complexes and with the published data [15, 16]. The analysis of the iron complex formed in dimethyl sulfoxide at a mole ratio of $n(\text{Fe}) : n(\text{Et}_2\text{dtc}^-) = 1 : 2$ has confirmed the presence of the Fe(III) oxidation state (the cathodic peak at potential $E_p = -0.39 \text{ V}$ with counterpeak $E_p = -0.32 \text{ V}$ and an anodic oxidation peak of the complex at potential $E_p = 0.43 \text{ V}$ with counterpeak $E_p = 0.38 \text{ V}$).

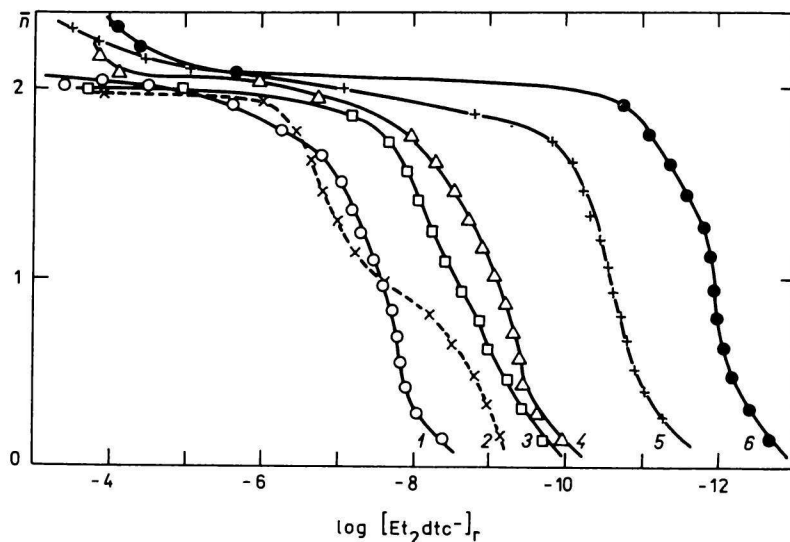


Fig. 2. Formation curves of complexes in the course of M^{2+} ion solution titration ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $V = 10 \text{ cm}^3$) by Et_2dtc^- solution ($c = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$). M: 1. Zn; 2. Pb; 3. Cd; 4. Ni; 5. Co; 6. Cu. Methanol, ionic strength 0.1 mol dm^{-3} , 25°C .

Oxidation to Co(III) was also observed in the case of cobalt both in dimethyl sulfoxide and in methanol. After adding Et_2dtc^- to the Co(II) solution up to a mole ratio of $n(\text{Co}) : n(\text{Et}_2\text{dtc}^-) = 1 : 2$ it was possible to record a cathodic peak at potential $E_p = -1.40 \text{ V}$ and an anodic peak at $E_p = 1.00 \text{ V}$ with counterpeak $E_p = 0.90 \text{ V}$. After a further addition of Et_2dtc^- there also appeared an anodic oxidation peak of an Et_2dtc^- free ion at potential $E_p = 0.10 \text{ V}$.

To calculate stability constants of complexes formed in dimethyl sulfoxide and methanol we used eqn (3). Fit of experimental points to the theoretical eqn (3) has been proved by high values of the correlation coefficient ($r > 0.99$). Values of stability constants are given in Table 1.

Titrations of the same ions as in methanol were carried out in an aqueous medium. In view of the slow potential stabilization process in buffer solutions, titrations were carried out in bufferless solutions ($\text{pH} = 6$) in which the potential was stabilized for 1 min. The resulting complexes were insoluble. Their formation curves are shown in Fig. 3.

Titrations in an aqueous medium determined the sequence of metal ion precipitation and the reaction stoichiometry besides providing an experimental basis for calculating the solubility product values of the appropriate diethyldithiocarbamates. A steep course of the formation curves is a necessary precondition for such a computation. Fig. 3 shows that this condition was met only in Cu(II),

Table 1

Stability constants of diethyldithiocarbamate complexes (ionic strength 0.1 mol dm⁻³, 25 °C)

Complex	Dimethyl sulfoxide			Methanol	
	log (β_1 /(mol ⁻¹ dm ³))	log (β_2 /(mol ⁻² dm ⁶))	log (β_3 /(mol ⁻³ dm ⁹))	log (β_1 /(mol ⁻¹ dm ³))	log (β_2 /(mol ⁻² dm ⁶))
Zn(Et ₂ dtc) ₂	7.83	15.7		7.7	15.1
Pb(Et ₂ dtc) ₂	8.3	15.9		8.7	15.4
Cd(Et ₂ dtc) ₂	8.4	16.7		9.1	17.1
Co(Et ₂ dtc) ₂ ⁺	10.2	20.8		10.6	21.1
Ni(Et ₂ dtc) ₂	10.3	21.5		9.4	18.2
Cu(Et ₂ dtc) ₂	12.3	25.0		11.7	23.9
Mn(Et ₂ dtc) ₃	4.9	9.3	12.6		
Fe(Et ₂ dtc) ₃	7.5	15.2	19.7		
Bi(Et ₂ dtc) ₃	11.2	21.6	29.6		

* Insoluble initial salts.

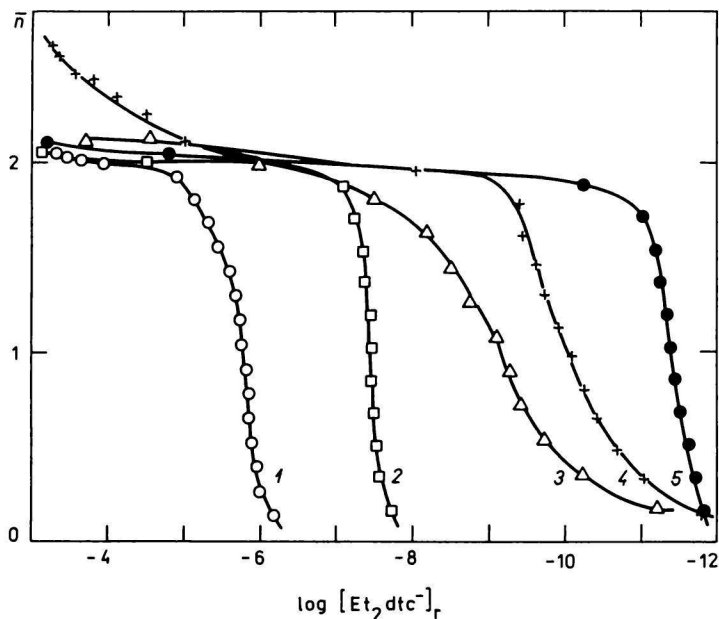


Fig. 3. Formation curves of complexes in the course of M^{2+} ion solution titration ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $V = 10 \text{ cm}^3$) by Et_2dtc^- solution ($c = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$). M: 1. Zn; 2. Cd; 3. Ni; 4. Co; 5. Cu. Water, ionic strength 0.1 mol dm^{-3} , 25°C .

Zn(II), and Cd(II) complexes. Calculations based on eqn (4) provided the following solubility product values (in terms of $\log(K_s/(\text{mol}^3 \text{ dm}^{-9}))$): $-14.8(\text{Zn}(\text{Et}_2\text{dtc})_2)$, $-18.2(\text{Cd}(\text{Et}_2\text{dtc})_2)$, and $-26.2(\text{Cu}(\text{Et}_2\text{dtc})_2)$. In these calculations titration data were taken into consideration up to the equivalent point. Side reactions (metal hydroxo complex formation and ligand protonization) were not taken into account because of the weak acidic medium ($\text{pH} = 6$).

Discussion

Maximum coordination numbers, resultant for central atoms from formation curves, have reached their usual values. In the case of Mn(II) titration, oxidation to Mn(III) and the coordination of three ligands have occurred, as evidenced also by the rapid change in colour of the solution to typically violet [17]. No formation of manganese triscomplex has, however, been observed [4, 5]. The iron-complex formation curve has, in accord with [4], confirmed the $\text{Fe}(\text{Et}_2\text{dtc})_2^+$ presence in a wider range of Et_2dtc^- concentration. The bond of a third ligand has been less

markedly apparent on the change of the potential which, with the exception of $\text{Fe}(\text{Et}_2\text{dte})_3$ and $\text{Fe}(\text{Et}_2\text{dte})_3^-$ formation [6, 16], may be also partially connected with a side redox reaction. Nonintegral value \bar{n} (between 2 and 3), recorded in the cobalt complex is also due to the central atom oxidation. Complex $\text{Co}(\text{II})$ can already be oxidized by traces of oxygen even in an inert atmosphere [6]. The resulting $\text{Co}(\text{III})$ is substitutionally inert, which retards the bonding of the third ligand as stated in paper [4]. In computing the stability constant, therefore, account was taken of the two-stage equilibrium and it was calculated from data up to $\bar{n} = 2$. In the case of copper the value of $\bar{n} = 2$ has remained unchanged in a relatively wide range of Et_2dte^- concentration and its increase ($\bar{n} > 3$) in the region of higher Et_2dte^- concentration (especially in dimethyl sulfoxide) is evidently due to side chemical or electrochemical phenomena.

Stability constant values thus obtained in principle confirm the published dithiocarbamate-complex formation sequences. Most of them numerically come close to stability constants that result from competitive reactions [1–5] but are strikingly higher in value than the stability constants defined in [6–9]. This inconsistency may be due to a lesser sensitivity of the spectrophotometric method as well as to a substantially different reaction medium [6–8]. The authors of paper [9] used the same technique as we did but in their case titration was done in dimethyl formamide and the unusual $\text{Ag}(\text{Et}_2\text{dte})_2$ complex formation was considered for the indicator ion. The presence of $\text{Ag}(\text{Et}_2\text{dte})$ was confirmed by a special study contained in paper [10]. The considered type of the indicator complex had a decisive influence on the established discrepancy in stability constant values. In our experiments with potentiometric titration in dimethylformamide we found that the reduction components, present in it, markedly altered the $\text{Ag}(\text{I})$ concentration and thus rendered impossible its reproducibility.

Using two solvents of different solvation capacity did not bring about, except in nickel complex, any substantial difference in stability constant values. To satisfy those interested in the characteristics of the type of complexes existing in aerobic media we refrained from using an inert atmosphere in our investigations. This, as well as the use of salt hydrates, caused a slight increase in water content in solvents, which according to [9] slightly decreases the stability of complexes.

Solubility product values of complexes, determined in water, were found to be higher than the data obtained under other conditions [8, 14]. The solubility sequence, however, of the complexes studied, was identical with that published in literature.

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