

New complexanes. XL.
D,L-N-(2,3-Dihydroxypropyl)-N-carboxymethylaminoacetic
acid — electrophoretic and potentiometric study
of the formation of the chelates with trivalent
central metal ions

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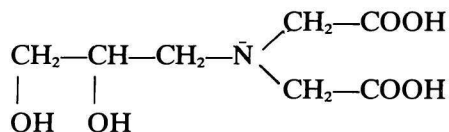
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A study of chelate-forming ligand of the monoaminic type, *i.e.* D,L-N-(2,3-dihydroxypropyl)-N-carboxymethylaminoacetic acid is described in this paper. By using the methods of paper electrophoresis and potentiometric pH measurements in equilibrium systems containing 2,2',2''-triaminotriethylamine, the formation of the chelate complexes with the ions of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), and Yb(III) was studied. The formation of the complexes with the cations of Al(III), Sc(III), Y(III), In(III), Fe(III), and Lu(III) was studied only by the method of paper electrophoresis. The substance investigated forms with the above ions ML and ML₂ chelates. The investigations were carried out under equal conditions, *i.e.* $I = 0.10 \text{ M (KNO}_3\text{)}$, $t = 20^\circ\text{C}$.

Описывается изучение хелатообразующего лиганда моноаминного типа D,L-N-(2,3-дигидроксипропил)-N-карбоксиметиламиноуксусной кислоты. Изучалось образование хелатных комплексов трехвалентных катионов La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III) и Yb(III) при использовании бумажного электрофореза и потенциометрического измерения pH равновесных систем с 2,2',2''-триаминотриэтиламином. Образование комплексов катионов Al(III), Sc(III), Y(III), In(III), Fe(III) и Lu(III) изучалось только методом бумажного электрофореза. Соединение образует с изучаемыми катионами хелаты типа ML и ML₂. Исследование было осуществлено при одинаковых условиях: $I = 0,10 \text{ M (KNO}_3\text{)}$, $t = 20^\circ\text{C}$.

The study of the acid-base properties of D,L-N-(2,3-dihydroxypropyl)-N-carboxymethylaminoacetic acid (DPKA)



as well as the study of formation of the chelates of this substance with the cations of alkaline earth metals (Mg and Ca) and some bivalent cations of heavy metals (Cd, Zn, Co, Ni, Pb, Cu, and Hg) is described in the previous paper [1].

This paper is concerned with the study of the formation of the chelates of the above agent with some trivalent cations. The formation of the complexes of this agent with a great number of trivalent cations of the rare earth elements, *i.e.* La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), and Yb(III) was evaluated on the basis of potentiometric data and electrophoretic measurements of the mobility curves. The formation of the complexes with Al(III), Sc(III), Y(III), In(III), Fe(III), and Lu(III) was investigated electrophoretically.

Experimental

The agent was prepared according to the procedure described in [1]. It was four times crystallized from 60% ethyl alcohol. The purity was checked by determining the melting point as well as by potentiometric neutralization titration. The solutions used for potentiometric and electrophoretic measurements were prepared from that preparation containing 99.70% of DPKA.

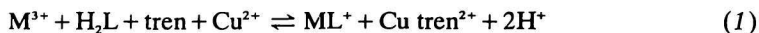
Electrophoretic measurements

The formation, composition, and approximate stability of the complexes with Al(III), Sc(III), Y(III), In(III), Fe(III) and the whole group of the trivalent cations of lanthanides (except Pm(III)) were investigated by paper electrophoresis.

The electrophoresis was carried out in the pH range 2—9 on a Whatman 2 paper using the 5×10^{-2} M solution of DPKA adjusted to required pH value and ionic strength ($I = 0.10$ M (KNO₃)) as a carrier electrolyte. The metal ions were applied in the form of 5×10^{-2} M nitrate solutions. The values of the relative electrophoretic mobility were related to the mobility of the tetraethylammonium cation and corrected with respect to electroosmosis. The working procedure and method of evaluation are described in [2, 3].

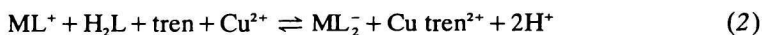
Potentiometric measurements

a) The concentration of the hydrogen ions liberated in the reaction



was measured on the basis of displacement reaction with 2,2',2''-triaminotriethylamine (tren) by the method according to *Schwarzenbach* and *Freitag* [4].

b) The concentration of the hydrogen ions released in the reaction



was measured by the method according to *Anderegg* [5].

As the equilibria of reactions (1) and (2) got established rapidly, we were able to titrate directly the solutions of the following composition

a)	5	ml	1×10^{-2} M	DPKA (H_2L)
	5	ml	1×10^{-2} M	nitrate of rare earth element (M)
	5	ml	1×10^{-2} M	$\text{Cu}(\text{NO}_3)_2$
	5	ml	1×10^{-2} M	tren
	8.2	ml	5×10^{-1} M	KNO_3
	21.8	ml	redistilled	water

50.0 ml initial volume

b)	10	ml	1×10^{-2} M	DPKA
	5	ml	1×10^{-2} M	nitrate of rare earth element
	5	ml	1×10^{-2} M	$\text{Cu}(\text{NO}_3)_2$
	5	ml	1×10^{-2} M	tren
	8.2	ml	5×10^{-1} M	KNO_3
	16.8	ml	redistilled	water

50.0 ml initial volume

The neutralization titrations were carried out in an equipment described in [1]. The carbonate-free 0.1 M-NaOH was used as titration agent. Each equilibrium was determined at least by three parallel titrations.

The experimental data were processed by calculation on a programming minicalculator Hewlett—Packard 97 by means of the programme according to *Dzurov* and *Benedikovič* [6]. The equilibrium constants of reactions (1) and (2) were evaluated. The data thus obtained, the protonation constants of DPKA, and the stability constant of DPKA with the ion of Cu(II) were used for calculating the stability constants β_1 , K_2 , and β_2 . The results are given in Table 2 as logarithms of the values of individual constants.

The intervals of reliability were calculated from standard deviation of the mean s_x by using the values of the Student characteristic t for the significance level $\alpha = 0.01$.

Results and discussion

As a matter of fact, already in the preceding study [1] we were interested in the problem of how two hydroxyl groups on vicinal carbon atoms influenced the acid-base and chelate-forming properties of the DPKA complexane. The compound DPKA may be compared with *N*-(2-hydroxyethyl)-iminodiacetic acid (HIDA). The 2,3-dihydroxypropyl group in the molecule of DPKA (in contradistinction to the 2-hydroxyethyl group in the molecule of HIDA) brings about a decrease in basicity of the nitrogen atom, which manifests itself in stability of the chelates of DPKA.

DPKA forms ML as well as ML_2 chelates with the trivalent cations of the rare earth elements. The composition of the arising chelates which depends on acidity conditions as well as the charge of the particles was studied by paper electrophoresis (Fig. 1).

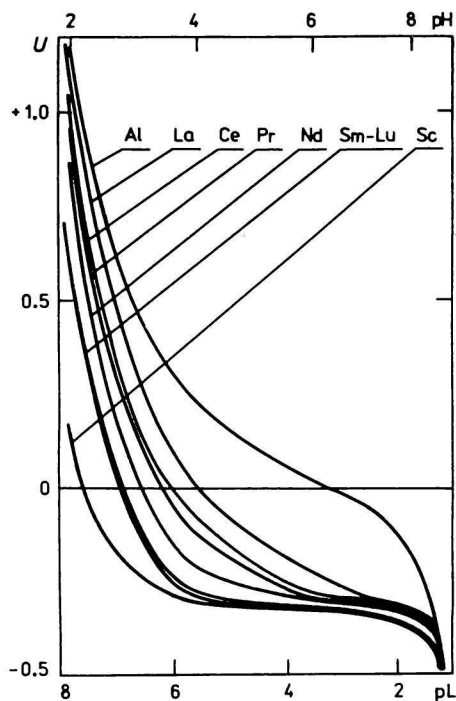


Fig. 1. Electrophoretic mobility of the DPKA complexes with lanthanides, aluminium, and scandium.

U — actual mobility related to $(C_2H_5)_4N^+$,
 $pL = -\log [L]$, $t = 20^\circ C$, $I = 0.1 M$ (KNO_3).

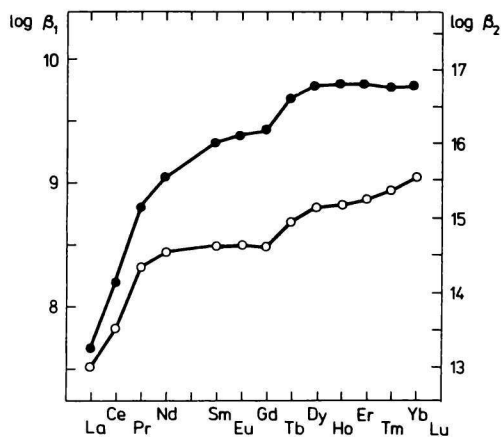


Fig. 2. Variation of the stability constants of DPKA with atomic number of the rare earth elements.

$\circ \log \beta_1 = f(\text{at. number})$; $\bullet \log \beta_2 = f(\text{at. number})$.

The character of the mobility curves of the DPKA complexes with the trivalent central metal ions of Fe(III), In(III), Sc(III), Y(III), and of lanthanides is almost identical. All the curves exhibit single wave terminated by a horizontal part in the mobility region from -0.3 to -0.4 which appears, according to stability of the complex, between pH 3 and pH 4 and remains nearly in the whole investigated pH region. Hence we may deduce that these ions form relatively stable complexes of the composition ML_2^- . This fact is also in good agreement with the results of investigation of the corresponding complexes of *N*-(2-hydroxyethyl)-iminodiacetic acid (HIDA) [3]. That is also confirmed by the values of mobility in the region of plateau which are in conformity with the theoretical values calculated according to the equation presented in the preceding paper [1]. In the region above pH 8, there is a suggestion of another wave indicating an increase in negative charge. Because of incompleteness of the curves, we cannot, however, draw conclusions about the composition of the arising particle.

On the curve of the Al(III) complex, a plateau with zero mobility is suggested on the basis of which a formation of the neutral $[Al(DPKA)OH]$ complex may be supposed.

The increase in anodic mobility in alkaline region may correspond to the formation either of the $[Al(DPKA)_2]^-$ complex or of the $[Al(DPKA)(OH)_2]^-$

Table 1

Approximate stability constants of the DPKA chelates evaluated from electrophoretic measurements

M(III)	$\log \beta_1$	$\log K_2$
In	>7.5	>7.5
Sc	>7.5	>7.5
Y	>7.5	7.1
La	7.2	6.3
Ce	7.45	6.5
Pr	7.5	6.6
Nd	7.55	6.8
Sm	>7.5	7.0
Eu	>7.5	7.0
Gd	>7.5	7.1
Tb	>7.5	7.15
Dy	>7.5	7.15
Ho	>7.5	7.25
Er	>7.5	7.3
Tm	>7.5	7.2
Yb	>7.5	7.2
Lu	>7.5	7.2
Fe	>7.5	>7.5

hydroxocomplex. However, we presume that a complex with two molecules of the agent ML_2^- arises from DPKA like from iminodiacetic acid (IDA) and (HIDA) [3].

In determining the stability constants of the chelates from the curves of electrophoretic mobility, the value of $\log K$ is read on the pL axis in the point where it holds $U = 1/2(u_1 + u_2)$, then $\log K = pL$. The symbols u_1 and u_2 stand for the mobilities of ML and ML_2 , respectively.

As no wave occurs for the ML complex on the curves of mobility, the values of u_1 were calculated only from the correlation according to [3], i.e. $u z^{-1} = 14.4 m^{-1/2} - 0.28$. The values of $\log K_2$ are thus loaded with a greater error and the values of $\log \beta_1$ are only approximate.

The stability constants of the DPKA complex with the investigated trivalent central metal ions evaluated from electrophoretic measurements are listed in Table 1.

The values of the stability constants of the DPKA complexes with the trivalent cations of the rare earth elements are comparable with the corresponding values found for HIDA in the same manner as it has been observed in case of the DPKA chelates with the bivalent cations of the alkaline earth metals and heavy metals [7], but all these values are a bit smaller. The values of the corresponding stability constants $\log \beta_1$ and $\log \beta_2$ determined on the basis of potentiometric measurements are given in Table 2.

DPKA behaves as a moderately strong 4-donor chelation agent. That results from the comparison of the stability constants found for DPKA with the values

Table 2

Stability constants of the DPKA chelates
 $t = 20^\circ\text{C}$, $I = 0.10 \text{ M (KNO}_3\text{)}$

M(III)	$\log \beta_1$	$\log K_2$	$\log \beta_2$
La	7.52 ± 0.01	5.73 ± 0.02	13.25 ± 0.03
Ce	7.84 ± 0.01	6.32 ± 0.02	14.16 ± 0.03
Pr	8.33 ± 0.02	6.85 ± 0.02	15.18 ± 0.04
Nd	8.45 ± 0.02	7.10 ± 0.02	15.55 ± 0.04
Sm	8.50 ± 0.02	7.52 ± 0.02	16.02 ± 0.04
Eu	8.51 ± 0.01	7.61 ± 0.02	16.12 ± 0.03
Gd	8.50 ± 0.02	7.70 ± 0.01	16.20 ± 0.03
Tb	8.70 ± 0.02	7.93 ± 0.02	16.63 ± 0.04
Dy	8.82 ± 0.02	7.99 ± 0.02	16.81 ± 0.04
Ho	8.84 ± 0.02	7.96 ± 0.01	16.80 ± 0.03
Er	8.88 ± 0.01	7.94 ± 0.01	16.82 ± 0.01
Tm	8.95 ± 0.02	7.82 ± 0.01	16.77 ± 0.03
Yb	9.06 ± 0.01	7.72 ± 0.02	16.78 ± 0.03

found for iminodiacetic acid (IDA) [7] which may afford only 3 donor spots in a molecule for a chelate. This fact confirms the participation of oxygen of the hydroxyethyl group in chelation. All values of the stability constants of DPKA are higher than the stability constants of the analogous IDA chelates.

The trivalent cations of the rare earth elements are fairly ready to attach the second DPKA molecule into the chelates to give the ML_2^- particles. It results from the relatively high values of $\log K_2$ which are quoted in Table 2. While the values of $\log \beta_1$ increase in the sequence from La to Yb (a small decrease is to be observed for Gd) (Fig. 2), the values of $\log K_2$ characterizing the attachment of the second ligand increase from La to Dy. Behind Dy, a small decrease appears in this regularity. The steric hindrance which is operative in coordination of the second molecule of agent to the metal ion increases with decreasing ionic radius of the lanthanides. This affects also the dependence of the overall constant of formation of the ML_2^- chelates on atomic number of the rare earth element ($\log \beta_2 = f(\text{at. number})$) (Fig. 2).

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