New complexanes. XLI. Study of equilibria of the chelate formation of N-(carbamoylmethyl)iminodiacetic and N-(2-carbamoylethyl)iminodiacetic acids with cations of the alkali earth metals

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The relative thermodynamic acid-base equilibria and equilibria of the complex formation of N-(carbamoylmethyl)iminodiacetic and N-(2-carbamoylethyl)iminodiacetic acid with the ions of Mg(II), Ca(II), Sr(II), and Ba(II) have been studied by direct potentiometric neutralization titration under unified conditions (I = 0.1 (KNO₃)) and at 15, 20, 25, 30 and 35°C. The resulting values of ΔH° and ΔS° are given for the protonation equilibria and equilibria of the complex formation with the above cations. The formation of these complexes has also been studied by ¹H-n.m.r. spectroscopy in D₂O solutions in the pD range 1.5–13.0. The results are discussed from the view-point of formation of a coordination bond between the amide group and central metal in a complex of the ML type.

Прямым потенциометрическим кислотно-основным титрованием при постоянных условиях I = 0,1 (KNO₃) и температурах 15, 20, 25, 30 и 35°C были изучены относительные термодинамические кислотно-основные равновесия и равновесия комплексообразования N-(карбамоилметил)иминодиуксусной и N-(2-карбамоилэтил)иминодиуксусной кислот с ионами металлов Mg(II), Ca(II), Sr(II), Ba(II). Приводятся полученные значения ΔH^0 и ΔS^0 термодинамических концентрационных констант протонизации и устойчивости комплексов указанных катионов. Образование этих комплексов было изучено далее методом ¹H-ЯМР в растворах D₂O в интервале pD = 1,5—13,0. Результаты обсуждаются с точки зрения образования координационной связи амидной группы с центральным металлом в комплексе типа ML.

In our preceding study [1] we investigated the acid-base and complex-forming properties of N-(carbamoylmethyl)iminodiacetic (KMIDA) and N-(2-carbamoylethyl)iminodiacetic (KEIDA) acid (HOOC—CH₂)₂NR where R = CH₂—CONH₂ (KMIDA), R = CH₂—COH₂ (KEIDA), respectively, with regard to a great number of cations of the bivalent metals by using potentiometric

neutralization titration, paper electrophoresis, ¹H-n.m.r. and infrared spectroscopy. The data of electrophoretic measurements obtained with ions of the alkali earth metals did not provide convincing evidence for the formation of complexes of the ML type. Though we proved the formation of these complexes potentiometrically, the question of coordination of the amide group remained open because the logarithm of the stability constant obtained log $K_{\rm ML}$ could not be correlated with the value log $K_{\rm HL}$ characterizing basicity of the amine nitrogen for a greater set of similar complexes owing to lack of data in literature, except for Mg(II). For this reason, we consider the determination of relative thermodynamic parameters of the formation of these complexes and the measurement of their ¹H-n.m.r. spectra to be necessary for the study of their formation and characterization of their structure in solution.

Experimental

Potentiometric measurements

We prepared the basic aqueous solutions of the investigated reagents with concentrations 4×10^{-3} mol dm⁻³. The initial concentration of the ligand in the titrated solutions was 2×10^{-3} mol dm⁻³ while the initial concentration of the nitrates of investigated metals was 1×10^{-2} mol dm⁻³. The initial volume in all titrations was 50 ml. The measurements were performed at 15, 20, 25, 30, and 35°C. The solutions of the reagents were prepared in redistilled water protected against CO₂ in air. A solution of NaOH of the concentration 1×10^{-1} mol dm⁻³ without carbonates was used as titration agent. During titration the solutions were stirred with a stream of purified nitrogen.

The pH values were measured on a Digital pH-meter pHM 52 (Radiometer, Denmark). The measuring cell consisted of a glass electrode G 202 C (usable in the temperature range $0-60^{\circ}$ C) and a calomel electrode K 401 (Radiometer, Denmark). A standard solution of potassium hydrogenphthalate for which the dependence of pH on temperature is represented in [2] was used for adjusting the instrument. At least three parallel measurements were carried out for each value.

The ionic strength was adjusted to the value I = 0.1 in all measurements by adding a 5×10^{-1} M solution of KNO₃ so that the solution possessed this ionic strength in the region chosen for evaluating the results.

The values of pH_{meas} found in individual measurements were corrected to the value of negative logarithm of the hydrogen ion concentration (pH_e value) by means of a correction term according to the subsequent equation

$$pH_{c} = pH_{meas} + \varepsilon \tag{1}$$

The correction term ε was determined experimentally by means of a 1×10^{-3} mol dm⁻³ solution with ionic strength I = 0.1 (KNO₃). The accurate concentration of HNO₃ was determined by titration. The correction term ε has the values -0.075 (for 15 and 20°C), -0.080 (for 25 and 30°C), and -0.085 (for 35°C).

In calculations, we used the ionic product of water quoted in literature for particular temperatures [2]. Other measuring, instrumental, and calculating techniques were like those used in our preceding work [1].

The values of ΔH° and ΔS° were determined from the temperature dependence of pertinent equilibrium constants and several experimental values by the method of least squares according to the programme constructed by us. Equal methodical approach was used by some authors [3, 4].

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'H-NMR spectroscopy

The instrumental technique used was like that described in [1]. The solutions for measurement were prepared by dissolving 5×10^{-4} moles of KEIDA and 5×10^{-4} moles of the nitrate of a certain alkali earth metal in 8.0 ml of D₂O in the presence of KOD. *Tert*-butyl alcohol (TBA) in the concentration of about 3.5 volume % was used as an internal standard. The solutions of the samples in the pD range 1.5—13.0 were prepared from the basic solutions by the use of KOD and DCl. The chemical shift δ was expressed with respect to the resonance frequency of protons of the methyl groups in TBA, $\delta_{\text{DSS}} = \delta_{\text{TBA}} + 1.233$.

Results and discussion

The arithmetic means of the values of $\log K_{\text{HL/H-L}}$, $\log K_{\text{H}_2\text{L/HL-H}}$, and $\log K_{\text{ML}}$ obtained from several points of the corresponding buffered regions of titration curves are given for individual temperatures in Table 1.

The values of ΔH^0 and ΔS^0 calculated from temperature dependence of log K_{ML} are presented in Table 2. For comparison, this table also contains literature data for

Table 1

Protonation constants and stability constants of KMIDA and KEIDA with ions of the alkali earth metals as a function of temperature [°C]

	KMIDA					KEIDA				
	15	20	25	30	35	15	20	25	30	35
log K _{HL/H·L}	6.77	6.71	6.66	6.63	6.60	8.55	8.52	8.44	8.39	8.33
log K _{H2L/HL} ·H	2.27	2.18	2.13	2.09	2.06	2.54	2.47	2.41	2.38	2.29
log KMaL	2.47	2.57	2.57	2.64	2.72	3.77	3.78	3.80	3.81	3.82
log K _{CaL}	4.07	4.06	4.02	4.01	4.03	3.95	3.93	3.91	3.89	3.88
log KsrL	2.94	2.95	2.94	2.92	2.89	2.95	2.94	2.95	2.93	2.92
$\log K_{Bal}$	2.84	2.84	2.81	2.81	2.76	2.92	2.90	2.89	2.87	2.86

 $I = 0.1 (KNO_3)$

π	~	h	6	2	
1	a	$\boldsymbol{\omega}$	e	4	

Equilibrium	KMIDA		KEIDA		IDA		HIDA		NTA	
	ΔH°	ΔS°	ΔH^{0}	ΔS°	ΔH ^o	ΔS°	ΔH ^o	ΔS°	ΔH°	ΔS ^o
HL/H·L	- 14.3	80	-20.5	93	- 34.3	63	-22.2	92	- 19.3	121
$H_2L/HL \cdot H$	-17.4	-17	- 19.4	- 19	- 5.0	34	-2.5	34	0.8	50
$H_3L/H_2L \cdot H$						—	—	_	0.8	38
MgL/Mg·L	19.4	115	5.1	90	12.1	100	11.7	105	18.4	176
CaL/Ca·L	-7.4	53	-6.2	54	1.3	54	-13.8	46	- 5.9	105
SrL/Sr · L	-4.4	41	-2.4	48	0.4	46	-12.6	29	-2.1	88
BaL/Ba·L	-6.4	32	- 5.1	38	0.4	34	-13.8	17	- 5.9	71

Thermodynamic equilibrium constants $I = 0.1 (\text{KNO}_3); t = 25^{\circ}\text{C}; \Delta H^0 \text{ in kJ mol}^{-1}; \Delta S^0 \text{ in J mol}^{-1} \text{ K}^{-1}$

the complexes of iminodiacetic (IDA), N-(2-hydroxyethyl)iminodiacetic (HIDA), and nitrilotriacetic (NTA) acid [5].

The data obtained by us are not true thermodynamic constants. They are the so-called concentration constants evaluated from measurements at a great excess of uni-univalent electrolyte which ensures constancy of the activity coefficients of reacting components.

It is obvious from Table 2 that the formation of the complex of KMIDA and KEIDA with Mg(II) is endothermic like in case of HIDA and NTA while this reaction with other ions of the alkali earth metals is exothermic.

The dependence of ΔS° on reciprocal value of the ionic radius is represented in Fig. 1. The values of r have been taken from literature [6]. For all ions of the alkali earth metals, the values of ΔS° found with KMIDA and KEIDA are linearly dependent on r^{-1} and their absolute magnitude varies in the range of the ΔS° values found for the complexes with IDA and HIDA. The values of ΔS° found for NTA are considerably higher, which is due to electrostatic interaction of three carboxylate groups with negative charge in contrast to IDA, HIDA, KMIDA, and KEIDA where an interaction of two negatively charged carboxylate groups with the ions of metals takes place. Thus our data confirm the theory of Martell [7] according to which the electrostatic interactions give a significant contribution to ΔS° .

The linearity of the relationship between ΔS^0 and r^{-1} found for all ions of the alkali earth metals has indicated that the character of coordination of the donor groups is likely to be equal for all above-mentioned ions.

The values of ΔH^0 belonging to the complexes of the investigated reagents with Mg(II) enable us to comprehend the remarkably rised stability of the complex of KEIDA when compared with that of the complex consisting of KMIDA and the above cation. It may be assumed [8] that the endothermic character of the reaction



Fig. 1. Variation of entropy with reciprocal value of the ionic radius of metal in the course of complex formation.
○ IDA ; △ KEIDA ; ● NTA ; □ HIDA ; ■ KMIDA.

with Mg(II) is caused by the strain of the chelate rings due to small ionic radius of Mg(II). The increased value of ΔH^0 of the complex consisting of KMIDA and Mg(II) indicates a greater strain than it is in the complex with KEIDA. The formation of one six-membered ring in the complex with KEIDA is likely to reduce the strain of the chelate rings, which results in an overall energy decrease and thus increase in its stability.

Though the above-mentioned thermodynamic study indirectly indicated the presence of three chelate rings in the complexes of KMIDA and KEIDA with ions of the alkali earth metals, we took it for necessary to confirm these results by a direct method, too. For the solutions, the ¹H-n.m.r. spectroscopy appeared to be the best method.

We investigated the chemical shifts in nonlabile protons of KEIDA in the solutions of D_2O and in the presence of metal ions as a function of pD. The spectra obtained were characteristic of the complexes in which all coordination bonds were labile from the view-point of ¹H-n.m.r. The chemical shifts of nonlabile protons are illustrated by Fig. 2, in which the results obtained with noncoordinated KEIDA and its equimolar solution containing Ca²⁺ are summarized. These relationships enable us to find out the pD region where the stable complex can exist. These values as well as the values of chemical shifts in the protons of KEIDA the denotation of which (a, b, c) follows from Fig. 2 are given in Table 3.

For all ions, the chemical shifts of the nonlabile protons in complexes differed from the chemical shifts in the protons of free ligand. The signal of the protons H^b was shifted to higher intensity of the magnetic field while the signal of the



Fig. 2. Chemical shifts of the nonlabile protons of KEIDA and its complex with Ca(II) as a function of the pD value of solutions.
KEIDA; --- KEIDA: Ca(II) = 1:1.

protons H^e was shifted to lower intensity when compared with the L²⁻ ion of the ligand. Not only the changes in electron densities on certain protons in the course of complex formation but also the changes in local magnetic fields on protons of the ligand due to magnetic anisotropy of the bonds may be responsible for the changes in chemical shifts. For this reason, it is difficult to estimate different directions of the shift in the signals H^b and H^e. Irrespective of this fact, the data obtained by us corroborate the coordination of the amide group in all complexes of KEIDA with ions of the alkali earth metals. It is interesting that the screening of the protons H^a and H^b in the complex of KEIDA with Mg(II) decreased with respect to the ion L²⁻ while it increased in other complexes of KEIDA with ions of the alkali earth metals. This information of the ¹H-n.m.r. spectroscopy is immediately coherent with the data of thermodynamic investigations and gives clear evidence that the structure of the complex of KEIDA with Mg(II) is different from that of the complexes with other ions of the alkali earth metals.

 Table 3

 Chemical shifts of the signals of the complexes of KEIDA and the pD regions of existence of the stable complex

Complex 1:1	nD of stable complex		δ/p.p.m.		
	pD of stable complex —	Hª	H۴	H	
Mg: KEIDA	8.0-10.0	2.07	1.69	1.26	
Ca: KEIDA	9.0-13.0	1.91	1.41	1.28	
Sr : KEIDA	9.5-13.5	1.88	1.48	1.25	
Ba : KEIDA	10.0—13.0	1.90	1.52	1.24	

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Conclusion

On the basis of determination of relative thermodynamic parameters, we have found that the formation of the complexes of KMIDA and KEIDA with Mg(II) is endothermic whereas the formation of these complexes with other alkali earth metals is an exothermic process, which is analogous to the observations obtained with similar complexes containing NTA and HIDA. The linear character of the relationship between ΔS^0 and reciprocal value of the ionic radius of metal confirms that the electrostatic bonds of the negatively charged carboxylate groups give a significant contribution to the values of ΔS^0 in the systems studied. The ¹H-n.m.r. spectroscopy has corroborated that KEIDA is a tetradentate ligand in all investigated complexes. It has also suggested that the structure of the complexes of KEIDA with Mg(II) is different from that of the complexes containing other ions of the alkali earth metals.

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