The Dissociation Constant of 5, 5-Diethylbarbituric Acid in Aqueous and Aqueous-Dioxane Solutions

Hitoshi OHTAKI, Hideki KATO and Kazuko KUNDA

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya

(Received October 28, 1966)

The dissociation constant of 5, 5-diethylbarbituric acid (DBA) has been determined by Manov, Schuette and Kirk[1] at various temperatures by means of emf measurements using hydrogen electrodes. They reported that the pK of BDA was 7.980 at zero ionic strength at 25°C. Biedermann, Newman and Ohtaki[2] used DBA as a reference substance in the determination of dissociation constants and amounts of protolytic impurities in aqueous ionic media. In 3 M $LiClO_4$, the pK of DBA was found to be 8.373 ± 0.005 at 25°C.

In most cases an accurate measurement of the hydrogen ion concentration with a glass electrode can be ensured only at pH values lower than about 8.2, because glass electrodes do not function well in more alkaline solutions. Therefore, the dissociation constant of a relatively weak acid should be determined in the region where the dissociation of the acid occurs to only a small extent. Thus, the amount of hydroxide ions added must be very accurately known. A technique of the coulometric generation of hydroxide ions explored by Ciavatta[3] is suitable for this purpose on condition that only water is electrolyzed. The technique employed in Ref. 2 in aqueous-solution systems was applied to aqueous-dioxane systems in the present work for the determination of the dissociation constant of DBA in a 3 M $LiClO_4$ medium.

Experimental

5, 5-Diethylbarbituric Acid. C. p. grade DBA was recrystallized three times from alcohol and dried at 110°C for an hour. The melting point of the purified substance was 189°C (188.8°C according to Ref. 1).

Lithium Perchlorate was prepared from Li_2CO_3 (Honjo Aen Kogyosho Co., Osaka) and $HClO_4$ (Hayashi Pure Chemical Industries, Ltd., Osaka) according to the method of Biedermann and Ciavatta.[4]

Dioxane (Hayashi Pure Chemical Industries, Ltd.) was purified according to the ordinary method[5] and stored over metallic sodium under an atmosphere of nitrogen gas. Mixtures of 0, 0.1 and 0.2 molar fractions of dioxane in water were used as the solvents.

A Coulometric Analyzer (Leeds & Northrup Co., Philadelphia) was employed as the current source. A constant current of 6.43 mA (4.000 microfaraday/min) was used. The variation of the current was within 0.05%.

A Radiometer PHM-4d (Radiometer Co., Copenhagen) was used in combination with Beckman-type 40498 glass electrodes for measurements of hydrogen ion concentrations.

A "Wilhelm"-type Half-cell[6] was used for emf measurements, and a modified one for the coulometric generation of hydroxide ions. The hydrogen ion concentration, h, in a solution was determined with the following equation, assuming that the activity factor of the hydrogen ion is kept constant and that the liquid junction potential is negligible:

$$E = E^\circ + 59.15 \log h \qquad (1)$$

where E° is a constant and is determined by means of the Gran plot[7] in the region of a negligible dissociation of DBA. In the present study the standard state of the solution was so chosen that activity factors of the reacting species approached unity when the composition of the solution approached 3 M $LiClO_4$ in a given solvent.

Results

The dissociation equilibrium of DBA is expressed by the following equation:

$$\mathrm{HB} = \mathrm{H}^+ + \mathrm{B}^-, \quad K_{\mathrm{HB}} = \frac{h[\mathrm{B}^-]}{[\mathrm{HB}]} \qquad (2)$$

where HB denotes DBA and where K_{HB} represents the dissociation constant of DBA. From Eq. (2), we have:

$$-\log K_{\mathrm{HB}} = -\log h + \log\left(\frac{[\mathrm{HB}]_{\mathrm{tot}}}{h-H} - 1\right) \qquad (3)$$

where H is an analytical excess of hydrogen ions. The value of K_{HB} was estimated in the region where the dissociation of protolytic impurities was negligible.

Typical results obtained are shown in Table 1, while the average values of $-\log K_{\mathrm{HB}}$ determined in different concentrations of DBA in various solutions are summarized in Table 2. The results in an aqueous solution agreed satisfactorily with the previous data.[2]

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Table 1. A typical run of experiments for determination oe dissociation constant of DBA (Concn. of DBA=40.04 mM in 0.2 molar fraction aqueous-dioxane of 3M $LiClO_4$ at 25°C)

$-\log h$	$-\log K_{HB}$	$-\log h$	$-\log K_{HB}$
7.354	9.426	7.806	9.465
7.410	9.433	7.836	9.465
7.508	9.446	7.866	9.467
7.586	9.452	7.893	9.467
7.669	9.460	7.926	9.467
7.738	9.464	7.956	9.466
7.773	9.465	7.991	9.465

Table 2. Dissociation constants of 5,5-diethylbarbituric acid, $-\log K_{HB}$, in aqueous and aqueous-dioxane solutions containing 3 M $LiClO_4$ at 25°C

Concn. of dioxane Mol. fraction (wt/wt%)	$-\log K_{HB}$
0.0 (0.00%)	8.374 ± 0.005
0.1 (35.21%)	9.093 ± 0.005
0.2 (55.01%)	9.471 ± 0.006

Table 3. Amounts and $-\log K_{HY}$ values of impurities estimated in solutions used

Concn. of dioxane Mol. fraction	$[HY]_{tot}\times10^6$ M	$-\log K_{HY}$ (at 25°C)
0.0	45 ± 10	5.4 ± 0.2
0.1	30 ± 10	4.6 ± 0.2
0.2	45 ± 10	4.5 ± 0.2

The variation in K_{HB} in the lower pH range may be attributed to the presence of protolytic impurities in solutions. If it is simply assumed that the impurity is a single monobasic acid whose dissociation equilibrium can be written as:

$$HY = H^+ + Y^-, \quad K_{HY} = \frac{h[Y^-]}{[HY]} \tag{4}$$

Equation (3) can, in combination with Eq. (2), be rewritten as:

$$h - H - \frac{[HB]_{tot}}{1+h/K_{BH}} = \frac{[HY]_{tot}}{1+h/K_{HY}} \tag{5}$$

The values of K_{HY} and $[HY]_{tot}$, the total amount of the impurity, were determined by means of the "curve fitting" method, comparing the data with a normalized function, $y=f(\log x)=-\log(1+x)$. The amounts and the pK_{HY} values of the impurities present in the solutions used are listed in Table 3. As compared with the results in Ref. 2 (3 M $LiClO_4$, $K_{HY}=6.4\pm0.2$, $[HY]_{tot}=(17\pm5)\times10^{-6}$ M), larger amounts of more acid impurities might exist in the solutions of the present study.

A test with a PAR (4-(2-pyridylazo)-resolcinol) solution[8] showed the presence of heavy metals; the total amount of the metals was estimated to be about 30 μM. Lead ions were detected by means of a dithizone test with KCN and sodium tartrate[9] after the extraction of the metal ions from the test solution with an oxine-chloroform solution at pH 9 and the decomposition of the oxinate by fusion with sodium carbonate.

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[8] W. J. Geary, G. Nickless and F. H. Pollard, *Anal. Chim. Acta,* **26**, 575 (1962).

[9] E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Pub. Inc., New York (1959), pp. 563—571.