Mixed organic solvent consisting of DEHPA and BDBuN yielded best synergetic coefficients if La and Nd ions were extracted and the extractants were present in the mixture in the ratio 1 1. Extraction of Pr ions proceeded with the maximum synergetic coefficient when the organic phase consisted of DEHPA and BDBuN in the ratio 1 : 4.

The mixed organic phase that contained TBP and BDBuN in the ratio 4 : 1 was found to be best suited for extraction of all four lanthanoids that were tested in this study.

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The Stability Constants of Complexes of L-Proline with Nickel(II), Cobalt(II), and Copper(II) Determined by the Potentiometric Method

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Protonation constants of L-proline, as well as stability constants of its complexes with Ni(II), Co(II), and Cu(II) were determined with the use of the potentiometric method.

L-Proline (2-pyrrolidinecarboxylic acid) is an amino acid interesting from the theoretical and biological point of view [1], its complexing properties are due to the ring nitrogen atom and COOH group in the molecule.

In the studies of *Albert* [2—4] dealing with L-proline complexes with some bivalent metal ions, the stability constants were determined by the potentiometric method. The complex formation between L-proline and Cu(II) was investigated in aqueous solution at the varying ionic strength values at the temperature of 20 °C; the found stability constant was equal to 6.31×10^{16} *Jacymirski* [5] determined using the above method the stability constants of L-proline complexes with Co(II), Ni(II) resp. Cu(II) listed in Table 1. *Karczyński* and *Kupryszewski* [6] also determined the stability constant of the L-proline complex with Cu(II) at constant ionic strength equal to 0.1 at the temperature of 20 °C using the spectrophotometric method. These authors obtained the 3.1×10^{15} value, different from that of *Albert* [2—4].

In the present work we determined the protonation constants of L-proline and stability constants of its complexes with Ni(II), Co(II), and Cu(II) using the potentiometric method described in literature [7]. The method applied by us is simple and convenient, we used it also in our previous investigation concerning determination of stability constants of some metal complexes; the obtained results were very good [8—12].

EXPERIMENTAL

The following reagents were used: L-proline (Reanal, Budapest), $[\alpha]$(D, 20 °C, ρ = 6 g dm^{-3}, 0.5 M-HCl) = 51°—54°, chromatographically homogeneous; 0.1—0.2 M solutions of NaOH, HCl, KNO_3, $Ni(NO_3)_2$, $Co(NO_3)_2$, $Cu(NO_3)_2$, all salts were of anal. grade purity.

The interaction of L-proline with metal ions was investigated by the potentiometric method in aqueous solution at a fixed ionic strength equal to 0.1 (at 15 °C) established by KNO_3 solution.

The measurements of pH (accuracy ± 0.01) were accomplished by means of pH-meter OP-211 (Radelkis, Budapest) using calomel and glass electrodes.

RESULTS AND DISCUSSION

The protonation constant K_a was found by titration of the 0.01 M L-proline with 0.1 M-HCl. The K_a value was calculated from the following equation

$$\log K_a = \log \frac{ac_L - [H^+] + [OH^-]}{(1-a)c_L + [H^+] - [OH^-]} + pH \quad (1)$$

where K_a is the protonation constant, a titration fraction (total amount of titrant to total amount of substance in solution), c_L concentration of ligand.

The protonation constant K_b was determined by titration of the 0.01 M L-proline with 0.1 M-NaOH. The K_b value was calculated from the relation

$$\log K_b = \log \frac{(1-a)c_{HL} - [H^+] + [OH^-]}{ac_{HL} + [H^+] - [OH^-]} + pH \quad (2)$$

where K_b is the protonation constant, c_{HL} concentration of the protonated form of L-proline.

The stability constants of complexes of L-proline with Cu(II), Ni(II), resp. Co(II) were determined potentiometrically by two titrations of 0.01 M L-proline: in the absence and in the presence of the given metal ion ($c_m = 2 \times 10^{-3}$ mol dm^{-3}) with 0.1 M-HCl or 0.1 M-NaOH. 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 and Melchior method [7] and is defined by the following expression

$$[L_{bound}] = (a - a°)c_{HL} \quad (3)$$

The concentration of the free ligand is given by the relation

$$[L_{free}] = \frac{c_{HL} - (a - a°)c_{HL}}{1 + [H^+]K_b} \quad (4)$$

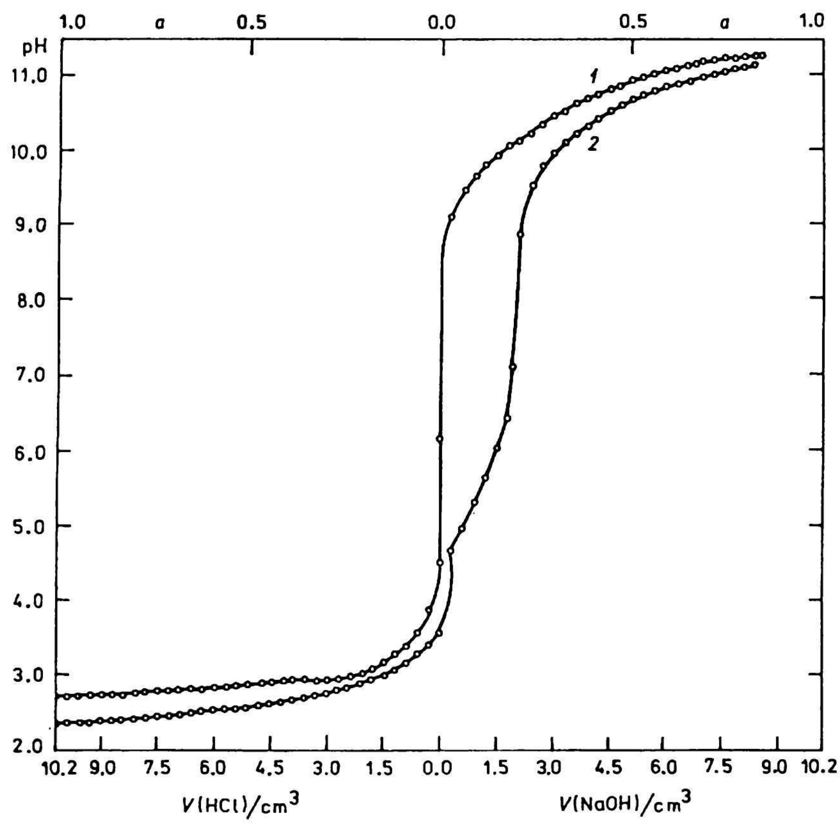

Fig. 1. Titration curves of L-proline with 0.01 M-HCl and 0.01 M-NaOH. *1.* In the absence of metal ion; 2. in the presence of Cu(II).

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

$$\bar{n} = \frac{(a - a^\circ)c_{HL}}{c_m} \quad (5)$$

where a° is the titration fraction of the protonated form of L-proline at the given pH value, a the titration fraction at the same pH value, in the presence of the investigated metal ion, c_m total metal ion concentration in solution, c_{HL} total L-proline concentration in solution.

Construction of curves of complex formation, *i.e.* plots of the relation of average number of ligand $\bar{n}$ against log [L] allowed to calculate the stability constants by the *Bjerrum* method [13].

Figs. 1—3 show titration curves of L-proline solution in the absence and in the presence of Cu(II), Ni(II), resp. Co(II). In all cases there was observed a strong shift between titration curves, in the absence and in the presence of the investigated metal ion.

In Fig. 4 the formation curves of complexes of L-proline with Cu(II), Ni(II), resp. Co(II) are shown. The results of the determination of stability constants are summarized in Table 1. The stability constant values of L-proline complexes with Cu(II), Ni(II), resp. Co(II) are different. The stability constant of the Cu(II) complex is higher than those of nickel(II) and cobalt(II) complexes. On the other hand, the stability constant of the Co(II) complex is lower than that of the Ni(II) complex. The found values are compatible with the *Irving* and *Williams* series [14].

Table 1. Protonation Constant (K) of L-Proline and Stability Constant (β) of its Complexes with Co(II), Ni(II), resp. Cu(II) (I = 0.1)

L-Proline		Metal	log β_1
log K_a	log K_b		
2.6	11.2	Co(II)	4.80
	10.48 [5]		4.89 [5]
2.01 [15]	11.4 [15]	Ni(II)	5.60
			6.15 [5]
		Cu(II)	7.60
			8.37 [5]

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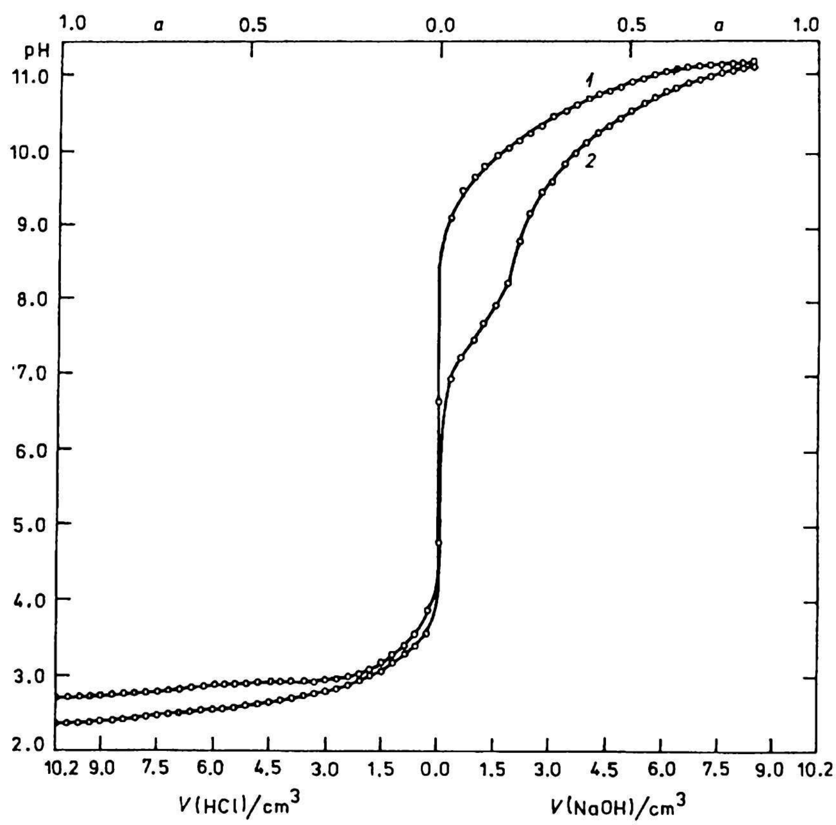

Fig. 2. Titration curves of L-proline with 0.01 M-HCl and 0.01 M-NaOH. *1.* In the absence of metal ion; *2.* in the presence of Ni(II).

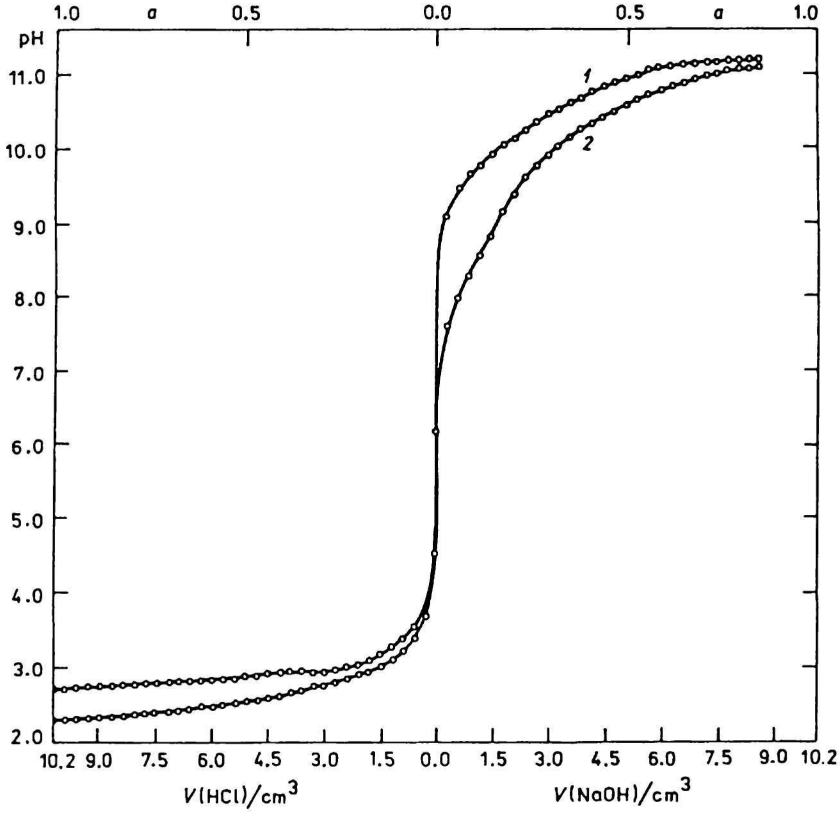

Fig. 3. Titration curves of L-proline with 0.01 M-HCl and 0.01 M-NaOH. *1.* In the absence of metal ion; *2.* in the presence of Co(II).

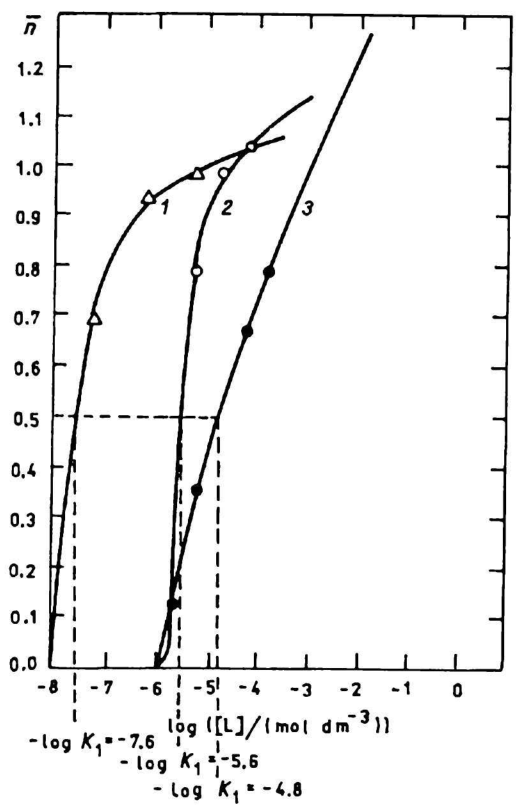

Fig. 4. Formation curves of the complex of L-proline with *1.* Cu(II), *2.* Ni(II), *3.* Co(II).

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