Chelate formation of N-(o-hydroxybenzyl)iminodiacetic acid with rare earth elements

J. MAJER, L. SIROTKOVÁ, and I. VALÁŠKOVÁ

Department of Analytical Chemistry, Faculty of Pharmacy,
Komenský University, CS-832 32 Bratislava

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In the framework of systematic study of chelate formation with rare earth elements the N-(o-hydroxybenzyl)iminodiacetic acid was selected as a ligand suitable for chelation with M(III) ions. The study was performed by potentiometric method and by paper electrophoresis. The stability constants of complexes of ML, MHL, and ML_2 type, respectively, were evaluated from neutralization curves measured at $I_c = 0.10 \, mol \, dm^{-3}$ (KNO$_3$) and $T = 293.2$ K.

The paper electrophoresis served for investigation of chelates formed in dependence on acidity and the charge of particles. The ionization constants of N-(o-hydroxybenzyl)iminodiacetic acid were determined by potentiometric method except the last one pK_{a3} being determined spectrophotometrically.

В рамках систематического изучения образования хелатов с редкоземельными элементами была выбрана N-(o-гидроксибензил)иминодиуксусная кислота (ГБИДУ) в качестве лиганда, удобного для образования металлических хелатов с M(III). Исследование проводилось потенциометрическим методом и электрофорезом на бумаге. Из нейтрализационных кривых были определены константы устойчивости комплексов типа ML, MHL, и ML_2 для $I_c = 0,10$ моль дм$^{-3}$ (KNO$_3$) и $T = 293,2$ K.

С помощью электрофореза на бумаге исследовался состав образующихся хелатов в зависимости от кислотных условий и заряда частиц. Ионизационные константы ГБИДУ были определены потенциометрически, а последняя pK_{a3} спектрофотометрически.

N-(o-hydroxybenzyl)iminodiacetic acid (HBIDA) is a complexone, which possesses in its molecule except the nitrogen atom and carboxyl group as donors also the phenolic functional group
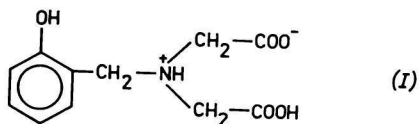
This compound was synthesized for the first time by *Schwarzenbach* [1], who has reported in his study the acid—base properties of HBIDA together with its stability constants of complexes with alkaline earth elements. The other authors have prepared HBIDA by different synthetic route [2]. That paper includes also the results of potentiometric study of chelate formation of HBIDA with divalent ions and spectrophotometic study of chelation with Fe(III). Polycondensation of HBIDA with phenol and formaldehyde yielded the new chelating resins [3].

Experimental

Potentiometric and spectrophotometric measurements

HBIDA was prepared according to the method described in [2] by reacting iminodiacetic acid with *o*-acetoxybenzylbromide. Solutions of rare earth elements used were prepared from their nitrates in 0.01 mol l^{-1} concentrations, verified by complexometry. The pH values were measured on PHM-26 (Radiometer) using G 202 B glass electrode and saturated calomel electrode as a measuring unit. Ionic strength of solutions was adjusted to $I_c = 0.10$ mol dm^{-3} by KNO_3, temperature was maintained at 293.2 K. Stirring of solutions was provided by bubbling the purified nitrogen throughout. Stability constants of HBIDA with lanthanoides were evaluated from neutralization curves for 2×10^{-3} mol l^{-1} HBIDA in the presence of metal ions in $c_L : c_M = 1:1$ and $2:1$ ratios, respectively. Calculations of stability constants were performed from separated buffer regions of neutralization curves. The K_{ML} values besides K_{MHL} ones were calculated from the first buffer region and K_{ML_2} from the other region using compiled programs, the algorithm of which was based on simple calculations of stability constants by elimination method. Values of the HBIDA ionization constants were determined under our experimental conditions at 293.2 K. K_{a1} and K_{a2} ionization constants were evaluated from neutralization curves of solution containing the agent alone. The third ionization constant K_{a3}, which corresponds to the phenolic hydroxyl group dissociation, was determined spectrophotometrically due to its very low value. Thus the absorption curves of HBIDA of $c_L = 2 \times 10^{-4}$ mol l^{-1} and $I_c = 0.10$ (NaCl) were measured in the spectral region of 37 000—30 000 cm^{-1} (245.7—333 nm) in dependence on pH. Measurements were performed on UNICAN SP-700 spectrometer and evaluation of ionization constants was made by routine calculation [4].

Electrophoretic measurements

These measurements were performed on apparatus without the electrode vessels. Electrolytes used for experiments contained investigated agent of 2×10^{-2} mol l^{-1} concentration, and they were pipetted onto chromatographic paper Whatman No. 2. Acidity of solutions being checked potentiometrically was adjusted to desirable pH values in such manner, that the individual experiments differed approximately by a unit of pH. Solutions of

pH < 2 were adjusted by HNO$_3$ of 1 mol l^{-1} and those of pH > 10 by KOH of 1 mol l^{-1}. The other solutions were adjusted by suitable buffering systems. Ionic strength was adjusted to I_c = 0.10 mol dm^{-3} (KNO$_3$). Solutions of rare earth elements were sampled in 5×10^{-2} mol l^{-1} concentrations. Detection of electrophoretograms was performed by alcoholic solution of alizarin followed by drying in vapours of ammonia.

The experimental conditions, the way of performing the electrophoresis, construction of mobility curves together with their evaluation are described by *Jokl* [5, 6].

Results and discussion

HBIDA is a dicarboxylic amino acid containing the phenolic functional group. This compound undergoes successive ionization in separated buffer regions during the titration. The first proton splits off in acidic environment, the second one is bound in betaine structure and it is placed on the lone electron pair of nitrogen atom. Proton of phenolic hydroxyl group splits off only in the strong alkali region. This phenomenon may be ascribed to the supposed intramolecular bond formed between the deprotonized nitrogen atom and phenolic oxygen atom. Comparing it with *N*-benzyliminodiacetic acid (BIDA), the influence of phenolic functional group in *o*-position of the benzene ring is expressed in lowering of the basicity of nitrogen atom, which results in increase of the second ionization constant. The final values of ionization constants are listed in Table 1. In the case of the first and the

Table 1

Values of ionization constants

	HBIDA $T = 293.2$ K	HBIDA [2] $T = 298.2$ K	BIDA [7] $T = 298.2$ K	
pK_{a1}	2.28	2.34	2.18	$I_c = 0.10$ (KNO$_3$)
pK_{a2}	8.09	8.07	8.90	$I_c = 0.10$ (KNO$_3$)
pK_{a3}	12.28	11.71		$I_c = 0.10$ (NaCl)

second ionization constants we have obtained values consistent with those in [2], but different value of the third one. The course of neutralization curves (Fig. 1) indicates that there proceeds the formation of complexes of ML and MHL$^+$ type. A characteristic feature of less functional ligands is the successive formation of complexes, which one may deduce from the shape of neutralization curves for systems containing a half content of metal ion. Their first buffer region corresponds to formation of MHL$^+$ and ML complexes
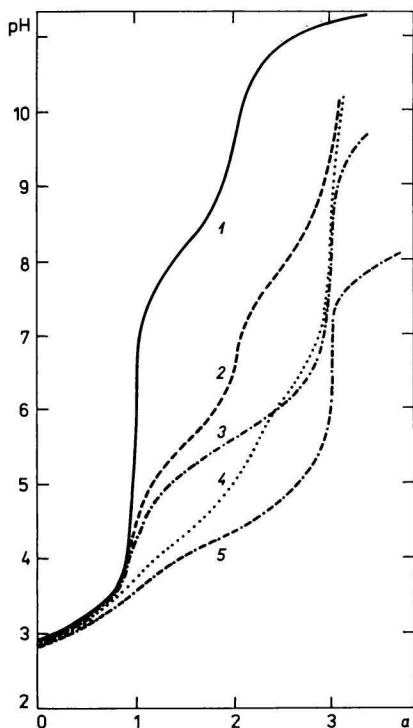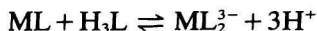
$$M^3 + H_3L \rightleftharpoons MHL^+ + 2H^+$$
$$M^{3+} + H_3L \rightleftharpoons ML + 3H^+$$
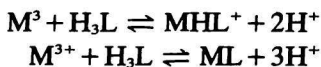
Fig. 1. Potentiometric neutralization curve of HBIDA (2×10^{-3} mol l^{-1}) (1) in the presence of La(III) $c_L : c_M = 2:1$ (2) and 1:1 (3) and Lu(III) $c_L : c_M = 2:1$ (4) and 1:1 (5). $a = $ mol NaOH/mol HBIDA.

and the second one corresponds to formation of ML_2^{3-} complexes

$$ML + H_3L \rightleftharpoons ML_2^{3-} + 3H^+$$

The dependence of composition of chelates formed on acidity conditions, as well as the charge of particles was investigated by means of paper electrophoresis. Fig. 2 shows the curves of electrophoretic mobilities of HBIDA complexes with a group of lanthanoides and Sc and Y, respectively, which were constructed as a dependence $U = f(pA)$ and simultaneously $U = f(pH)$. The shape of curves for the individual metal ions is, in general, the same, which results from very similar chemical and physical properties of the group of rare earth elements. The value of anodic mobility in the plateau region ($u = -0.90$) indicates the existence of complex formed by a central ion and two molecules of the agent — ML_2^{3-}. Stability constants determined electrophoretically (log K_{ML_2} — Table 2) are in a good agreement with those obtained by potentiometric method. With exception of scandium, the curves of electrophoretic mobility do not reveal the formation of complexes of ML type, which is connected with the shift of equilibrium favouring the ML_2^{3-} complex formation in the presence of an excess of ligand. Values of log K_{ML} listed in Table 2 were calculated by extrapolation of electrophoretic data,
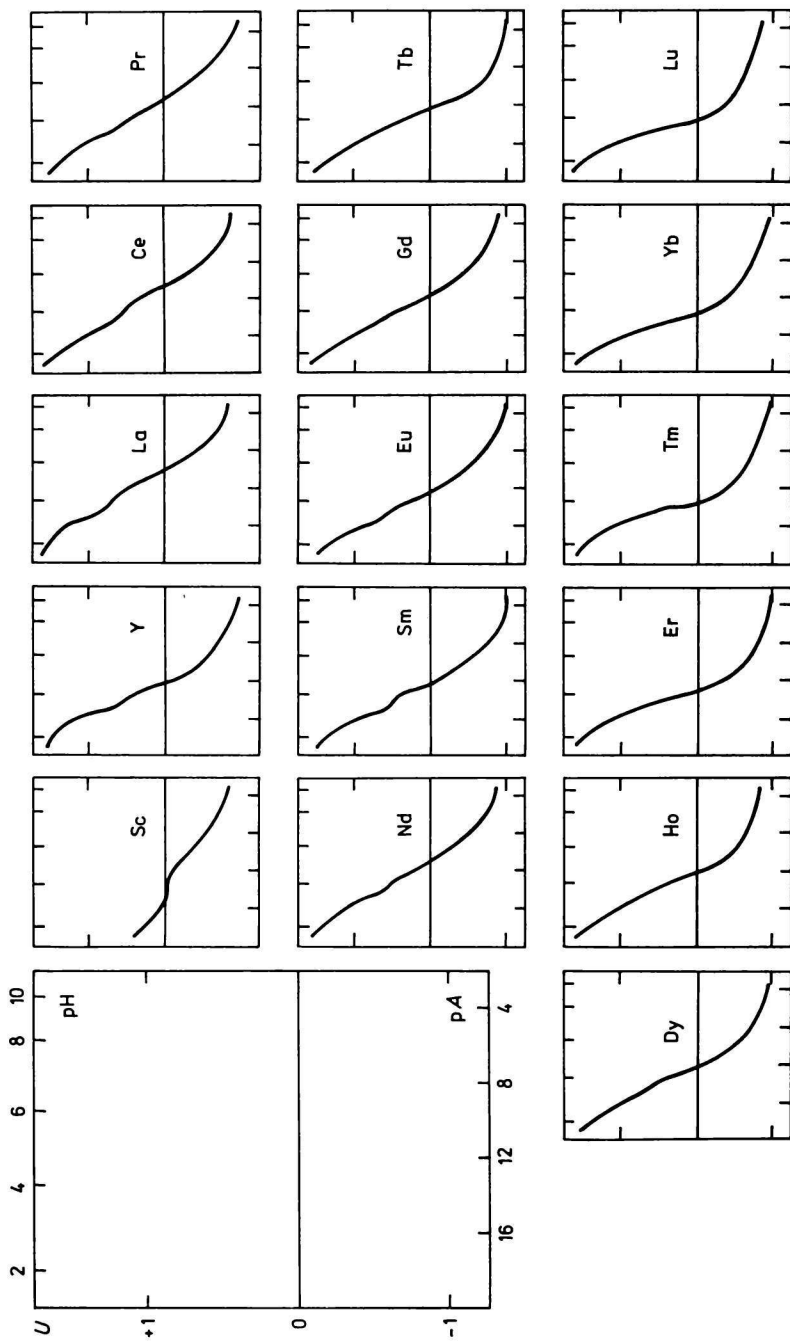
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Fig. 2. Curves of electrophoretic mobilities of complexes of HBIDA with a group of rare earths.
[A] = concentration of the free ligand, [U] = actual electrophoretic mobility, relative to $(C_2H_5)N^+$
$(u = +1.00)$, $T = 293.2$ K, $I_c = 0.1$ mol dm^{-3} (KNO$_3$).

Table 2

Stability constants ($T = 293.2$ K; $I_c = 0.10$ mol dm^{-3})

M(III)	log K_{ML}		BIDA [7][b]	log K_{MHL} HBIDA	log K_{ML_2} HBIDA		BIDA [7][b]
	HBIDA	BIDA [7][b]					
Sc		(>18)[a]				(9.4)[a]	
Y		(14.5)				(10.3)	
La	12.14	(11.6)	5.42	5.30	7.67	(8.0)	3.99
Ce	12.68	(12.2)	5.75	5.14	8.37	(8.4)	4.26
Pr	12.92	(12.8)	5.84	5.16	8.79	(8.6)	4.51
Nd	13.27	(13.0)	5.99	5.16	9.31	(9.0)	4.44
Sm	13.62	(13.3)	6.06	4.62	10.06	(9.8)	4.64
Eu	13.75	(13.5)	6.07	4.24	10.34	(10.2)	4.60
Gd	13.82	(13.3)	6.09	4.30	10.54	(9.6)	4.60
Tb	14.04	(13.4)	6.33	3.88	10.66	(10.5)	4.85
Dy	14.25	(13.5)	6.36	3.88	10.83	(10.5)	4.85
Ho	14.24	(13.4)	6.35	3.82	10.96	(10.9)	4.90
Er	14.32	(13.5)	6.54	3.82	11.04	(10.9)	5.09
Tm	14.53	(13.6)	6.59	3.82	11.24	(11.1)	5.15
Yb	14.57	(14.3)	6.69	3.85	11.26	(11.1)	5.26
Lu	14.62	(14.3)	6.70	3.80	11.26	(11.6)	5.32

a) The values obtained by paper electrophoresis method.
b) $T = 298.2$ K, $I_c = 0.10$ mol dm^{-3}.

supposing the zero mobility of electroneutral particles of ML complexes. Differences in the data, when compared with results of potentiometric study, do not in majority exceed the deviations caused by less accuracy of electrophoretic method. In the region of cathodic mobility there is seen a clear contour of plateau which may be ascribed to the formation of hydrogen complex MHL$^+$.

Comparing the chelating properties of HBIDA with those of BIDA as a representative of similar type complexone without phenolic group, the complexes of HBIDA are substantially more stable than one would expect according to the difference of the last ionization constants of both agents ($\Delta pK_a = 12.28 - 8.90 = 3.38$). Relatively high values of stability constants K_{ML_2} indicate that ions of rare earth elements easily coordinate with the second molecule of HBIDA. All these results indicate that HBIDA behaves as a strong chelating agent against ions of rare earth elements and the oxygen of phenolic hydroxyl group takes part in coordination as well.

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