*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 110 (4), pp. 425–427 (1982)*

# THE INFLUENCE OF THE IONIC STRENGTH ON THE DISSOCIATION CONSTANT OF HYDROGEN CYANIDE

*(SHORT COMMUNICATION)*

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Received June 17, 1981
Accepted for publication September 18, 1981

For the study of the photoaquation of hexacyanoferrate(II) and octacyanomolybdate(IV) [1] the dissociation constant of hydrogen cyanide ($K_d$) was determined at several ionic strengths in the range from 0.1 to 5.0 mol dm$^{-3}$ $NaClO_4$ ($T = 298$ K).

Data in the literature are available only in the range of the Debye-Hückel theory and were extrapolated to zero ionic strength [2, 3, 4]. Different methods were used for the determination of $K_d$. Britton and Robinson calculated $pK_d = 9.31$ by measuring the saturated vapor pressure of HCN, Pang determined $pK_d = 9.22$ by spectrophotometric measurements and Izatt *et al.* got $pK_d = 9.21$ by monitoring the pH with glass electrode [2].

In our study the dissociation constant was determined by a potentiometric titration method using cyanide selective and glass electrodes. A linearized form of titration curve was used for calculations [5].

## Experimental

0.1 mol dm$^{-3}$ sodium cyanide (Reanal product) stock solutions were freshly prepared and used only if no yellowish colouration occurred. The solutions were kept in plastic vessels in the dark and cold, under $N_2$ atmosphere.

1.0 mol dm$^{-3}$ perchloric acid stock solutions were prepared by diluting 60% (Merck product) perchloric acid. The concentration was determined by titration potassium hydrogencarbonate (Reanal product) using methylorange as an indicator.

For titration at different ionic strengths 0.1 mol dm$^{-3}$ perchloric acid and about 0.01 mol dm$^{-3}$ sodium cyanide solutions were diluted from the stock solutions.

The ionic strength of different samples was adjusted with 6.0 mol dm$^{-3}$ sodium perchlorate (Merck product) stock solution.

The cyanide concentration was determined with an OP-201 Universal Radelkis pH-meter using OP-711-D-IRadelkis ionselective electrode and K 401 Radiometer S.C.E. (filled with saturated sodium chloride to avoid the precipitation of potassium perchlorate).

The pH value of the same sample was determined with PHM-51 Radiometer pH meter using GK 2301 combined electrode (filled also with saturated sodium chloride).

The constant temperature was 298 ± 0.1 K.

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## Calculations

A linearized form of the titration curve can be written as follows:

$$\frac{V+V_0}{C_{\mathrm{HClO_4}}}[\mathrm{CN^-}] = V_{\mathrm{eq}} - \frac{1}{K_\mathrm{d}}\frac{V+V_0}{C_{\mathrm{HClO_4}}}[\mathrm{CN^-}][\mathrm{H^+}] \tag{1}$$

where

$V_0$ volume of a titrated sodium cyanide solution (generally 50 mL), $C_{\mathrm{CN^-}}$ 0.01 mol dm$^{-3}$, $I = 0.1, \ldots, 5.0$ mol dm$^{-3}$ $\mathrm{NaClO_4}$.

$C_{\mathrm{HClO_4}}$ concentration of perchloric acid solution used for titration (0.1 mol dm$^{-3}$, $I = 0.1, \ldots, 5.0$ mol dm$^{-3}$ $\mathrm{NaClO_4}$),

$V$ volume of added acid (mL)

$V_{\mathrm{eq}}$ equivalence volume of perchloric acid, defined as: $V_{\mathrm{eq}} = \frac{V_0[C_{\mathrm{CN^-}}]}{C_{\mathrm{HClO_4}}}$ (mL),

$K_\mathrm{d}$ the dissociation constant of HCN (mol dm$^{-3}$).

The $K_\mathrm{d}$ values were calculated from the slope of (1) type lines by least squares method. The cyanide and hydrogen ion concentrations were calculated only in the first part of the titration curves, because of the well-known anomalous character of the cyanide selective electrode below pH = 8.5 [6].

## Results

Linearized titration curves at different ionic strengths are shown in Fig. 1.

The first part of the titration curves was linear in the whole range of the ionic strength from 0.1 to 5.0 mol dm$^{-3}$ $\mathrm{NaClO_4}$.

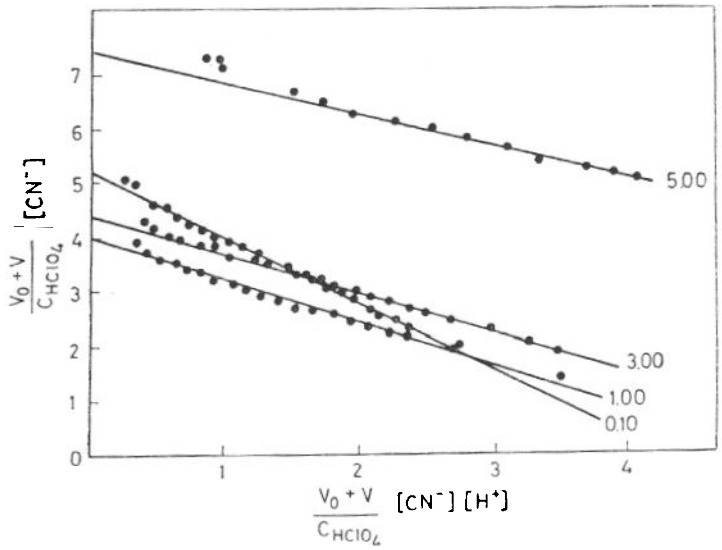

*Fig. 1.* Linearized titration curves at different ionic strengths

The results of the calculations are summarized as follows:

| $I$ (mol dm$^{-3}$ $NaClO_4$) | $\overline{pK_d}$ |
|---|---|
| 0.00 | 9.21 ± 0.01 (extrapolated) |
| 0.10 | 9.06 ± 0.02 |
| 1.00 | 8.88 ± 0.02 |
| 3.00 | 8.81 ± 0.02 |
| 5.00 | 8.78 ± 0.02 |

The mean values were calculated from the results of three parallel measurements.

There is a good agreement between the DH theory and experimental results: the dissociation constant strongly increased with increasing the ionic strength.

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