New complexanes
VL. Acid-base and chelate-forming properties of surface-active complexanes of the type of 2-alkyl-nitrilotriacetic acids

S. LÜBKEOVÁ, P. BALGAVÝ, E. FÜLEOVÁ, V. NOVÁK, M. SVIČEKOVÁ,
I. VALÁŠKOVÁ, and J. MAJER

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

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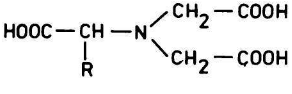
In this study, the acid-base and chelate-forming properties of surface-active complexanes of the type of 2-alkyl-nitrilotriacetic acids have been investigated by the use of ^{1}H NMR spectroscopy, potentiometry, polarography, and paper electrophoresis. The values of dissociation constants and stability constants obtained for 25 bivalent and trivalent ions give evidence that the investigated substances preserve the chelate-forming properties of the original complexone NTA.

В работе изучаются кислотно-основные и хелатообразующие свойства комплексанов типа 2-алкил-нитрилотриуксусных кислот с поверхностноактивными свойствами с помощью ^{1}H ЯМР-спектроскопии, потенциометрии, полярографии и электрофореза на бумаге. Найденные величины констант диссоциации и констант устойчивости комплексов с 25 двух- и трехвалентными ионами являются доказательством того, что исследуемые поверхностноактивные вещества сохраняют хелатообразующие свойства исходного комплексона НТА.

This paper is concerned with investigations of acid-base and chelate-forming properties of a group of complexanes of the type of 2-alkyl-nitrilotriacetic acids



where R is CH_3—$(CH_2)_5$—, CH_3—$(CH_2)_9$—, CH_3—$(CH_2)_{13}$—, or CH_3—$(CH_2)_{15}$—, which corresponds to the investigated complexanes 2-hexyl-nitrilotriacetic (KaDA), 2-decyl-nitrilotriacetic (LaDA), 2-tetradecyl-nitrilotriacetic (PaDA), or 2-hexadecyl-nitrilotriacetic acid (SDA), respectively.

These new complexanes, only the synthesis of which has been hitherto described [1, 2], represent a particular group in the class of reagents derived from the model complexone NTA. The introduction of a long aliphatic chain into the molecule of complexone changes its character. The hydrophobic component consisting of a long aliphatic chain C-6, C-10, C-14, or C-16 and the hydrophilic component represented by the chelate-forming iminodiacetic group are joined in a molecule. The formed amphipatic structure influences the anomalous behaviour of these substances in solutions and enhances the surface activity. The structure of the donor groups of NTA that has not been impaired by substitution is the prerequisite for preserving the complex-forming properties.

The acid-base properties of the investigated acids were examined by ^{1}H NMR spectroscopy and potentiometry. Some mutually complementary methods of investigation of complex compounds in solution, *i.e.* potentiometry, polarography, and electrophoresis were used for investigating the chelate-forming properties.

The basic theoretical relationships used for determining the dissociation constants of the acids themselves as well as the stability constants of the investigated chelates were presented in the preceding papers of the series "New complexanes" [3—5] and, for this reason, we give in the subsequent text only the obtained results or their interpretation.

Experimental

^{1}H NMR spectroscopic measurements

The samples for measuring the ^{1}H NMR spectra of the investigated substances were prepared by dissolving the substances in an alkaline solution (D_2O) in concentrations $c(\mathrm{KaDA}) = 3.6 \times 10^{-1}$ mol dm^{-3}; $c(\mathrm{LaDA}) = 3.0 \times 10^{-1}$ mol dm^{-3}; $c(\mathrm{PaDA}) = 1.3 \times \times 10^{-1}$ mol dm^{-3}; $c(\mathrm{SDA}) = 1.2 \times 10^{-1}$ mol dm^{-3}. The sodium salt of trimethylsilylpropionic-d$_4$ acid (TSP) was used as internal standard. The pD value of solutions was adjusted with KOD and DCl. The pD values [6] were calculated from the formula $\mathrm{pD} = \mathrm{pH_m} + 0.4$ where $\mathrm{pH_m}$ is the value read on a pH-meter Radelkis OP-205 equipped with a combined microelectrode EA-125 (Metrohm). The ^{1}H NMR spectra were taken with a spectrometer Tesla BS 487 A by using the working frequency of 80 MHz at 25 °C for KaDA and LaDA and at 80 °C for PaDA and SDA.

Electrophoretic measurements

The experimental procedures of electrophoretic investigation, method of construction of the curves and their evaluation are described in more detail in papers [7, 8].

The electrophoretic measurements were performed in an apparatus without electrode vessels in fundamental electrolytes containing KaDA in concentration 2×10^{-2} mol dm^{-3} by using chromatographic paper Whatman 2. The ions were applied in the form of nitrates in concentration 5×10^{-2} mol dm^{-3}.

Potentiometric measurements

The dissociation constants of KaDA were evaluated from the potentiometric neutralization curves of a given acid ($c = 1 \times 10^{-3}$ mol dm^{-3}) in the solution of KNO_3 ($c = 1 \times 10^{-1}$ mol dm^{-3}) by using several points in the pertinent buffer region. Owing to small solubility of LaDA, the investigations were carried out in the medium of 40 volume % of methanol while the concentration of acid as well as the medium was like for KaDA.

For studying the chelate-forming properties of KaDA with the ions of alkali earth metals, we used the method of exchange reaction with proton by using the technique of titration curves. The ratio c(metal) : c(ligand) was 10 : 1 and 1 : 1 for Ca(II) and Mg(II), respectively.

The formation of the chelates of KaDA with the Cu(II), Cd(II), Zn(II), and Ni(II) ions was investigated by the method of exchange equilibrium systems with 2,2′,2″-trisaminotriethylamine (tren) using Ca(II) or Cu(II) as auxiliary ion.

All experimental data were processed by means of a programming minicalculator HP-97 (Hewlett—Packard) according to the programs designed by us.

Polarographic measurements

In order to determine the logarithms of stability constants (log K) of the chelates of KaDA with lanthanoides La—Lu and Pb(II), we used the method of exchange equilibrium systems. The ratio c(reference ion) : c(fundamental ion) : c(ligand) was 1 : 1 : 1 for all systems. We used Pb(II), La(III), and Lu(III) as fundamental ions, Cu(II), Pb(II), and Eu(III) as reference ions and the disodium salt of KaDA as a ligand. The measurements were performed with 43 equilibrium systems. The pH value of individual systems varied within the range 3.8—4.0. The basic value used for calculating the logarithms of stability constants was the stability constant of the copper(II) chelate of KaDA determined potentiometrically by the method of exchange reaction with "tren".

For investigating the mercury(II) chelates of KaDA, we used the method based on the shift in half-wave potential of a reversible polarographic wave as a function of pH. The relationship $E_{1/2} = f(\text{pH})$ was investigated for 10 systems with regularly graded pH values in the range 3.6—5.6. The anodic waves were measured in the medium of acetate and Britton—Robinson buffer solution. The values of $E_{1/2}$ used for calculating log K as well as verification of reversibility of the reactions in the investigated systems were measured by the method of three electrodes [9].

Results and discussion

The investigated substitution of alkyls in a molecule of the model complexone NTA produces a decrease in solubility of a given ligand. The solubility σ decreases in the order $\sigma(\text{KaDA}) > \sigma(\text{LaDA}) > \sigma(\text{PaDA}) > \sigma(\text{SDA})$ with increasing length of the alkyl substituent so that it gets unsuitable for conditions of the potentiometric investigation of acid-base and chelate-forming properties of LaDA, PaDA, and SDA in solution.

Thus we have started from the properties of KaDA as model complexone in order to appreciate the acid-base and chelate-forming properties of 2-alkyl-nitrilotriacetic acids with surface-active properties.

For evaluating of the dissociation constants of KaDA and insufficiently soluble higher homologues LaDA, PaDA, and SDA the data obtained by ^{1}H NMR spectroscopy have been conveniently used.

The dependence of chemical shifts in nonlabile protons of KaDA in D_2O solutions on pD is represented in Fig. 1. The dependence of chemical shifts of nonlabile protons of LaDA, PaDA, and SDA on pD of solutions is not given because it is not significantly different from the above-mentioned one.

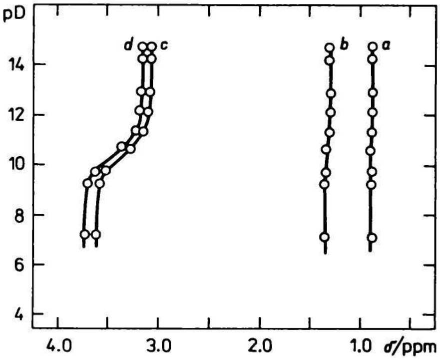


Fig. 1. Variation of chemical shifts δ of nonlabile protons of KaDA with pD in D_2O solution at 25 °C.
a) $—CH_3$; *b*) $—(CH_2)_5—$; *c*) $—\overset{|}{C}H—COO^-$; *d*) $—CH_2—COO^-$

In all cases, a considerable change in chemical shift of nonlabile protons of the fragments $—CH_2—COO^-$, and $—\overset{|}{C}H—COO^-$ appears in the region of pK_{a3}. In the first case, the chemical shift changed by $\Delta\delta = 0.52$ ppm and in the second one by $\Delta\delta = 0.45—0.50$ ppm. In both cases, the signal shifted towards lower values of the intensity of magnetic field, from which it resulted that the electron density on nonlabile protons gradually decreased with decreasing pH value. Nearly equal change in chemical shift in the pK_{a3} region for both types of nonlabile protons indicates that the increasing concentration of the deuterium ions in the region pD = 12.0—9.0 brings about a bonding of these ions to amine nitrogen of the investigated compounds, owing to which a structure of the betaine type arises.

The signal of protons of the CH_3 groups in the investigated compounds did not practically change. The change in chemical shift due to its dependence on pD varied in the region pD = 14.0—7.0 only in the scope of experimental error. A certain indication of a change in chemical shifts in signals of the methylene protons of aliphatic chains were obvious from the change in form of the spectra in dependence on pD. The chemical shift in maximum of the signal of these protons which was an unresolved multiplet at all pD values is plotted in Fig. 1. This relationship shows that a change in chemical shift appears in the region pD =

= 12.0—9.0 though it is not so conspicuous as for the protons of —CH_2—COO^-, and —$\overset{|}{\mathrm{C}}\mathrm{H}$—$COO^-$, which is comprehensible in connection with a decrease in induction effect due to increasing distance from the place of protonization. The change in form of the spectrum of these protons is thus caused by unequal change in chemical shifts of individual methylene groups in aliphatic chain. The corresponding spectra represented in Fig. 2 serve for example. For quantitative evaluation of this change the width of signal in a half of its amplitude ($\Delta\nu_{1/2}$) was used as parameter. The determination of this parameter of the spectrum is to be seen in Fig. 2. It is obvious that the width of signal increases with decreasing value of pD in the region of pD = 12.0—9.0. However, the change in signal width is not monotonous in the whole pD range. It may be due to inaccuracy of measurements (relative error ±0.2 Hz) as well as to possible formation of molecular cluster aggregates and change in their structure depending on pD. The change in structure brings about a variation of the relaxation times T_1 and T_2, which results in a change of signal width. A certain suggestion of the second alternative is the ^{1}H NMR spectrum of KaDA measured in D_2O at pD = 3.32. This spectrum is represented in Fig. 3 and consists of a broad unresolved line in the region $\delta = 0$—3.0 ppm.

The difference between the values of pK_{a3} determined graphically from the shifts in signals of —CH_2—COO^- and —$\overset{|}{\mathrm{C}}\mathrm{H}$—$COO^-$ at varying pD and the values of

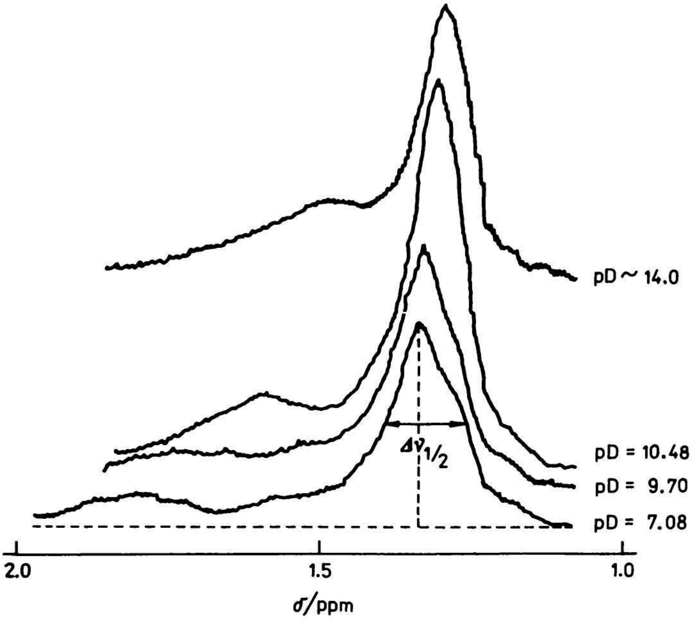


Fig. 2. ^{1}H NMR spectra expressing the shift δ in nonlabile protons of the methylene groups of aliphatic chain of KaDA in D_2O solution as a function of pD.

pK_{a3} obtained potentiometrically (Table 1) is comprehensible because of considerably higher concentration of solutions used for ^1H NMR measurements and different ionic strength.

Table 1

Dissociation constants
$I_c(KNO_3) = 0.10\ mol\ dm^{-3}$; $\theta = 20\ °C$

pK_a	AMDA [10]		KaDA		LaDA		PaDA		SDA		NTA [11]
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*
pK_{a1}	1.59	—	1.9	—	1.82^c	—	—	—	—	—	1.8
pK_{a2}	2.48	—	2.51	—	3.26^c	—	—	—	—	—	2.48
pK_{a3}	9.88	10.1	10.08	10.3	10.29^c	10.5	—	10.3	—	10.3	9.71

a) Data from potentiometric measurements; *b*) data obtained by ^1H NMR spectroscopy; *c*) measured in the medium of 40 volume % of methanol.
AMDA = 2-ethyl-nitrilotriacetic acid.

If we compare the values of dissociation constants of KaDA with the corresponding values of the model complexone NTA (Table 1), we can see that the 2-hexyl substitution in skeleton has produced an increase in basicity of the amine nitrogen, which may be attributed to the induction effect of the particular alkyl substituent. The values of pK_{a1} and pK_{a2} remain on the level of the pertinent values of the

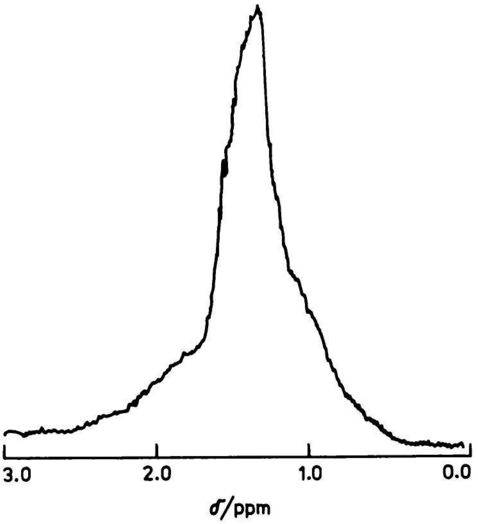


Fig. 3. ^1H NMR spectrum of KaDA in D_2O at pD = 3.32.

model complexone. The values of pK_{a3} found for higher members of the homologous series of compounds (with C-10, C-14, and C-16) indicate that further extension of the aliphatic chain does not bring any change in acid-base properties.

The distribution diagram (Fig. 4) constructed on the basis of the obtained pK values gives the percentage of the nonionized form and individual ionized forms of KaDA as a function of pH. It results from this graph that there are three components present in the solution in the following proportions: H_3A 3 %, H_2A^- 27 %, and HA^{2-} 70 % if KaDA is dissolved in the form of free tricarboxylic acid in water (pH = 2.90).

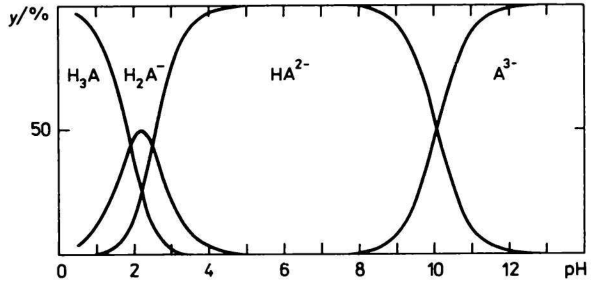


Fig. 4. Distribution diagram for KaDA and its individual ionization forms.

The potentiometric titration curves of pure KaDA as well as in the presence of alkali earth metals indicate the absence of the processes involving formation of hydrogen and hydroxo complexes in the whole investigated pH region and confirm only the formation of complexes of the ML^- type.

The curves describing the electrophoretic mobility of the complexes of KaDA with the investigated bivalent and trivalent central ions are represented in Fig. 5.

The analysis of these curves enables us to draw conclusions about composition and stability of the complexes of KaDA with 25 bivalent and trivalent central atoms including the whole group of lanthanoides (except Pm). The bivalent ions — Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) — interact with KaDA and form chelates of the ML^- type. As for Ca(II) and Mg(II), complexes of analogous composition arise, of course, in strongly alkaline region. No formation of any complexes in the investigated pH region was proved for Ba(II) and Sr(II). The character of the curves of electrophoretic mobility for the chelates of lanthanoides is, in principle, always identical and, for this reason, only the curves of some representatives are presented in Fig. 5. In all cases, the formation of a neutral complex $[ML]^0$ in the region of pH < 4.0 and formation of complexes of the $[ML_2]^{3-}$ type (1 : 2) at pH > 4.5 was evidenced for lanthanoides. The character of the curves of mobility of the Al(III) and Fe(III) ion is analogous. The plateau in the region of zero mobility corresponds to the existence of a neutral complex with the

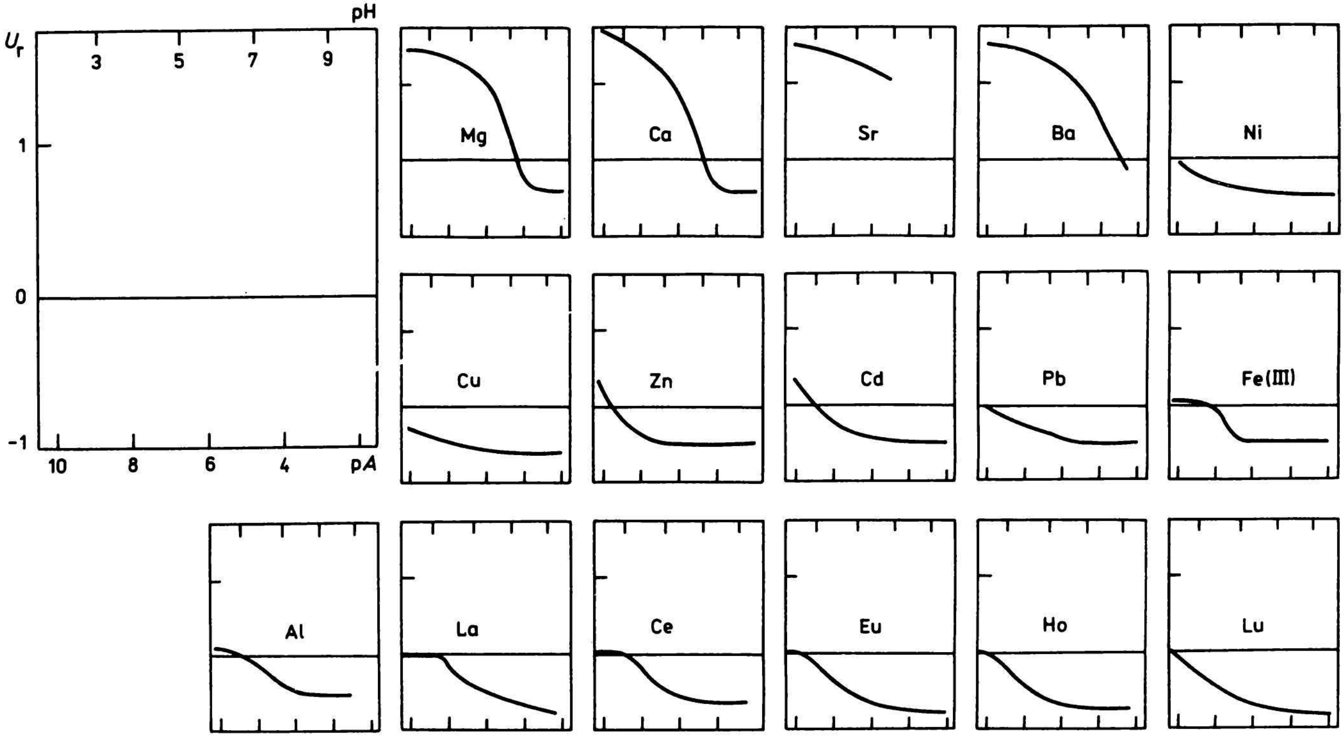


Fig. 5. Electrophoretic mobility of KaDA complexes.
A = concentration of free ligand, U_r = real relative electrophoretic mobility with respect to $(C_2H_5)N^+$ ($u = +1.0$), $\theta = 20$ °C, $I_c(KNO_3) = 0.10$ mol dm^{-3}.
Analytical concentration of KaDA in fundamental electrolyte $c_L = 2 \times 10^{-2}$ mol dm^{-3}, analytical concentration of metals for spotting $c_M = 5 \times 10^{-2}$ mol dm^{-3}.

Table 2

Experimental values of the function $E_{1/2} = f(\text{pH})$ for Hg(II) complex of KaDA
$I_c(\text{KNO}_3) = 0.10\ \text{mol dm}^{-3}$; $\theta = 20\ °\text{C}$

No.	pH	$E_{1/2}$/mV	log [A]	Logarithm of stability constant
1	3.62	375	6.49	14.28
2	3.81	366	6.29	14.32
3	4.07	361	6.02	14.29
4	4.23	350	5.86	14.52
5	4.40	340	5.69	14.69
6	4.61	338	5.47	14.54
7	4.79	336	5.29	14.42
8	5.01	331	5.08	14.39
9	5.18	328	4.90	14.31
10	5.54	311	4.58	14.58
Mean value				14.44

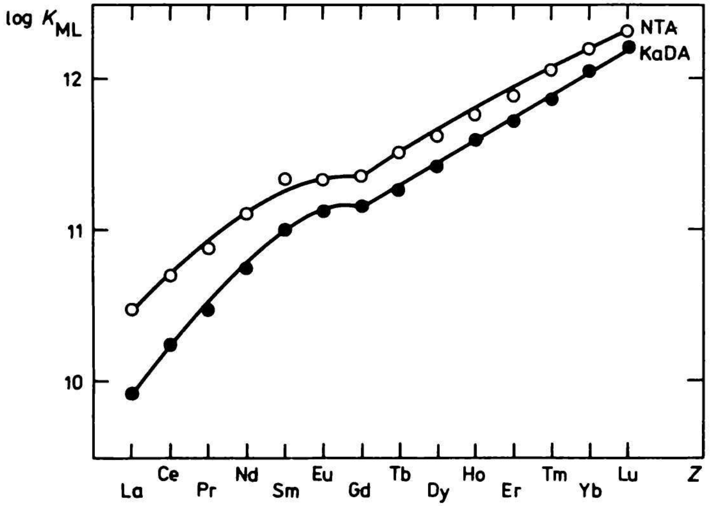


Fig. 6. Numerical values of the logarithms of stability constants of the complexes containing lanthanoides and KaDA as a function of proton number of the lanthanoide representing the central ion of complex.

ratio $v(\mathrm{M}):v(\mathrm{L}) = 1:1$ while the plateau in the region of anodic mobility corresponds to a complex of the $[\mathrm{ML}_2]^{3-}$ type. The values of stability constants of the investigated complexes determined by electrophoresis are in good agreement with the values obtained by the potentiometric or polarographic method. The differences do not exceed the scope of deviations caused by smaller precision of the electrophoretic method. The investigation of the polarographic functional relation $E_{1/2} = f(\mathrm{pH})$ has given evidence that KaDA interacts with Hg(II) in the region of pH = 3.6—5.6 to give chelates of the HgL^- type. However, formation of hydroxo complexes was observed at pH > 6. The experimental values of the function $E_{1/2} = f(\mathrm{pH})$ as well as the resulting numerical value of the logarithm of stability constant of the Hg(II) chelate of KaDA are given in Table 2.

The course of numerical values of the logarithms of stability constants of the chelates of KaDA with trivalent ions of the lanthanoide group as a function of

Table 3

Resulting values of stability constants (log K_{ML})
$I_c(\mathrm{KNO_3}) = 0.10$ mol dm^{-3}; $\theta = 20$ °C

M	KaDA	AMDA [10]	NTA [11]
Mg(II)	5.44	5.36	5.41
Ca(II)	6.47	6.46	6.41
Sr(II)	4.62	4.52	4.98
Ba(II)	4.40	4.48	4.82
Zn(II)	10.21	10.35	10.67
Cd(II)	9.84	9.96	9.83
Pb(II)	11.29*	11.55	11.39
Cu(II)	13.01	13.11	12.96
Ni(II)	11.23	11.24	11.53
La(III)	9.84	9.98	10.47
Ce(III)	10.18*	10.48	10.70
Pr(III)	10.40*	10.67	10.88
Nd(III)	10.68*	10.82	11.11
Sm(III)	10.93*	11.13	11.33
Eu(III)	11.06*	—	11.33
Gd(III)	11.08*	11.25	11.36
Tb(III)	11.19*	11.29	11.51
Dy(III)	11.34*	11.45	11.62
Ho(III)	11.53*	11.58	11.75
Er(III)	11.65*	11.77	11.89
Tm(III)	11.80*	12.07	12.06
Yb(III)	11.99*	12.19	12.20
Lu(III)	12.17*	—	12.32

The values designated with * were measured polarographically and the other ones potentiometrically.

proton number of the lanthanoide (Fig. 6) representing the central atom of complex is analogous to that one found for NTA. The values of the logarithms of stability constants increase from lanthanum up to lutecium and exhibit evident irregularity in the region of gadolinium by the so-called gadolinium break.

The resulting values of the logarithms of stability constants of the chelates of KaDA with the alkali earth metals (Mg(II), Ca(II), Sr(II), and Ba(II)), selected representatives of bivalent ions (Zn(II), Cd(II), Pb(II), Cu(II), and Ni(II)), and trivalent ions (all lanthanoides except Pm) are given in Table 3. They are confronted with the corresponding values given in literature [11] for the model complexone NTA. It results that all investigated ions form with KaDA less stable chelates than with NTA. This piece of knowledge may be explained in agreement with the theory of coordination compounds by the fact that the investigated alkyl substitution has favourable influence on the increase in basicity of the amine nitrogen but, on the other hand, the voluminous substituent gives rise to steric hindrance for chelation.

KaDA used as a model complexane of the investigated group of 2-alkyl-nitrilotriacetic acids with surface-active properties exhibits acid-base and chelate-forming properties on the level of analogous alkyl derivatives of NTA with the number of carbon atoms up to C-6 [10]. Therefore we may justly expect that the higher homologues of LaDA, PaDA, and SDA should exhibit properties very similar to those of the model complexane.

The results obtained by investigating the surface-active properties of 2-alkyl-nitrilotriacetic acids will be published in subsequent papers.

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