# DETERMINATION OF THE STABILITY CONSTANTS OF THE COMPLEX OF COBALT WITH PYRIDINE

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The stability constants of the binary complex of cobalt with pyridine, $\log K_1(CoPy^{2+}) = 1{\cdot}16 \pm 0{\cdot}13$ (1·30), $\log K_2(CoPy_2^{2+}) = 0{\cdot}61 \pm 0{\cdot}35$ (0·70), $\log K_3(CoPy_3^{2+}) = (0{\cdot}58)$, were determined by potentiometry and by an extraction method (the values in brackets). Also determined were the dissociation constant of pyridine $pK_a(C_5H_5NH^+) = 5{\cdot}31 \pm 0{\cdot}03$ and its partition constant in the system benzene–water, $K_D = 2{\cdot}83 \pm 0{\cdot}07$. All the equilibrium constants are valid for 25°C and $I$ 0·1 ($NaClO_4$) and were measured under conditions corresponding to the extraction — photometric determination of cobalt with α-furilmonoxime.

The presence of pyridine (Py) plays an important role during the photometric determination of cobalt with α-furilmonoxime[1]. During study of the reactions taking place in this determination, it is necessary to assume that the ternary complex Co–α-furilmonoxime–Py can be formed. In order to enable the equilibria, valid for the mentioned photometric determination, to be described, it is necessary to know the values of the required equilibrium constants for the formation of the binary complexes Co–α-furilmonoxime and Co–Py. The determination of the former was the topic of our previous communication[2].

In this work we determined the equilibrium constants in the Co(II)–Py system, which would be valid in the extraction-photometric determination of cobalt. Values of the stability constant of the binary complex Co–Py have been given by various authors[3-11]. The conditions, under which these constants were determined, however, do not correspond to conditions during the mentioned extraction-photometric determination.

## EXPERIMENTAL

### Reagents and Apparatus

Pyridine was obtained from the commercial p.a. material by drying with KOH and distillation. Cobalt(II) perchlorate was prepared from cobalt(II) acetate p.a. by repeated evaporation with perchloric acid and was recrystallized from water. Other chemicals and solvents used were of p.a. purity.

For measuring pH, the pH meter OP-205 (Radelkis, Budapest) was employed with a glass electrode of the same make and a saturated calomel electrode (Radiometer, Copenhagen). The measuring element was calibrated according to the method of Biedermann and Sillén[12], so that the measured values correspond to $-\log [H^+]$. All measurements were carried out at a temperature of 25 ± 1°C and with an ionic strength of $I = 0{\cdot}1$ ($NaClO_4$).

The dissociation constant of pyridine $K(C_5H_5NH^+)$ was determined potentiometrically[13,14] in a nitrogen atmosphere by two methods. An aqueous pyridine solution, acidified with perchloric acid, was titrated with 0·1M-NaOH. The value of $\log K(C_5H_5NH^+)$ was read as an intercept in the graph of the $\log [Py]/[HPy^+]$ dependence on $-\log [H^+]$. A further determination was carried out by titration of a pyridine solution by 0·1M-$HClO_4$. The $K_a$ value was determined by calculation. The partition constant $K_D$ and distribution ratio $D$ of pyridine between aqueous (0·1M-$NaClO_4$) and benzene phases were determined at pH > 7·5. 15 ml of a pyridine solution in 0·1M-$NaClO_4$ was extracted with 15 ml of benzene until equilibrium was attained (5 min). The pyridine content in both phases was determined by titration using 0·1M-$HClO_4$. In the aqueous phase, the end-point of the titration was determined potentiometrically; in the organic phase, pyridine was determined by titration in glacial acetic acid using methyl violet[15].

*The potentiometric determination of the stability constant of the complex of cobalt with pyridine.* A solution containing $Co(ClO_4)_2$ ($1·0 . 10^{-2}$—$8·5 . 10^{-2}$M) and perchloric acid ($6 . 10^{-3}$ to $1 . 10^{-2}$M) was titrated with a 2M aqueous pyridine solution. The function $\bar{n} = (c_{Py} - [Py])/c_{Co}$ was calculated and the values of $\log K_1$ and $\log K_2$ were determined from the graph of the dependence of $\bar{n}$ on p[Py], and were further refined by the method of successive approximations[16].

*Determination of the stability constant of the complex of cobalt with pyridine by the extraction method.* An aqueous solution of $Co(ClO_4)_2$ ($1 . 10^{-2}$M) and pyridine ($4 . 10^{-2}$—2M) was extracted with benzene to attainment of equilibrium (5 min). After extraction, the pH of the aqueous phase was measured and the concentration of free pyridine in the organic phase was determined by titration with 0·1M-$HClO_4$ in glacial acetic acid. The stability constant values were determined from a graph of the dependence of $\bar{n}$ on p[Py] and refined by the method of successive approximations[16].

## RESULTS

The dissociation constant of pyridine was determined in aqueous solution at the ionic strength and temperature employed in the ensuing measurement of the stability constant values of the complex of cobalt with pyridine. The value $pK_a = 5·20 \pm 0·18$

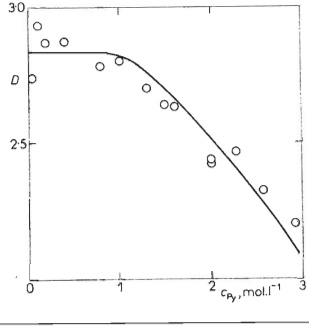


FIG. 1

Dependence of the Distribution Ratio $D$ of Pyridine on Its Original Concentration in the Aqueous Phase

($n = 4$) was determined graphically. The reliability of this and further results is expressed by the 95% confidence limits. By calculation according to[14], the value $pK_a = 5{\cdot}28 \pm 0{\cdot}03$ was obtained. The first of the two values, determined graphically, is closer to the most frequently cited value $pK_a(C_5H_5NH^+)$ (5·17, see[17]); its precision is, however, rather low. The second value is sufficiently precise and its accuracy is comparable with the results of several authors (5·29 – see[18], 5·32 – see[19]).

The partition of pyridine in the system water (0·1M-$NaClO_4$)–benzene was studied at pH > 7·5, *i.e.* in the region in which pyridine is practically not protonized (at pH 7·5, 0·5% of the pyridine is protonized). At a pyridine concentration $c_{Py} \leqq 1$M, its partition is independent of its concentration, so that in the given pH region $D = K_D = 2{\cdot}83 \pm 0{\cdot}07$. At $c_{Py} > 1$M, the distribution ratio of pyridine depends on its original concentration (Fig. 1). During calculation of $D$, the change in the volume of both phases after attainment of extraction equilibrium was taken into account.

Pyridine forms a number of complexes $CoPy_n^{2+}$ with cobalt(II) salts. As opposed to ammine complexes, cobalt remains in its original oxidation state. The stability constants $K_n(CoPy_{n-1}^{2+} + Py \rightleftarrows CoPy_n^{2+})$ were determined both by the common potentiometric method and using extraction, during which the distribution of the free ligand (pyridine) between the two phases is followed, and it is assumed that no species containing cobalt and pyridine (*e.g.* the ion-associate $\{CoPy^{2+}, 2\,ClO_4^-\}$) is perceptibly extracted in the concentration range employed. This assumption was verified by the fact that no cobalt content was found in the organic phase, employing atomic absorption. Use of the extraction method was advantageous because of the simple composition of the organic phase, in which the concentration of pyridine was determined by titration. From the determined values of the partition constant of pyridine and the pH values of the aqueous phase, the concentration of pyridine and protonated pyridine in the aqueous phases were calculated. From the material balance, the concentration of pyridine bound to cobalt and the function $\bar{n}$, necessary for graphical determination of $K_n$, were determined. The following values of $\log K_n$ were determined potentiometrically: $\log K_1 = 1{\cdot}18 \pm 0{\cdot}14$; $\log K_2 = 0{\cdot}66 \pm 0{\cdot}48$ by extraction: $\log K_1 = 1{\cdot}30$; $\log K_2 = 0{\cdot}70$; $\log K_3 = 0{\cdot}58$.

The $K_1$ and $K_2$ values are comparable with those published earlier. The $K_3$ value is larger than the so far published values[7,8,10]. Although the $K_3$ value, determined in the given way, is not too reliable, with respect to its magnitude, it is apparently not erroneous. This follows from comparison of the values of the ratios $K_1/K_2$ and $K_2/K_3$ for the ammine complexes (0·33 and 0·26) and for the pyridine complexes of cobalt (0·25 and 0·76). The value found here for $K_2/K_3$ is larger for the pyridine complex than for the ammine complex, which is also true of the $K_3$ values found by other authors[7,8,10]. The value $K_2/K_3 = 0{\cdot}76$ is even larger than the statistical value of this ratio (0·533), which is also valid for the $K_2$ and $K_3$ values found by two earlier authors[8,10].

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Translated by M. Štulíková.