Complexes of benzimidazole with nickel(II) and cobalt(II)

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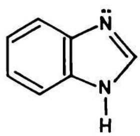
Using the potentiometric method, the protonation constant of benzimidazole, as well as the stability constants of its complexes with nickel(II) and cobalt(II) were determined.

Benzimidazole, a heterocyclic compound of basic character, is interesting for its use as an intermediate in organic synthesis. In the molecule there are two nitrogen atoms; it possesses complexing properties.



Complexes of benzimidazole were studied by *Ghosh et al.*; they obtained solid complexes with several metal ions [1—3]. *Prajapati*, *Bhatt*, and *Soni* described the complex of benzimidazole with copper(II) formed in the ratio 4 : 1 in aqueous solution [4]. *Lenarcik* and *Maciejewski* investigated formation of benzimidazole complexes with some metal ions in aqueous solutions; these authors determined their stability constants with the use of potentiometric method [5].

In the present work we determined the protonation constants of benzimidazole and stability constants of its complexes with Ni(II) and Co(II) using potentiometric method of the other type than that utilized in [5].

The method applied by us proved to be simple and convenient, we used it in our former research for determination of stability constants of complexes of ethylenediamine [6], and three isomeric benzo[*h*]naphthyridines [7—9] with a variety of transition metal ions; the obtained results were good.

In the present work we have made also the statistical evaluation of the found data.

Experimental

The reagents used, 0.005 M benzimidazole, 0.05 M-NaOH, 0.05 M-HNO_3, 1 M-KNO_3, $Co(NO_3)_2 \cdot 6H_2O$, and $Ni(NO_3)_2 \cdot 6H_2O$, were of the anal. grade purity.

Measurements and apparatus

An aqueous solution of benzimidazole in HNO_3 was titrated with NaOH. Titrations were performed at the constant ionic strength equal to 0.5 using digital pH-meter N-517 Mera-Tronik with the calomel and glass electrodes, the pH accuracy was ± 0.01 ($\theta = 20\,°C$).

Protonation constant of benzimidazole as well as stability constants of its complexes with Ni(II) and Co(II) have been determined by the potentiometric method using two titrations of protonated benzimidazole solution with a strong base in the absence and in the presence of corresponding metal ion [10].

Results and discussion

The protonation constant of benzimidazole was calculated from the following equation

$$\log K = \log \frac{(1-a)\,c_{HL} - [H^+] + [OH^-]}{a c_{HL} + [H^+] - [OH^-]} + pH \qquad (1)$$

where K is the protonation constant, a titration fraction, and c_{HL} concentration of the protonated benzimidazole. The calculations were made for titration fraction in the range of 0.2—1.5. The statistical evaluation of the potentiometric determination of protonation constant of benzimidazole is presented in Table 1.

Table 1

The statistical evaluations of the potentiometric determinations of the constants of benzimidazole

Constant of	Number	$\bar{x}$	K_i	r	$L_{1,2} = \bar{x} \pm K_i r$
protonation	5	5.2570	0.51	0.1911	5.26 ± 0.97
stability for Ni(II) complex	3	2.450	1.3	0.430	2.45 ± 0.56
stability forCo(II) complex	3	2.4407	1.3	0.399	2.44 ± 0.52

In the potentiometric determination of the stability constants of the benzimidazole complexes with nickel(II) and cobalt(II) in the pH range 5—9 a strong shift of the titration curves was observed. The concentration of the bound ligand was determined directly from the plot using the Calvin—Melchior method [11]. Plots of the titrations of protonated benzimidazole in the absence and in the presence of Ni(II) and Co(II) ions are shown in Figs. 1 and 2.

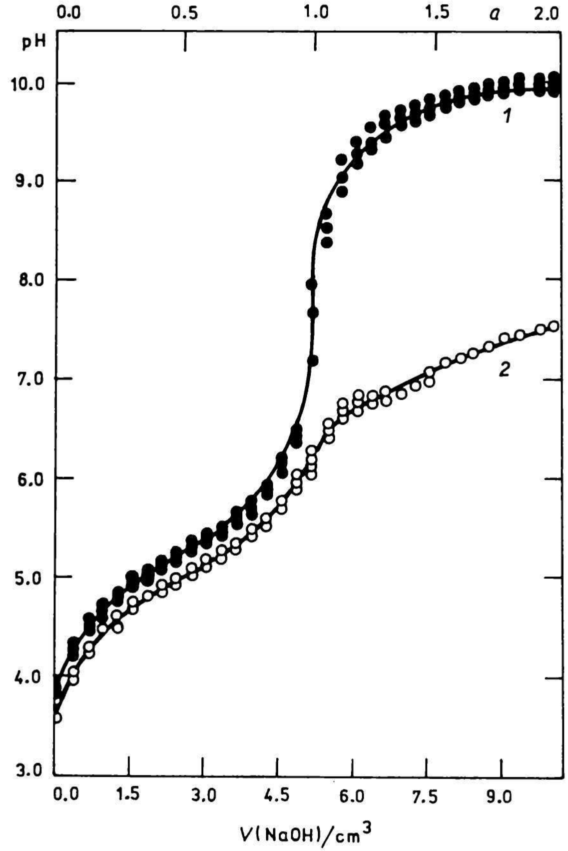


Fig. 1. Titration curves of benzimidazole with 0.05 M-NaOH in the absence (*1*) and in the presence (*2*) of 0.005 M-$Co(NO_3)_2$; *a* titration fraction.

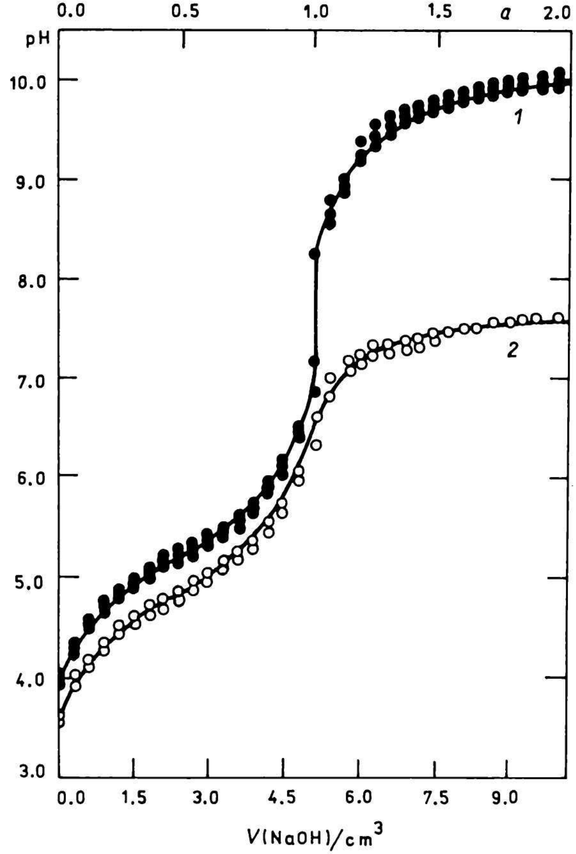


Fig. 2. Titration curves of benzimidazole with 0.05 M-NaOH in the absence (*1*) and in the presence (*2*) of 0.005 M-$Ni(NO_3)_2$; *a* titration fraction.

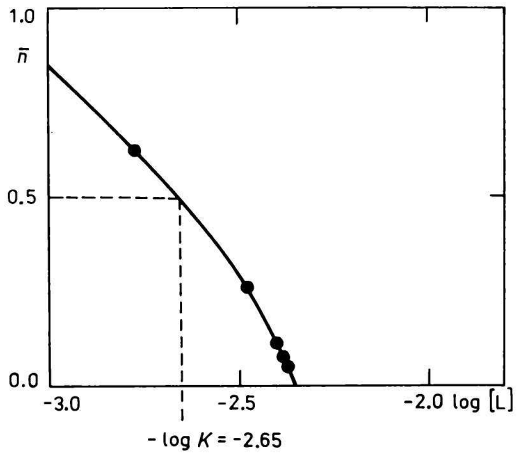


Fig. 3. Formation curve of the complex of benzimidazole with Ni(II).

The concentration of the bound ligand is defined by the following expression

$$[L_{bound}] = (a - a^{\circ})c_{HL} \tag{2}$$

The concentration of the free ligand is given by the relation

$$[L_{free}] = \frac{c_{HL} - (a - a^{\circ})}{1 + [H^{+}]K} \tag{3}$$

Thus, the average number of ligand molecules $\bar{n}$ is given by the relationship

$$\bar{n} = \frac{(a - a^{\circ})c_{HL}}{c_m} \tag{4}$$

where a° is the titration fraction of the protonated base at the given pH value,

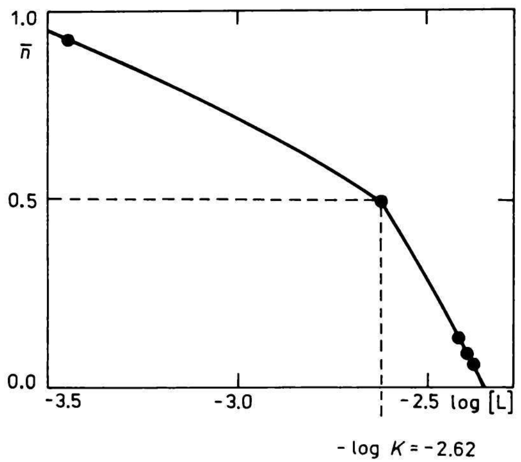


Fig. 4. Formation curve of the complex of benzimidazole with Co(II).

a the titration fraction of the protonated ligand at the same pH value in the presence of the metal ion and c_m total metal ion concentration in the solution. Plots of $\bar{n}$ *vs.* log [L] (Figs. 3 and 4) allowed calculation of the complex stability constants by the *Bjerrum* method [12].

The statistical evaluation of potentiometric determination data of nickel(II) and cobalt(II) complexes of benzimidazole was made and the results are given in Table 1.

References

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