Determination of the values of solubility product of some ethylenebisdithiocarbamates

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The values of solubility product of some salts of ethylenebisdithiocarbamic acid (Ag^+, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}) were determined potentiometrically by the use of silver indication electrode. The data obtained are in line with the published properties of the investigated substances (solubility, stability, biological activity).

Потенциометрически при помощи серебряного электрода были определены продукты растворимости некоторых солей этиленбис-дитиокарбаматовой кислоты (Ag^+, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}). Полученные данные в хорошем согласии с литературными данными изучаемых соединений (растворимость, устойчивость, биологическая активность).

The excellent fungicidal properties of some salts of ethylenebisdithiocarbamic acid are known for a few decades. It is especially valid for the salts with bivalent cation, *e.g.* Zn(II) [1], Mn(II) [2], and Cu(II) [3] salts or their combinations, namely Mn + Zn combination [4—6].

The above-mentioned salts with bonded bivalent cation are rather poorly soluble substances the solubility of which decreases in the order Mn, Zn, Cu. Though these compounds have been known for fairly long period of time, no data have been hitherto published in available literature on the basis of which we could compare the solubilities of individual salts of ethylenebisdithiocarbamic acid containing bonded bivalent cations with each other.

The aim of this study has been to determine the values of solubility product of the salts of ethylenebisdithiocarbamic acid containing the following cations: Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Ag^+. For this purpose we used the potentiometric method with silver indication electrode.

Experimental

Chemicals and solvents

The hexahydrate of the disodium salt of ethylenebisdithiocarbamic acid ($Na_2C_4H_6$-$N_2S_4 \cdot 6H_2O$) was prepared according to *Klöpping* [7]. This procedure was extended by the use of 3-fold recrystallization from the aqueous solution saturated at 50 °C. The numerical values of mass fractions of C, N, H obtained from two determinations are as follows: w_i(found)/% (w_i(calc.)/%): C 13.24 (13.19), N 7.83 (7.69), H 4.94 (4.98). The aqueous solutions of the pertinent cations were prepared by dissolving the corresponding nitrates in redistilled water. NaCl was made ready by heating an anal. grade chemical for 10 min at 400 °C and cooling it in a desiccator over P_4O_{10}. Anal. grade $Pb(NO_3)_2$ and Chelaton III were used for complexometric determinations.

Instrumental equipment

The potential was measured with a digital pH-meter OP 211/1 (Radelkis, Budapest); its declared error being ± 1 mV. The following electrodes were used: 1. An indication Ag-electrode, type OH-944. Before measurement the electrode was mechanically cleaned with chalk. After rinsing it was dipped into acidified solution of thiourea and afterwards for 3 min into solution of NH_4OH (V(concentrated solution of NH_4OH): $V(H_2O)$ = = 1 : 1). Then it was washed with water and ethanol and dried up with filter paper. 2. Reference electrode. A saturated calomel electrode joined with the measured solution by means of a bridge filled with 0.1 mol dm^{-3} solution of $NaClO_4$. The influence of diffusion potential was neglected with respect to the instrument and magnitude of the measured values of potentials. The temperature was held at (25.0 ± 0.1) °C by the use of a thermostat VEB-Prüfgeräte Wert (GDR). The undesirable gases (oxygen, carbon monoxide) were removed from the measured system by a flow of pure nitrogen which simultaneously effectuated stirring of the solution before measurement. The solution of $AgNO_3$ was standardized with NaCl once a day. The ionic strength of solutions was adjusted to 0.1 mol dm^{-3} concentration with $NaClO_4$.

Results and discussion

In order to determine the values of solubility product of the investigated substances, it was necessary first to find out the values of formal potential of the silver electrode E'(Ag) and silver—ethylenebisdithiocarbamate electrode E'(Ag$_2$EBDTC).

The value of E'(Ag) was obtained by solving eqn (*1*) for 10—15 pairs of the values of the Ag$^+$ concentration and corresponding potential E(Ag). Altogether five series of measurements were performed. Thus 5 pairs of the values of E'(Ag)

and parameter $b(Ag)$ were obtained. The value of correlation coefficient in individual series varied within the range 0.9980—0.9998.

$$E(Ag) = E'(Ag) + b(Ag) \log([Ag^+]/(mol\,dm^{-3})) \qquad (1)$$

The obtained value of the parameter $b(Ag)$ is equal to $(59.07 \pm 1.12)\,mV$, which is in good agreement with the theoretical value $59.15\,mV$ for $25.0\,°C$. It was ascertained that the value of formal potential of the silver electrode in $0.1\,M\text{-}NaClO_4$ was $E'(Ag) = (574.2 \pm 5.1)\,mV$.

The value of the formal potential $E'(Ag_2EBDTC)$ (Ag_2EBDTC means the disilver salt of ethylenebisdithiocarbamic acid the formation and existence of which was confirmed by preparation and isolation of this substance) was determined analogously by measuring the dependence of the potential of Ag--electrode on $EBDTC^{2-}$ (anion of ethylenebisdithiocarbamic acid). The equilibrium concentration of $[EBDTC^{2-}]$ was calculated from eqn (2). The contribution originating from dissociation was neglected with respect to a low value of the solubility product of Ag_2EBDTC as found in preliminary experiments.

$$[EBDTC^{2-}] = \frac{V(EBDTC)\,c(EBDTC) - 0.5c(Ag)\,V(Ag)}{V_0 + V(Ag) + V(EBDTC)} \qquad (2)$$

The meaning of the symbols in eqn (2) is as follows: $V(Ag)$ is the volume of the $AgNO_3$ solution of $c(Ag)$ concentration which has been used for preparation of the electrode of the second sort, *i.e.* silver—ethylenebisdithiocarbamate electrode. $V(EBDTC)$ is the volume of the $EBDTC^{2-}$ solution of $c(EBDTC)$ concentration which has been altogether added into the solution. V_0 stands for the initial volume of the solution.

The following values were used in our experiments:
$c(EBDTC) = 1 \times 10^{-2}\,mol\,dm^{-3}$, $c(Ag) = 2 \times 10^{-3}\,mol\,dm^{-3}$, $V(Ag) = 0.50\,cm^3$, $V(EBDTC) = 0.00$—$5.00\,cm^3$, during measurements the potential varied within the range (-420)—$(-486)\,mV$. On the whole ten series of measurements were performed. The solution of eqn (3) by the method of least squares gave ten values of $E'(Ag_2EBDTC)$ and $b(Ag_2EBDTC)$.

$$E(Ag) = E'(Ag_2EBDTC) + b(Ag_2EBDTC) \log([EBDTC^{-2}]/(mol\,dm^{-3})) \qquad (3)$$

The following values were obtained: $E'(Ag_2EBDTC) = (-578.2 \pm 3.9)\,mV$, $b(Ag_2EBDTC) = (-31.09 \pm 0.62)\,mV$. In spite of a small deviation from the theoretical value $-29.58\,mV$, the obtained value of the parameter $b(Ag_2EBDTC)$ indicates the transfer of two electrons in the electrode process on the cathode and may be regarded as one of the evidences of existence of the compound Ag_2EBDTC.

On the basis of the obtained values we may determine the value of the solubility product of Ag_2EBDTC from eqn (4)

$$\log K(\mathrm{Ag_2EBDTC}) = \frac{E'(\mathrm{Ag_2EBDTC}) - E'(\mathrm{Ag})}{b(\mathrm{Ag_2EBDTC})} \qquad (4)$$

If we insert the pertinent values in eqn (4), we obtain $K = 8.6 \times 10^{-38}$.

The values of the solubility products of other cations were determined by the method according to *Hulanicky* [8], which was also used in paper [9]. For the value of solubility product the following equation was derived

$$\log K(\mathrm{MEBDTC}) = \frac{E'(\mathrm{Ag_2EBDTC}) - E(\mathrm{Ag})}{b(\mathrm{Ag_2EBDTC})} + \log([\mathrm{M^{2+}}]/(\mathrm{mol\,dm^{-3}})) \qquad (5)$$

In the first approximation, the concentration of the free metal cation was calculated after each addition of the standard solution of cation without respecting the dissociation of salt. In subsequent iterations, the contribution from dissociation was calculated from the last value of the solubility product. It appeared that this correction practically had no significance because of considerable relative error (50—80 %). The values of solubility product were calculated for individual cations in 8—10 points of "titration curve" while the ratio $V_{\mathrm{M}}/V_{\mathrm{M,e}}$ varied within the range 0.1—0.5 ($V_{\mathrm{M,e}}$ is the volume of the solution of cation necessary for stoichiometric course of the reaction with the $\mathrm{EBDTC^{2-}}$ anion). The mean values of solubility product found for individual salts are as follows: $\log K_{\mathrm{s}}$ (error): Mn: $-6.56(0.24)$, Zn: $-9.53(0.20)$, Ni: $-13.41(0.42)$, Co: $-18.47(0.19)$, Cu: $-27.84(0.18)$. It may be assumed that the major cause of the error of measurement consists in very slow establishment of the potential of the indication electrode. While it lasted 3—6 s in measurements of the formal potentials $E'(\mathrm{Ag})$ and $E'(\mathrm{Ag_2EBDTC})$, it required a few minutes in the presence of other cations. The rate of establishment of potential depended on the type of cation as well as on the value of "titration degree". The establishment of equilibrium is fairly rapid for the boundary values of "titration degree" (10 —20 s).

The presented values of solubility product of some salts of ethylenebisdithio-carbamic acid are in good correlation not only with the observed properties of these substances but also with the published data about the corresponding diethyl dithiocarbamates [9]. The obtained values of solubility product account for the biological activity of the Zn(II) and Mn(II) salts of ethylenebisdithiocarbamic acid as well as for easy degradation of these substances when compared with other salts of this acid [4, 10, 11].

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