Determination of the values of ionization constants of ethylenebisdithiocarbamic acid

Š. GERGELY

*Department of Analytical Chemistry, Slovak Technical University,
CS-812 37 Bratislava*

The values of ionization constants $K_{T,1}$ and $K_{T,2}$ of dibasic ethylenebisdithiocarbamic acid were determined potentiometrically. The calculated values enable us to conclude that the hydrogen atoms in both dithiocarbamide groups are practically equivalent in protolytic reactions taking place in aqueous medium.

Потенциометрическим методом были определены константы ионизации $K_{T,1}$ и $K_{T,2}$ этиленбисдитиокарбаматовой кислоты. Выходя из полученных данных можно сделать вывод о том, что атомы водорода в обоих дитиокарбаматовых группах практически эквивалентны в протолитических реакциях в водной среде.

Some salts of ethylenebisdithiocarbamic acid, especially manganese(II) and zinc(II) salts, have been known as excellent fungicide agents for several decades. For this reason, considerable attention has been paid to these substances which manifests itself by a great number of original communications dealing with individual properties and practical application of these compounds [1—5].

As for ethylenebisdithiocarbamic acid (H₂EBDTC), the situation is much worse because besides the paper by *Yakubovich* and *Klimova* [6] issued in 1939 (containing only short information about preparation and appearance of H₂EBDTC acid) no data concerning other properties of this compound (UV, IR, and NMR spectra, thermal properties, *etc.*) have been published.

The aim of this study was to determine the values of ionization constants K_1 and K_2 of this dibasic acid on the basis of the course of titration curve obtained by titrating with a KOH solution.

Experimental

Chemicals and solvents

Pure H_2EBDTC acid was prepared by acidifying an aqueous solution of the disodium salt of this acid, isolating the arisen white crystalline substance and drying it in a desiccator. The contents of C, N, H obtained from six determinations are as follows for $C_4H_8N_2S_4$: w_i(found)/% (w_i(calc.)/%): 22.50 (22.62) C, 13.17 (13.19) N, 3.86 (3.79) H.

Carbonate-free solution of KOH was prepared according to the procedure described by *Albert* and *Serjeant* [7]. Solid $BaCl_2$ was added into a solution of KOH and the free Ba^{2+} cations were removed by letting the solution flow through a ionex column packed with Amberlit IR 120H in K^+ cycle. The carbonate-free solution of KOH was collected in a polyethylene bottle filled with gaseous nitrogen. The burette was filled with the solution of KOH immediately from the stock bottle by means of pressure nitrogen.

The precise concentration of the solution of KOH was determined by standardization with the potassium hydrogen phthalate solution. According to the data given in paper [7], the content of CO_3^{2-} in a solution of KOH thus prepared is less than 1 ppm. Boiled and cooled redistilled water was used for preparation of all solutions. The ionic strength of solutions was not adjusted.

Instrumental equipment

A digital pH-meter OP-211/1 (Radelkis, Budapest) with the declared error ± 0.01 pH was used for pH measurements. *Electrodes: 1.* Indication glass electrode CRY-TUR 01—19; *2.* reference electrode CRYTUR RCE 101. The temperature was held at (20.0 ± 0.1) °C by means of a thermostat. The used pH-meter was once a day calibrated by means of the borax and hydrogen phthalate buffer solutions with the values of pH = 9.00 and pH = 4.00, respectively. These buffer solutions were prepared by diluting the commercially produced concentrated buffer solutions (products of the Institute of Drugs and Vaccination Sera, Prague).

Results and discussion

A typical course of titration curve for titration of the solution of H_2EBDTC acid with the solution of KOH is represented in Fig. 1.

On the basis of the presented experimental data as well as additional measurements, it has been ascertained that:

1. The consumption of KOH in the point of equivalence corresponds to the total substance amount of H_2EBDTC acid present in the investigated solution.

2. Freshly prepared solutions of H_2EBDTC acid saturated at the temperature of 20 °C exhibit pH value of 3.20, approximately.

3. H₂EBDTC acid is instable in aqueous medium, the half-life of decomposition being approximately 25 min. (A more precise determination of this value is not important for the purpose of this study and because of the used experimental arrangement it was not possible.) One titration requires 6—7 min and for this reason the time moment of the point of equivalence may be determined only approximately. Moreover, the rate of decomposition of H₂EBDTC acid decreases during titration because the stability of ethylenebisdithiocarbamates considerably increases with pH value [8].

In spite of a great number of repetitions we did not succeed in obtaining a titration curve with two points of equivalence which should correspond to two degrees of ionization of H₂EBDTC. Only one acceptable conclusion results from this fact, *i.e.* the values of K_1 and K_2 must be of equal decimal order.
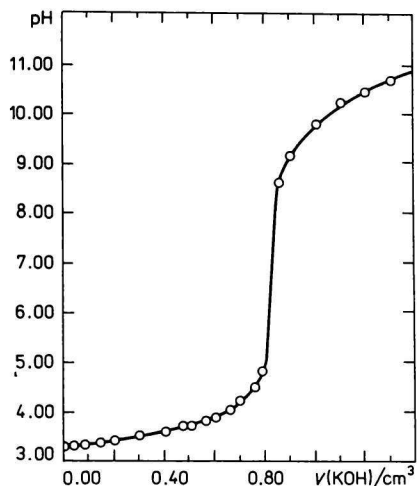

Fig. 1. Course of titration curve for titration of H₂EBDTC acid with KOH solution.
$V_e = 0.835$ cm³; $c(KOH) = 33.94$ mmol dm⁻³;
$V(H_2EBDTC) = 25.0$ cm³.

Under these conditions we used the iterative method described in paper [7] for calculating the ionization constants. The basis of this method consists in solution of the following equation

$$\frac{1}{K_{M,1}} \cdot \frac{F(a(H^+))^2}{2-F} - K_{M,2} = \frac{1-F}{2-F} \cdot (a(H^+))^2 \qquad (1)$$

where $a(H^+)$ is activity of the H⁺ ions, $K_{M,1}$ and $K_{M,2}$ are values of the mixed ionization constants and $F = ([K^+] + [H^+] - [OH^-])/c(H_2EBDTC)$. The symbol $c(H_2EBDTC)$ stands for the analytical concentration of H₂EBDTC acid with respect to the volume change arising in the course of titration.

The known values of $K_{M,1}$ and $K_{M,2}$ are used for calculating the values of [HEBDTC⁻], [EBDTC²⁻], ionic strength I, [H⁺] and [OH⁻] which are applied to the solution of eqn (1) in subsequent iteration.

The calculation terminates if the difference between the values of the mixed ionization constants in two successive iterations is smaller than a small number chosen beforehand (*e.g.* $0.001\ K_{M,1}$ or $0.001\ K_{M,2}$).

The final values of $K_{M,1}$ and $K_{M,2}$ are used for calculating the thermodynamic values according to eqns (*2*) and (*3*)

$$K_{T,1} = K_{M,1} \cdot f(\text{HEBDTC}^-) \tag{2}$$

$$K_{T,2} = K_{M,2} \cdot f(\text{HEBDTC}^-)^3 \tag{3}$$

where $f(\text{HEBDTC}^-)$ is the value of activity coefficient of the HEBDTC^- anion.

Owing to the observed instability of the aqueous solution of acid during titration, it is obvious that the calculated values of $K_{T,1}$ and $K_{T,2}$ are subject to a greater error than "a priori" allowed by experimental arrangement. The error in determination of the constants $K_{T,1}$ and $K_{T,2}$ was estimated on the basis of the error originating in calculation of the constants $K_{M,1}$ and $K_{M,2}$ from eqn (*1*). The relative error was 10 % and 6 %.

With respect to the above-mentioned facts, the resulting values of ionization constants are as follows

$$K_{T,1} = (6.7 \pm 0.7) \times 10^{-4}; \quad K_{T,2} = (3.2 \pm 0.2) \times 10^{-4}$$

These values of ionization constants are in good agreement with the shape of titration curve (Fig. 1) and at the same time give evidence that both thiol groups in a molecule of H_2EBDTC acid dissolved in aqueous medium are practically of equal value as regards protolytic reactions.

References

1. Aagrunol, N. V., *Brit.* 748291 (1956).
2. Flenner, A. L., *USA* 2504404 (1950).
3. Montecatini, *Ger.* 1081446 (1967).
4. Barrientos, C. F., Carbacho, H., and Contreras, J. G., *J. Inorg. Nucl. Chem. 40*, 926 (1979).
5. Lyalikov, Yu. S. and Kitovskaya, M. I., *J. Therm. Anal. 4*, 271 (1972).
6. Yakubovich, A. Ya. and Klimova, V. A., *Zh. Obshch. Khim. 9*, 1777 (1939).
7. Albert, A. and Serjeant, E. P., *The Determination of Ionization Constants.* Academic Press, London, 1971.
8. Klisenko, M. A. and Vekhstein, M. S., *Zh. Obshch. Khim. 41*, 1122 (1971).