

Influence of Ligand Concentration and Reaction Medium on Protonation Constants and Stability Constants of Nickel(II) and Copper(II) Benzo[*h*]naphthyridine Complexes

A. GAUDYN and W. ŚLIWA

*Institute of Chemistry, Pedagogical University,
PL-42-201 Częstochowa*

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Using the potentiometric method the influence of ligand concentration and reaction medium on the stability constants of Ni(II) and Cu(II) complexes of 1,6- and 4,6-benzo[*h*]naphthyridines and on their compositions was examined, as well as the influence of the reaction medium on protonation constants for these ligands.

In experiments water—alcohol solutions ($\phi_r = V(\text{H}_2\text{O}) : V(\text{alcohol}) = 2 : 3$) have been applied. The protonation and stability constant values obtained in water—alcohol systems were compared with those determined in aqueous solution. Measurements were carried out at the constant ionic strength $I(\text{KNO}_3) = 0.1 \text{ mol dm}^{-3}$ and 25°C .

The present paper is a continuation of our research concerning complexing properties of benzo[*h*]naphthyridines (bn) [1—4], compounds interesting for their reactivity [5, 6] and biological activities [7].

Bn's are isomeric with 1,10-phenanthroline (phen), a widely used complexing agent; due to the lower symmetry of molecule than in the case of phen, the reactivity of bn's is more dependent on electronic and steric factors.



In our former study the protonation constant values of bn's and stability constant values of their complexes with transition metal ions (Fe, Co, Ni, Cu, Cd, Zn) were determined by the potentiometric method in aqueous solutions; here water—alcohol solutions ($\phi_r = 2 : 3$) are used.

The protonation constants of ligands and stability constants of their Ni(II) and Cu(II) complexes obtained in aqueous and in water—alcohol solutions have been compared and the influence of the ligand concentration and reaction medium on stability constants of complexes and on their composition is discussed, as well as the effect of the reaction medium on the protonation constants of bn's.

EXPERIMENTAL

The stability constants of Ni(II) and Cu(II) com-

plexes of 1,6- and 4,6-bn's have been determined potentiometrically. The measurements were carried out as in our previous work, at 25°C and at the constant ionic strength $I(\text{KNO}_3) = 0.1 \text{ mol dm}^{-3}$, using water—alcohol systems ($\phi_r = 2 : 3$).

The applied reagents $\text{C}_2\text{H}_5\text{OH}$ ($w = 96\%$), 0.1 M-NaOH , $0.01 \text{ M-Ni}(\text{NO}_3)_2$, and $0.01 \text{ M-Cu}(\text{NO}_3)_2$ were of anal. grade quality, 1,6- and 4,6-bn's have been recrystallized from cyclohexane and n-heptane, respectively, their melting points being 95°C and 114°C [2, 3].

The protonation constants were found by titration of the protonated bases (0.0268 M solutions in HNO_3) with 0.1 M-NaOH^* .

According to literature data [8], the concentration of the ligand in the sample should be 10 times lower than that of the titrating agent; so the concentration of the ligand in the sample is 0.01 mol dm^{-3} .

For determination of stability constants of complexes, two titrations of protonated bn's were accomplished, the first one in the absence, and the second in the presence of Ni(II) or Cu(II) ions. The measurements were performed using an OP-211 digital pH-meter (Radelkis, Budapest) (pH accuracy to ± 0.01 units) at 25°C with calomel and glass electrodes. Before the experiment the characteristics of the glass electrode was made. The characteristics of the glass electrode was performed in water and in water—alcohol solution ($\phi_r = 2 : 3$) by titrating $0.1\text{—}0.0001 \text{ M-HNO}_3$ with NaOH of appropriate concen-

* HNO_3 was used in the amount sufficient to protonation of bn, its excess being back titrated with 0.1 M-NaOH ; this was taken into account in calculations.

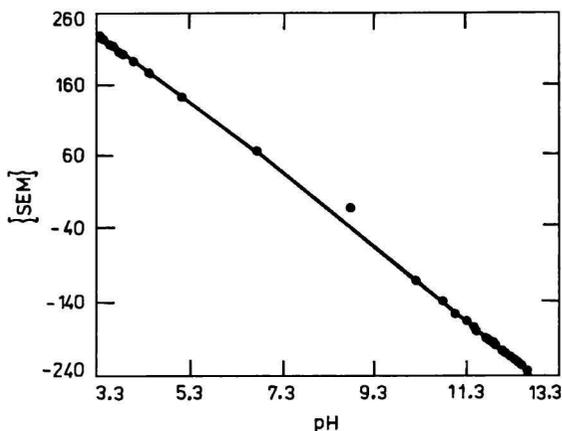


Fig. 1. Characteristics of the glass electrode in aqueous solution for 0.01 M-HNO₃ titrated with 0.1 M-NaOH.

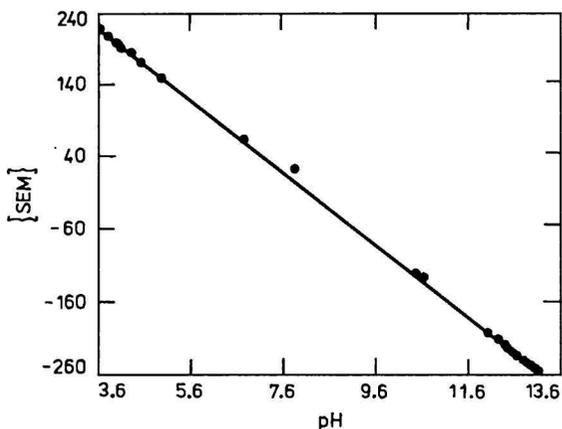


Fig. 2. Characteristics of the glass electrode in water—alcohol ($\varphi_1 = 2 : 3$) solution for 0.01 M-HNO₃ titrated with 0.1 M-NaOH.

tration, and the curves were constructed. For characteristics of the electrode presented in Figs. 1 and

2 curves from the titration of 0.01 M-HNO₃ were chosen. For calculations pK_w at 25 °C equal to 13.996 was taken.

The concentration of hydrogen ions was measured on a compensation pH-meter with glass-calomel electrode system. The standard potential values E_0 calculated prior to each measurement were read from the glass electrode characteristics curve made as a plot of $\{E\} + 59.162 \log \{[H^+]\}$ vs. $\{[H^+]\}$.

The activity of hydrogen ions released during complexation was determined from Nernst's equation. Then the bound and free ligand concentrations, $[L]_{\text{bound}}$ and $[L]_{\text{free}}$, respectively, along with the average number of ligands \bar{n} were calculated using Calvin—Melchior method [9] in order to construct titration curves. Stability constants were determined by the Bjerrum method [10].

The average activity coefficients $f_{\pm} = B/[H^+]$ (B = activity of hydrogen ions read on the pH-meter, $[H^+]$ = concentration of introduced hydrogen ions), were determined according to van Uiter and Davis [11, 12]; these values were used for calculation of activities and thermodynamical stability constants.

The dissociation constants of bn's under investigation were determined also in water—alcohol medium and calculated in the same way. In all cases average of five measurements was taken. The accuracy of protonation and stability constants calculations is 0.01.

RESULTS AND DISCUSSION

The determined values of average f_{\pm} activity coefficient practically are the same in water and in water—alcohol solutions. In water and in water—alco-

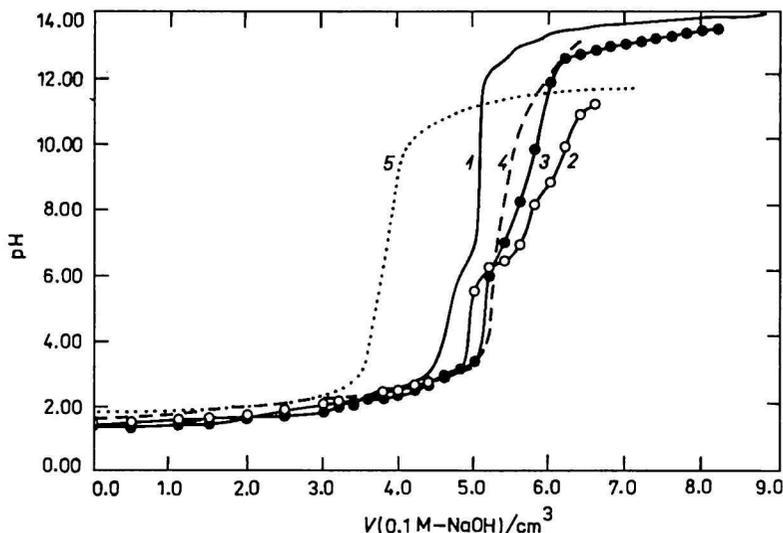


Fig. 3. Titration curve of the protonated 1,6-bn titrated with 0.1 M-NaOH in water—alcohol solution (1), and such curves taken in the presence of 0.025 M (2), 0.017 M (3), and 0.0014 M (4) Ni(II) ion solutions. Titration curve of 0.01 M-HNO₃ titrated with 0.1 M-NaOH (5).

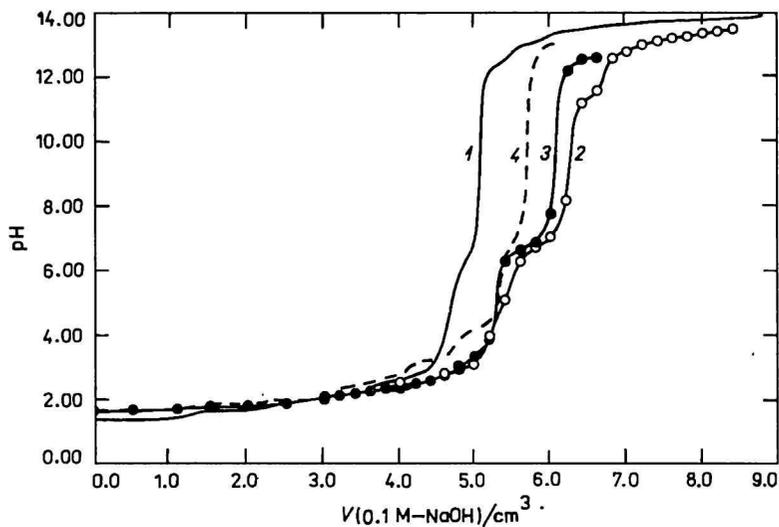


Fig. 4. Titration curve of the protonated 1,6-bn titrated with 0.1 M-NaOH in water—alcohol solution (1), and such curves taken in the presence of 0.025 M (2), 0.017 M (3), and 0.0014 M (4) Cu(II) ion solutions.

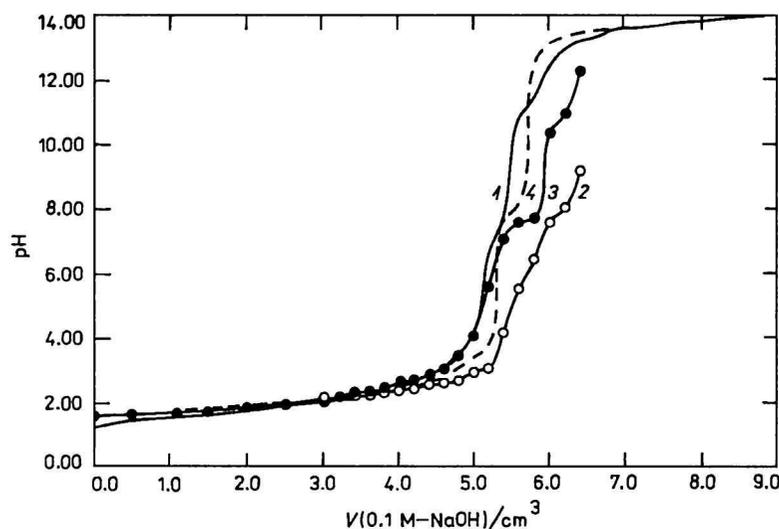


Fig. 5. Titration curve of the protonated 4,6-bn titrated with 0.1 M-NaOH in water—alcohol solution (1), and such curves taken in the presence of 0.025 M (2), 0.017 M (3), and 0.0014 M (4) Ni(II) ion solutions.

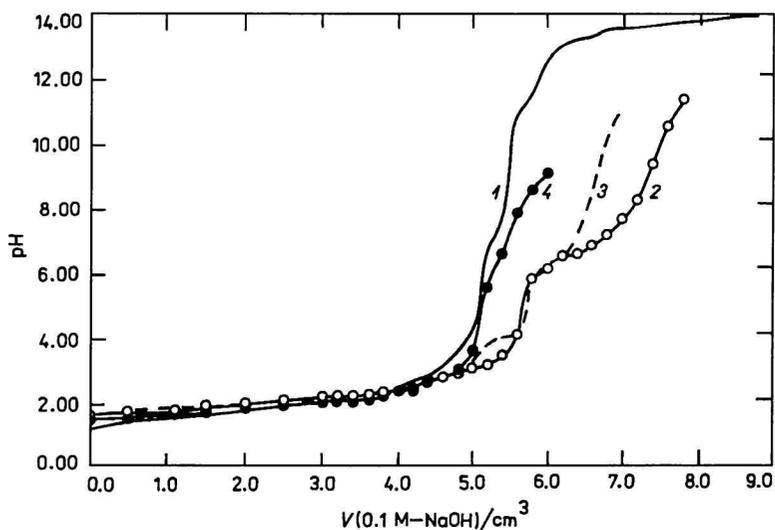


Fig. 6. Titration curve of the protonated 4,6-bn titrated with 0.1 M-NaOH in water—alcohol solution (1), and such curves taken in the presence of 0.025 M (2), 0.017 M (3), and 0.0014 M (4) Cu(II) ion solutions.

Table 1. Protonation Constants of 1,6- and 4,6-bn's and Stability Constants of Their Ni(II) and Cu(II) Complexes in Water—Alcohol and in Aqueous Solutions at Various Metal Ion—Ligand Ratio $c_M : c_L$ ($I = 0.1 \text{ mol dm}^{-3}$)

| Ligand | Medium | $\log K_1$ | $\log K_2$ | Metal ion | $c_M : c_L$ | Stability constants | | | | | | | |
|--------|---------------|------------|------------|-----------|---------------|---------------------|----------------|----------------|----------------|-------|-------|-------|-------|
| | | | | | | $\log \beta_1$ | $\log \beta_2$ | $\log \beta_3$ | $\log \beta_4$ | | | | |
| 1,6-bn | Water—alcohol | 11.06 | 3.29 | Ni(II) | 1 : 4 | 9.95 | 19.62 | 29.07 | — | | | | |
| | | | | | 1 : 6 | 9.62 | 16.44 | — | — | | | | |
| | | | | | 1 : 7 | 7.25 | 14.00 | — | — | | | | |
| | Water | 10.80 | 3.86 | Ni(II) | 1 : 7 | 4.82 | — | — | — | | | | |
| | | | | | Water—alcohol | 11.06 | 3.29 | Cu(II) | 1 : 4 | — | — | — | |
| | | | | | | | | | 1 : 6 | 6.91 | 13.76 | — | — |
| Water | 10.80 | 3.86 | Cu(II) | 1 : 7 | 9.65 | 16.75 | — | — | | | | | |
| | | | | 1 : 7 | 7.97 | 14.02 | — | — | | | | | |
| 4,6-bn | Water—alcohol | 10.56 | 3.67 | Ni(II) | 1 : 4 | 10.85 | 18.35 | — | — | | | | |
| | | | | | 1 : 6 | 6.87 | — | — | — | | | | |
| | | | | | 1 : 7 | 8.15 | — | — | — | | | | |
| | Water | 10.60 | 3.04 | Ni(II) | 1 : 4 | 10.25 | 15.31 | — | — | | | | |
| | | | | | Water—alcohol | 10.56 | 3.67 | Cu(II) | 1 : 4 | 10.50 | 17.50 | 24.65 | 31.70 |
| | | | | | | | | | 1 : 6 | 7.09 | — | — | — |
| Water | 10.60 | 3.04 | Cu(II) | 1 : 7 | — | 7.17 | — | — | | | | | |
| | | | | 1 : 4 | 10.10 | 17.20 | — | — | | | | | |
| phen | Water | 4.95 | — | Ni(II) | — | 7.66 | 14.06 | 18.61 | — | | | | |
| | | | | Cu(II) | — | 10.55 | 19.60 | — | — | | | | |

hol solutions the experimental error is 0.01 pH units; we have checked that this is true for solutions containing $\leq 50\%$ of alcohol.

For the determination of protonation constants and of stability constants the equations and relationships presented in our earlier works were applied [1, 2].

The protonation constants were also determined graphically using the titration curve; the average value of n , denoted by \bar{n} , was calculated from the relation

$$\bar{n} = \frac{(n-a)c_{H_nL} + [OH^-] + [H^+]}{c_{H_nL}}$$

Fig. 3 shows titration curves of the protonated 1,6-bn titrated with 0.1 M-NaOH in water—alcohol solution (1) and such curves taken in the presence of 0.025 M (2), 0.017 M (3) or 0.0014 M (4) Ni(II) ion solutions, as well as the titration curve of 0.01 M-HNO₃ titrated with 0.1 M-NaOH (5). In Fig. 4 analogous curves for Cu(II) complexes of 1,6-bn are presented. The same plots as in Figs. 3 and 4 for 1,6-bn are shown in Figs. 5 and 6 for 4,6-bn.

The found protonation constants of 1,6-bn and 4,6-bn in water—alcohol solutions and stability constants of their Ni(II) and Cu(II) complexes are summarized in Table 1.

The present results were compared with those obtained in aqueous solution. It was observed that the stability constants of Cu(II) complexes of 1,6-bn increase with the higher ligand concentration in water—alcohol solutions. The most stable Cu(II) complexes of 1,6-bn are formed at the ratio of metal ion to ligand $x_r = 1 : 7$.

Stability constants of 4,6-bn complexes with Ni(II)

and Cu(II) ions are higher than those for 1,6-bn complexes.

Comparing the results of potentiometric measurements of stability constants of Ni(II) and Cu(II) complexes of investigated bn's in alcohol—water and in aqueous solutions, it was observed that the stability constants of Ni(II) and Cu(II) complexes determined in alcohol—water solution are higher than those formed in aqueous solution; this fact is in accordance with literature data [13, 14].

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