

# New complexanes. XXXV.

## Properties of 1,2-diaminooctane-*N,N,N',N'*-tetraacetic acid

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The acid-base and, in particular, complexing properties of the new chelate-forming agent ODTA have been studied by using potentiometric and polarographic methods as well as paper electrophoresis. The values of dissociation constants of this multidentate ligand and the stability constants of its chelates with 25 bivalent and trivalent cations including the alkaline earth ions and lanthanides determined under unified conditions ( $I_c = 0.10$  (KNO<sub>3</sub>);  $T = 293$  K) are the results of this study. The properties of ODTA are compared with those of structurally analogous substances of the EDTA and DCTA complexane type. It appears that ODTA invariably forms more stable chelates than EDTA the stabilities of which are comparable with those of the DCTA.

Изучаются кислотно-основные и преимущественно комплексообразовательные свойства нового хелатообразующего реагента – 1,2-диаминооктан-*N,N,N',N'*-тетрауксусной кислоты (ODTA) при использовании потенциометрического и полярографического методов, а также электрофореза на бумаге. Результатом данной работы являются значения констант диссоциации этого шестидентатного лиганда и константы устойчивости хелатов ODTA с 25 двух- и трехвалентными катионами, включительно ионов щелочных земель и лантаноидов, которые были получены при одинаковых условиях ( $I_c = 0,10$  (KNO<sub>3</sub>),  $T = 293$  K). Свойства ODTA сравниваются с комплексообразователями аналогичной структуры EDTA и DCTA, причем вообще ODTA образует более прочные хелаты по сравнению с EDTA и их устойчивость сравнима с хелатами DCTA.

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### Abbreviations:

ODTA 1,2-Diaminooctane-*N,N,N',N'*-tetraacetic acid.

DCTA 1,2-Diaminocyclohexane-*N,N,N',N'*-tetraacetic acid.

In the scope of a complex and systematic study of the monosubstituted and disubstituted monotopic and ditopic alkyl, isoalkyl, and aryl derivatives of EDTA we have been hitherto concerned with the properties of the alkyl derivatives of EDTA in three papers of this series [1—3]. As this substitution resulted in the preparation of some agents exhibiting an increased chelating ability when compared with EDTA, another complexane with a long aliphatic chain in the skeleton of the molecule was prepared. It was 1,2-diaminooctane-*N,N,N',N'*-tetraacetic acid [4].

In this study, we concentrated our attention upon the acid-base and chelating properties of ODTA by using both electrochemical instrumental methods, *i.e.* polarography and potentiometry, and paper electrophoresis. By evaluating the potentiometric neutralization titration curves, the values of dissociation constants of the acid itself as well as the stability constants of its chelates with Ca(II), Mg(II), Sr(II), and Ba(II) were determined. The stability constants of the complexes containing Cd(II) and Cu(II) were determined potentiometrically by the "tren" method of exchange equilibrium. The chelates containing the trivalent ions of lanthanides (La→Lu) or particular bivalent cations Cu(II), Pb(II), Zn(II), Co(II), Mn(II) were investigated by using the polarographic method of exchange equilibrium systems. The complexes containing Hg(II) and partly the dissociation constants of the acid were investigated on the basis of the polarographic relationship  $E_{1/2} = f(\text{pH})$ . The composition, charge, and region of existence of individual complexes were verified by electrophoretic investigation of the relationship  $U = f(\text{pH})$ .

As the theoretical relations, experimental accomplishment of particular physicochemical measurements, and method of evaluation of the results is like in our preceding studies [1—3], we shall immediately give the resulting constants and characterization of the properties of the investigated complexane.

## Experimental

The dissociation constants were evaluated from neutralization curves of  $1 \times 10^{-3}$  M solutions of the acid in usual way. The resulting  $\text{p}K_{a1} - \text{p}K_{a4}$  values of ODTA and for comparison those of EDTA [5] and DCTA [6] are given in Table 1.

The neutralization curves of the  $1 \times 10^{-3}$  M solutions of ODTA containing tenfold excess of the salt of metal ion or in case of Ca(II) and Mg(II), the neutralization curves corresponding to equimolar concentration of the metal ion with respect to the complex were used for determining the stability constants of the chelates containing alkaline earth metals (Table 1).

The results of potentiometric measurements were evaluated on a computer by means of a universal program for calculating the dissociation constants and stability constants of complexes containing metal ions [7].

Table 1

pK Values and stability constants  
 $I_c = 0.10$  (KNO<sub>3</sub>);  $T = 293$  K

	ODTA	EDTA [5, 8]	DCTA [6, 8]
pK <sub>a1</sub>	2.28 ± 0.10*	2.00*	2.43*
pK <sub>a2</sub>	2.98 ± 0.03*	2.67*	3.52*
pK <sub>a3</sub>	6.05 ± 0.03*	6.16*	6.12*
pK <sub>a4</sub>	10.95 ± 0.02*	10.26*	11.70*
Mg	10.16 ± 0.03*	8.69*	10.32*
Ca	11.70 ± 0.02*	10.69*	12.50*
Sr	9.80 ± 0.03*	8.63*	10.69*
Ba	8.65 ± 0.03*	7.76*	7.99*
Zn	18.12 ± 0.09	16.66 ± 0.02	18.67 ± 0.06
Cd	18.02 ± 0.03*	16.62 ± 0.02*	19.23 ± 0.02*
Hg	22.77	21.80	24.30
Mn	15.51 ± 0.10	14.20 ± 0.20	16.78 ± 0.15
Co	17.90 ± 0.09	16.47 ± 0.05	18.92 ± 0.05
Cu	20.44 ± 0.11	18.96 ± 0.14	21.30 ± 0.07
Pb	19.20 ± 0.09	18.20 ± 0.14	19.68 ± 0.05
La	16.47 ± 0.15	15.66 ± 0.05	16.26 ± 0.17
Ce	17.05 ± 0.14	16.14 ± 0.05	16.76 ± 0.17
Pr	17.28 ± 0.13	16.56 ± 0.05	17.31 ± 0.12
Nd	17.65 ± 0.12	16.77 ± 0.05	17.68 ± 0.07
Sm	18.17 ± 0.10	17.30 ± 0.05	18.38 ± 0.07
Eu	18.31 ± 0.10	17.51 ± 0.06	18.62 ± 0.06
Gd	18.43 ± 0.10	17.53 ± 0.05	18.77 ± 0.06
Tb	19.00 ± 0.10	18.09 ± 0.05	19.50 ± 0.06
Dy	19.57 ± 0.11	18.46 ± 0.05	19.69 ± 0.06
Ho	19.67 ± 0.12	—	—
Er	19.83 ± 0.13	19.01 ± 0.06	20.68 ± 0.09
Tm	20.39 ± 0.17	19.48 ± 0.05	20.96 ± 0.06
Yb	20.58 ± 0.14	19.67 ± 0.07	21.12 ± 0.09
Lu	20.75 ± 0.15	19.99 ± 0.07	21.51 ± 0.09

\* The values were measured potentiometrically.

The stability constants of the complexes of lanthanides (La → Lu) and other bivalent ions listed in Table 1 were determined polarographically by the method of equilibrium systems (53 equilibrium systems; internal polarographic standards: Pb(II), Cu(II), Eu(III)); the pH values of the systems varied in the range 4.1—4.4). The fundamental value for the calculation of these constants was the stability constant of the cadmium(II) complex of ODTA determined potentiometrically (by the "tren" method).

The electrophoretic measurements served mainly for investigating the formation, composition, and charge of complexes as functions of pH. The experimental conditions of these measurements and the method of their evaluation are described in [9]. The curves of electrophoretic mobility of the complexes containing particular representatives of bivalent ions and lanthanides are shown in Fig. 1.



A comparison between the values of dissociation constants of ODTA and EDTA (Table 1) in the function of model complexane shows clearly that, besides a slight increase in  $pK_{a1}$  and  $pK_{a2}$ , the *n*-hexyl substitution performed in skeleton of the molecule resulted in a considerable change in the  $pK_{a4}$  value corresponding to hydrogen dissociation in one of the ammonium groups, which might be attributed to induction effect of particular alkyl substituent. The percentage of individual dissociation forms of ODTA at varying pH is illustrated by the distribution diagram (Fig. 2) from which could be seen that three components are present in the solution in the subsequent proportions provided this complexane in the form of free tetracarboxylic acid is dissolved in H<sub>2</sub>O (pH 2.95): H<sub>4</sub>A 10%, H<sub>3</sub>A<sup>-</sup> 45%, H<sub>2</sub>A<sup>2-</sup> 45%.

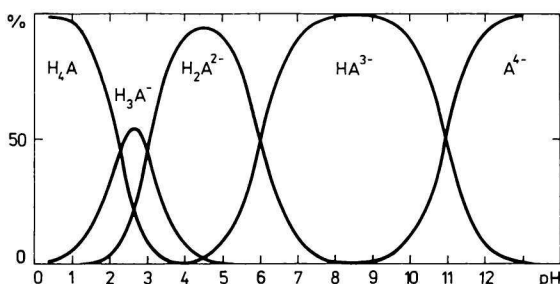


Fig. 2. Distribution diagram of ODTA and its dissociation forms.

The curves of relative electrophoretic mobility (Fig. 1) of the ODTA complexes with the whole group of lanthanides exhibit a qualitatively analogous course and confirm that the interaction of this ligand with lanthanides results in formation of chelates of the  $ML^-$  type in the ratio  $M:L = 1:1$ . All curves obtained by using strongly alkaline medium reveal increasing anodic mobility, which indicates the formation of hydroxo complexes. Bivalent ions give rise to the complexes with anodic mobility corresponding to the composition  $ML^{2-}$ . The region of existence of these complexes is within the pH range 3–10.

The dependence of logarithms of stability constants of the lanthanide complexes on atomic number of the pertinent central ion (Fig. 3) shows that ODTA forms with all lanthanides chelates which are almost by one decimal order more stable than the chelates formed by EDTA. These complexes attain the stability of the DCTA complexes for light lanthanides. The difference between stability constants of the  $LaL^-$  and  $LuL^-$  complexes exceeds four  $\log K$  units for ODTA.

All investigated complex-forming characteristics of ODTA with lanthanides and bivalent ions have been compared with respect to a model complexane (Fig. 4) on the basis of the *Irving–Rossotti* relationship [10]. In our case, this functional

Fig. 3. Dependence of the logarithms of stability constants of the lanthanide complexes of ODTA on atomic number  $Z$  of the lanthanide constituting central ion of the complex.  
1. ODTA; 2. EDTA; 3. DCTA.

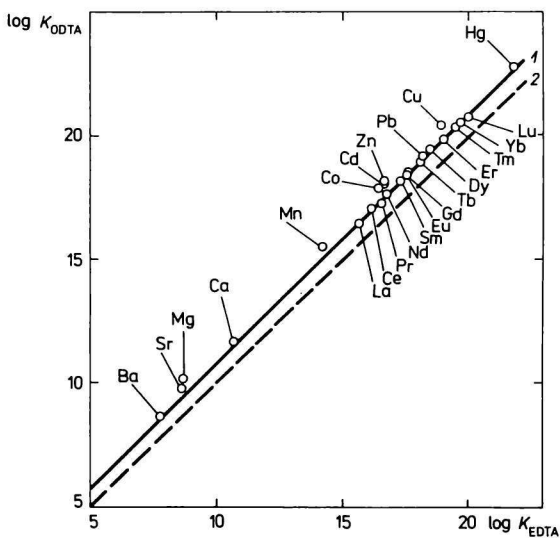
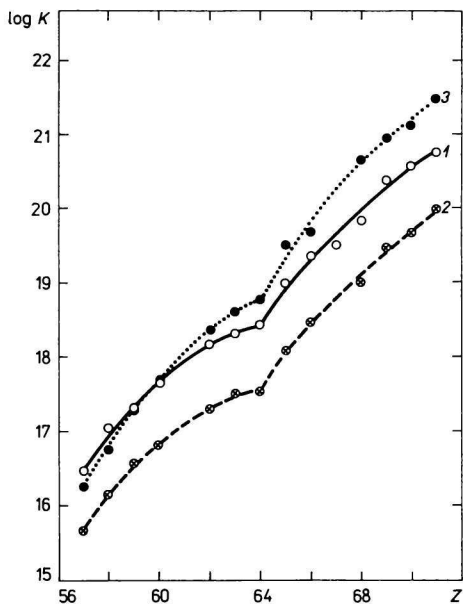


Fig. 4. Logarithms of stability constants of the complexes of ODTA as functions of corresponding values of the complexes containing EDTA.

$$\log K_{M-ODTA} = f(\log K_{M-EDTA}).$$

1. Theoretical curve; 2. EDTA.

relationship is very conclusive owing to a considerable number of investigated complexes and the range of complexity constants covering 14 units ( $\log K_{\text{BaL}^{-2}} - \log K_{\text{HgL}^{-2}}$ ) and confirms that the higher stability of the ODTA chelates when compared with the EDTA chelates is, in principle, determined by the difference between the  $\text{p}K_{\text{a}4}$  values of the constituent complexanes.

### References

1. Novák, V., Lučanský, J., and Majer, J., *Chem. Zvesti* **22**, 721 (1968).
2. Novák, V., Dvořáková, E., and Majer, J., *Chem. Zvesti* **23**, 161 (1969).
3. Novák, V., Lučanský, J., Svičková, M., and Majer, J., *Chem. Zvesti* **28**, 324 (1974).
4. Majer, J. and Butvin, P., unpublished results.
5. Schwarzenbach, G. and Ackermann, H., *Helv. Chim. Acta* **30**, 1798 (1947).
6. Schwarzenbach, G. and Ackermann, H., *Helv. Chim. Acta* **32**, 1682 (1949).
7. Oravský, V., unpublished results.
8. Schwarzenbach, G., Gut, R., and Anderegg, G., *Helv. Chim. Acta* **37**, 937 (1954).
9. Jokl, V., Majer, J., and Mazáčová, M., *Chem. Zvesti* **18**, 584 (1964).
10. Irving, H. and Rossotti, H., *Acta Chem. Scand.* **10**, 72 (1956).

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