Mixed Ligand complexes of Zinc (II) with NTA, EDTA and HEDTA as primary Ligands and Glutamic acid as secondary Ligand

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Summary: Formation of mixed ligand complexes of Zn(II) with NTA, EDTA and HEDTA as primary ligands and glutamic acid as a secondary ligand has been studied potentiometrically. The K_{MLA} values are larger than K_1 and K_2 values of simple Zn(II) - glutamate chelates. Further the stability sequence with respect to primary ligands is EDTA > HEDTA > NTA.

Introduction

Mixed ligand complexes have aroused much interest in recent years (1 - 14). Many workers hav studied and reported number of mixed ligand systems potentiometrically, spectrophotometrically and by solvent extraction (15, 16). It is noticed that polydentate aminopolycarboxylic acids, viz., NTA, HEDTA and EDTA, etc. in general form stronger chelates and serves as primary ligands whereas many other ligands which form comparatively less stable chelates behave as secondary ligands.

The present paper describes a potentiometric study of some mixed complexes of zinc with NTA, HEDTA and EDTA as primary ligands and glutamic acid as a secondary ligand.

Experimental

Reagents

Glutamic acid (BDH-England), zinc perchlorate, perchloric acid (Riedel), sodium perchlorate (Riedel), sodium hydroxide (S. Merck), EDTA disodium salt (AR, BDH), NTA (BDH, England) and HEDTA (BDH, England).

All solutions were prepared in CO_2 - free doubly distilled water, and standardized by the standard methods. pH measurements were done at 25°C on a Beckman pH meter H 5 fitted with glass and calomel electrode assembly and the accuracy of pH meter was ± 0.05.

Titration Procedure

Mixtures containing (i) H: acid (0.001M perchloric acid) (ii) L: primary ligand (0.001 M, NTA or EDTA or HEDTA) (iii) A: Secondary ligand (0.001M glutamic acid) (iv) ML: (1:1 molar ratio of Zn^{++}, NTA or EDTA or HEDTA) (v) MA: (1:1 molar ratio of Zn^{++}, and secondary ligand) (vi) MLA (1:1:1 molar ratio of Zn^{++} glutamic acid any of the primary ligand) were prepared, and the total volume was kept 50.0 ml. in each case. The ionic strength of the mixture solution was kept constant by using 0.1 M sodium perchlorate. All of these also contained equal concentration of free perchloric acid (0.001 M) The above mixture solutions were then separately titrated with a standard carbonate-free 0.1 M sodium hydroxide solution.

The typical pH titration curves for mixed ligand systems Zn^{++} - glutamic acid and NTA, EDTA and HEDTA are shown in Figs.1 - 3 respectively. Figures 1 - 3 also depict the composite curves (4-6) for the mixed ligand systems, which were calculated on the assumption that no mixed ligand chelate is formed and the only species present during titration was a 1:1 Zn^{++} - NTA, EDTA or HEDTA (ML) chelate and free secondary ligand (HA). Thus the graphical addition of the free secondary ligand (HA) to 1:1 (ML) chelate titration curves yields the composite curves. Since the experimental titration curves for the mixed ligand systems (MLA) are quite different from the composite curves, it indicates the formation of mixed ligand chelates in these systems. K_{MLA} values were claculated as described by Ozer (6).

Results and Discussion

Zn^{++} - NTA-Glutamic acid system - Figure 1 contains the potentiometric titration curves for 1:1 Zn^{++} -NTA (ML), 1:1 Zn^{++} - glutamic acid (MA) and 1:1:1 Zn^{++} NTA-glutamic acid (MLA) system respectively. The ML titration curve shows an inflexion at a=4, but the mixed complex (MLA) curve does not show any inflexion at a=4, instead of a well marked inflexion is observed at a=5. The formation of the mixed chelate is inferred by

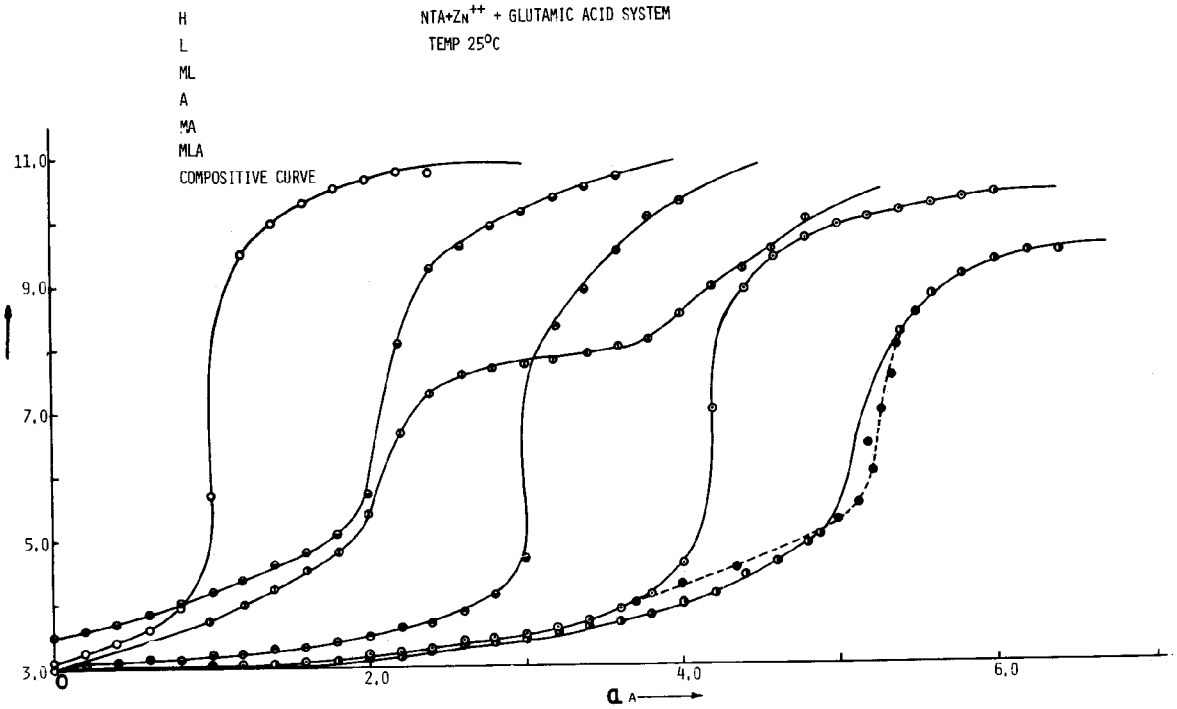
NTA+Zn++ + GLUTAMIC ACID SYSTEM
TEMP 25°C
H
L
ML
A
MA
MLA
COMPOSITIVE CURVE
11.0
9.0
7.0
5.0
3.0
0
2.0
4.0
6.0
a A

Fig. 1

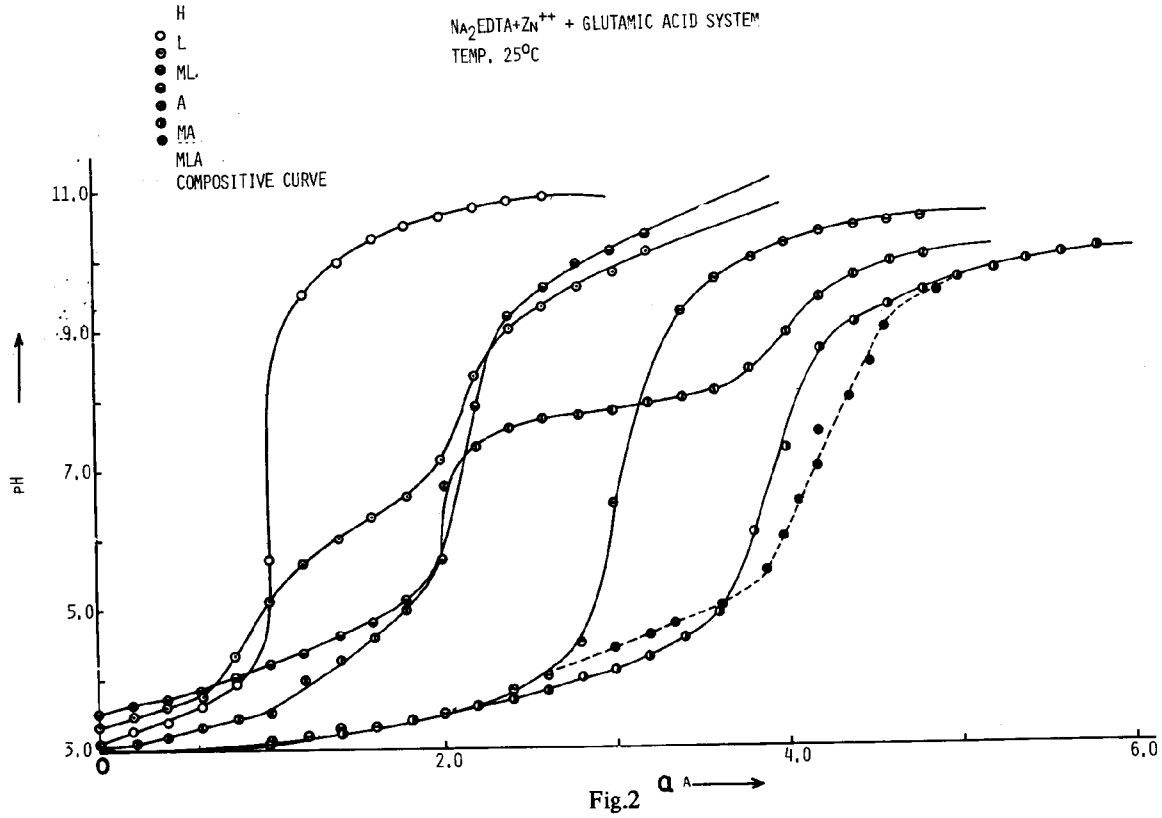
Na2EDTA+Zn++ + GLUTAMIC ACID SYSTEM
TEMP. 25°C
H
L
ML
A
MA
MLA
COMPOSITIVE CURVE
pH
11.0
9.0
7.0
5.0
3.0
0
2.0
4.0
6.0
a A

Fig.2

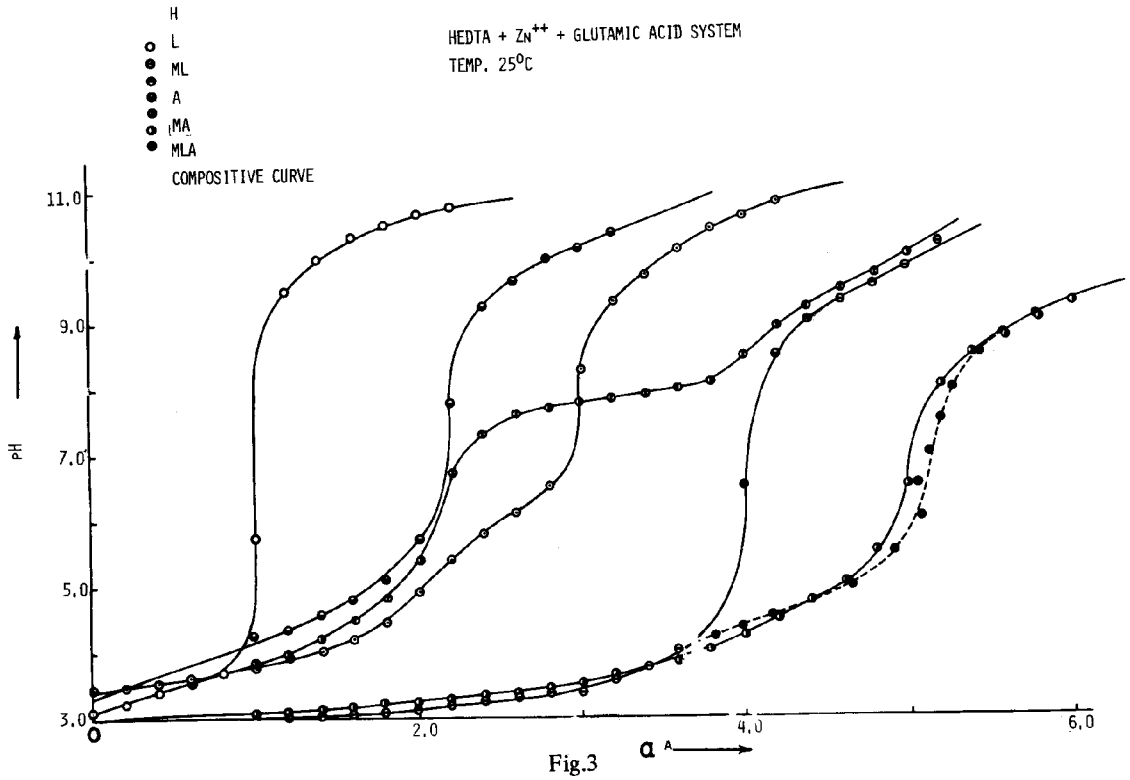

Fig.3

a comparison of the experimental MLA titration curve with the compositive curve, obtained as described earlier. It is noted that the experimental MLA curve runs along with the composite curve up to pH 5 but afterwards it separates and run above the composite curve up to pH 8.

Similarly, Figs. 2 and 3 obtain the pH titration curves for Zn^{++} EDTA-glutamic acid and Zn^{++} - HEDTA -glutamic acid systems respectively. For Zn^{++} -EDTA complex, the ML curve shows an inflexion at a=3, which is not observed in the mixed ligand chelate system which instead shows an inflexion at a=4. In this case also the experimental MLA curve runs along the composite curve upto pH 5, after it runs above the composite curve.

In Fig. 3 the ML curve (Zn^{++} - HEDTA - Complex) shows an inflexion at a=4, which is again absent in the mixed complex system, where an inflexion is noted at a=5. In this system the experimental MLA curve runs along with the composite curve up to pH 5, after which it separates and runs above the composite curve.

Thus a comparison of the experimental MLA curves with the composite curves indicates that mixed ligand chelates are formed in all the three systems. Their stability constants (log K_{MLA} values) are given in table 1.

Table 1.

Stability constants of mixed ligand complexes of Zn(II) (Temperature 25°C, μ = 0.1 M $NaClO_4$)

Primary ligand	Secondary ligand	log K_{MLA}
NTA	glutamic acid	6.67
EDTA	glutamic acid	7.88
HEDTA	glutamic acid	8.42

A comparison of these K_{MLA} values with stability constants of Zn(II) - glutamate chelates shows that these values are larger than K_1 and K_2 values of simple chelates (17, 18).

Further a comparison of K_{MLA} values with different primary ligands shows the following sequence EDTA > HEDTA > NTA.

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