

New complexanes
XLIV. Potentiometric study
of chelate formation of *N,N*-bis(2-hydroxyethyl)glycine
and *D,L-N,N*-bis(2-hydroxyethyl)- α -alanine with rare earth
elements

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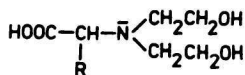
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The chelate stability constants of *N,N*-bis(2-hydroxyethyl)glycine and *D,L-N,N*-bis(2-hydroxyethyl)- α -alanine with La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), and Lu(III) were determined using the potentiometric method at ionic strength $I = 0.10 \text{ mol dm}^{-3}$ (KNO_3) and 293.2 K. The mole ratio of central ion to ligand in the formed complexes was found to be 1:1 and 1:2, respectively.

Методом потенциометрических кривых нейтрализации ($I = 0,10$ моль дм^{-3} (KNO_3); 293,2 К) были определены константы устойчивости хелатов *N,N*-бис(2-гидроксиэтил)глицина и *D,L-N,N*-бис(2-гидроксиэтил)- α -аланина с катионами La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III). В образующихся комплексах молярное отношение центральный атом:лиганд составляет 1:1 и 1:2.

In this paper we deal with the complex formation of two complexanes belonging to the monoamine type



where $\text{R} = \text{H}$ for *N,N*-bis(2-hydroxyethyl)glycine (BHG) and $\text{R} = \text{CH}_3$ for *D,L-N,N*-bis(2-hydroxyethyl)- α -alanine (BHA_α).

The compounds BHG and BHA_α correspond to complexanes possessing the nitrogen atom, a carboxylic group, and two hydroxyethyl groups as donors. Coordination of these various donating groups to the central metal ions, the stability of bodies formed as well as the spatial arrangement of ligands have

attracted attention of many investigators. Acid-base properties of BHG have been studied in papers [1—3]. The chelate formation of BHG with bivalent central ions has been studied by a number of authors who have used the potentiometric measurements of pH [1], spectrophotometric study in the case of coloured cations [3] as well as the paper electrophoresis [4].

Jokl et al. [5] studied the formation and composition of BHG and *N*-(2-hydroxyethyl)iminodiacetic acid complexes with cations of rare earth elements using paper electrophoresis. The possibility of rare earth elements separation in the presence of these complexanes has been also investigated. *Kostromina* and *Romanenko* [6] were concerned with the character of alcoholic hydroxyl group bond of BHG onto trivalent rare earth element cations in both aqueous and methanol—aqueous media. *Masuda et al.* [7] studied the ML and ML₂ complex formations, respectively, of BHG with rare earth elements using the potentiometric method.

Previously we investigated the acid-base properties as well as the complex formation of the compound BHA_α [8]. *Pikulíková et al.* [9] studied the complex formation of BHA_α with a series of bivalent and trivalent central metal ions. The possibility of utilization of BHA_α and *N*-(2-hydroxyethyl)-*N*-carboxymethyl-2-aminopropane acid for the separation of complicated mixtures involving bivalent and trivalent cations has been studied with the aid of paper electrophoresis.

Complex formation of BHA_α with rare earth elements is the object of the present paper. Since there are remarkable differences in data of complex stability constants of BHG with rare earth elements published so far, we studied also this ligand.

Experimental

The compound BHG was prepared according to *Khramov* and *Remizov* [10] in the reaction of diethanolamine with monochloroacetic acid. It was four times crystallized from 60 mass % methanol. Compound BHA_α was prepared by reacting the diethanolamine with α -bromopropane acid as described in our previous paper [8]. The compound was four times crystallized from 50 mass % ethanol.

The purity of both compounds was verified by melting point measurements and by potentiometric determination of neutralization equivalents as well. The content of BHG and BHA_α used for preparation of solutions was 99.9 and 99.7 mass %, respectively.

Potentiometric measurements

We have used direct potentiometric neutralization titrating technique. Using mole ratio metal to ligand equal to 1:4 we studied chelate formation of the type ML and ML₂. The

starting concentration of BHG and BHA_a , respectively, was $4 \times 10^{-3} \text{ mol dm}^{-3}$, while that of nitrates of the studied rare earth elements was $10^{-3} \text{ mol dm}^{-3}$. The reagent solution was prepared in redistilled water protected against airborne carbon dioxide.

The titrations were carried out in the neutral electrolyte environment at a constant ionic strength $I = 0.1 \text{ mol dm}^{-3}$ and the temperature maintained at $293.2 \pm 0.2 \text{ K}$. The carbonate-free NaOH solution in concentration $10^{-1} \text{ mol dm}^{-3}$ was used as a titrating agent. The solutions were agitated by bubbling the purified nitrogen throughout.

The pH values were measured by pHM 26 Radiometer. The measuring cell consisted of a glass electrode G 202 B and a standard calomel electrode K 401 (Radiometer, Denmark).

The calculations of complex stability constants were carried out with the aid of programmable calculator Hewlett—Packard HP 97 using a tailor-made program [11] based on the relationships describing successive complex formation as described by *Schwarzenbach* and *Baur* [12]. The program enables to compute the K_{ML} and K_{ML_2} stability constants from the experimental data.

Results and discussion

Both the preliminary measurements and the published data have revealed that BHG and BHA_a form with trivalent rare earth element cations the complexes with mole ratio metal to ligand 1:1 and 1:2, whereas the differences between the stability constants of successive complex formation of ML and ML_2 appeared to be small enough (approximately of an order). Therefore, we have selected the method developed by *Schwarzenbach* and *Baur* [12] for the study of these complexes. The measurements were carried out in solutions containing an excess of ligand, in mole ratio metal to ligand 1:4. The complex stability constants were evaluated from linear regression of negative logarithms of free ligand concentration (pL) as a function of mean ligand number (\bar{n}).

Table 1 shows the resulting values of complex stability constants (their logarithms).

Compounds BHG and BHA_a are relatively weak chelating agents and they can act as tetradentate substances assuming that nitrogen atom, carboxylic group, and both alcoholic hydroxyl groups take place in chelation. Figs. 1 and 2 show dependences of $\log \beta_1$ and $\log K_2$, respectively, on the atomic number of rare earth elements. For the sake of comparison, these figures also contain the values for iminodiacetic acid (IDA) as well as the data for glycine, available from literature, since the latter is the parent amino acid from which both BHG and BHA_a are derived.

All the $\log \beta_1$ and $\log K_2$ are for BHG and BHA_a lower when compared with those for IDA — a typical tridentate ligand. The course of BHG and BHA_a relationships is also different when compared with that for IDA. The values of $\log \beta_1$ for BHG and BHA_a increase from La to Eu, at Gd there is a little drop and

Table 1
Stability constants; $T = 293.2 \text{ K}$; $I = 0.10 \text{ mol dm}^{-3} (\text{KNO}_3)$

M(III)	BHG			BHA _α		
	log β ₁	log K ₂	log β ₂	log β ₁	log K ₂	log β ₂
La	4.99	3.41	8.40	4.49	3.01	7.50
Ce	5.32	3.71	9.03	4.91	3.61	8.52
Pr	5.46	3.95	9.41	5.21	3.86	9.07
Nd	5.66	4.09	9.75	5.28	3.96	9.24
Sm	5.72	4.58	10.30	5.36	4.39	9.75
Eu	5.73	4.74	10.47	5.36	4.45	9.81
Gd	5.58	4.85	10.43	5.26	4.54	9.80
Tb	5.43	5.06	10.49	5.28	4.76	10.04
Dy	5.41	5.04	10.45	5.18	4.70	9.88
Ho	5.36	5.01	10.37	5.10	4.67	9.77
Er	5.36	4.87	10.23	5.13	4.58	9.71
Tm	5.35	4.55	9.90	5.07	4.51	9.58
Yb	5.42	4.40	9.82	5.19	4.43	9.62
Lu	5.46	4.30	9.76	—	—	—

$$\beta_1 = \frac{[\text{ML}]}{[\text{M}][\text{L}]}; \quad K_2 = \frac{[\text{ML}_2]}{[\text{ML}][\text{L}]}; \quad \beta_2 = \frac{[\text{ML}_2]}{[\text{M}][\text{L}]^2}$$

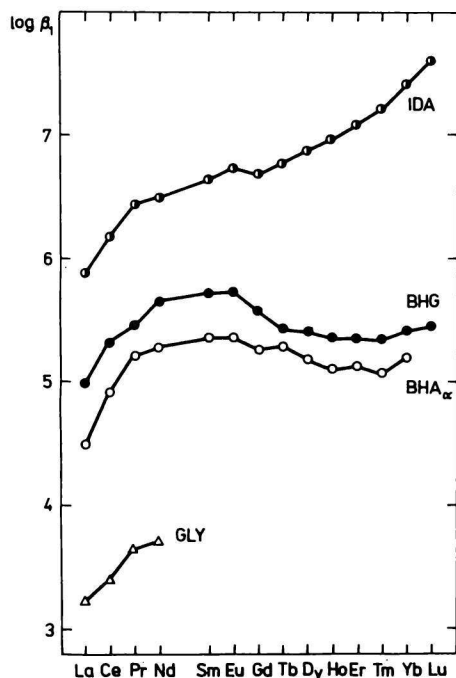


Fig. 1. Dependence of the logarithms of stability constants of chelates in the ratio metal : ligand = 1 : 1 on atomic number of lanthanides.

GLY — glycine [14];
 BHG — this paper;
 BHA_α — this paper;
 IDA — iminodiacetic acid [13].

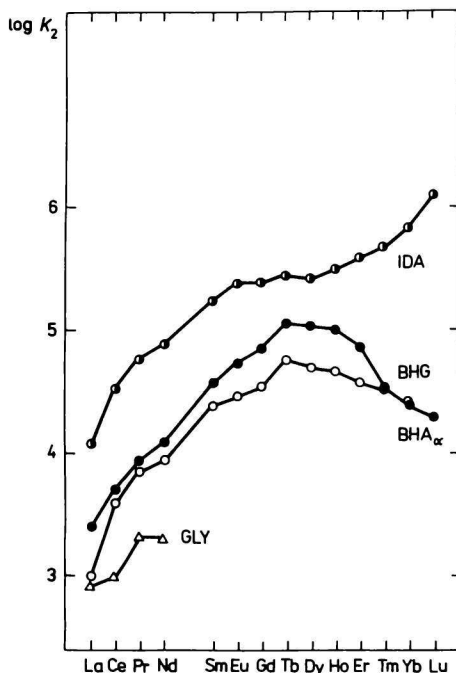


Fig. 2. Dependence of the logarithms of stability constants of chelates in the ratio metal: ligand = 1:2 on atomic number of lanthanides.

GLY — glycine [14];
 BHG — this paper;
 BHA_α — this paper;
 IDA — iminodiacetic acid [13].

then they are approximately on the same level up to Lu. The values of $\log K_2$ for both BHG and BHA_α reveal a relatively sharp increase from La to Tb and then follow the drop of these relationships. It is known that with reducing radius of cations studied increase the spatial hindrances, which can be noted from the course of relationships in Figs. 1 and 2.

The potentiometric [1, 8] and electrophoretic [5, 9] measurements show that coordination of alcoholic hydroxyl groups proceeds without splitting the proton off.

Our observations lead to statements that both the compounds BHG and BHA_α are probably acting as tridentate ligands, whereby besides the nitrogen atom and carboxylic group, one of the alcoholic hydroxyl groups takes part in coordination. Compound BHG seems to form slightly more stable complexes than BHA_α. The influence of induction effect of the methyl group in BHA_α has not been expressed in complex stability constants of BHA_α complexes with lanthanides studied, regardless of the influenced basicity of nitrogen atom ($\log K_{HL}$ for BHG is 8.19 [13], that for BHA_α is 8.47 [13]).

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