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On Thallium(I) Chelates of 1,2-Cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic Acid and Diethylenetriaminepentaacetic Acid

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Synopsis. The stability constants of the complexes mentioned in the title obtained by us by potentiometric pH measurements are compared with those of Kodama *et al.* Because sodium ion forms quite a stable 1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetate (CyDTA) complex, the discrepancy of the values can be explained. Further new calculations confirm the formation of protonated chelate with CyDTA but in a very limited pH range.

Kodama *et al.* have determined the stability constants of thallium(I) complexes with diethylenetriaminepentaacetate (DTPA)1) and 1,2-cyclohexanetetraacetate (CyDTA)2) ions using polarographic measurements. Their values (K. and T.) are given together with those obtained by us3) (A. and B.) with pH measurements in the Table 1. The difference between the results of the two works can be partly caused by the different ionic strengths used but the discrepancies with CyDTA as ligand is too large to be explained in this manner. The preference given by us to the potassium nitrate as inert salt is justified by the fact that potassium ion forms very weak complexes with amino polycarboxylate ligands and the ligand protonation constants in this medium at $I=0.1$ are known.4,5) Kodama and Tominaga have preferred $NaClO_4$ solutions ($I=0.4$ resp. 0.3) in spite of the greater stability of the sodium complexes4,7) and have calculated the dissociation constants of the acids using the pK values of Schwarzenbach and Ackermann,6) correcting for the change in the ionic strength by means of the Davies equation. The calculation of the activity coefficients of high charged ions as those involved here can only give very approximative results. Further the pK value of $HCyDTA^{3-}$ of the above work was found to be too low.5) The better agreement of the results in the case of DTPA indicates that the discrepancies for CyDTA cannot be due only to these reasons.

K. and T. followed from the constancy of $(E_{1/2})_{TlZ}$ in the pH range from 10 to 11.7 the formation of the protonated chelate $TlHZ^{2-}$. This constancy is due to the fact that beside the unprotonated complex TlZ^{3-} "uncomplexed" ligand is mainly present as sodium complex NaZ^{3-} in that pH range. Indeed from our pK values4,5) and some new measurements—the pK of $HCyDTA^{3-}$ at $I=0.1$ ($NaNO_3$) and 20 °C is found to be 9.80—for that complex a stability constant of approximately $10^{2.7}$ is estimated. Therefore in 0.3 ($NaClO_4$) and pH=10 already more than 80% of the uncomplexed ligand is present as NaZ^{3-}. As described in our work3) for the determination of the stability of the thallium(I) complexes alkalimetric titration have been used, in which solutions containing the diprotonated ligand H_2Z^- and thallium(I) nitrate have been titrated with 0.1 M KOH. In Fig. 1 of reference3) the curve obtained with EDTA as ligand is given. Starting from 100 ml of a solution containing 10^{-4} mol H_2CyDTA and Tl^+ by addition of 0.1 M KOH the following data have been obtained: (ml/pH): 0.4/5.919: 0.6/6.259: 0.8/6.686: 0.9/6.986: 0.95/7.178: 1.0/7.409: 1.05/7.637: 1.1/7.823: 1.2/8.136: 1.3/8.399: 1.4/8.626: 1.5/8.858: 1.6/9.098: 1.65/9.218: 1.7/9.478: 1.8/9.605. The calculations were done considering the following equilibria:

$$H_2L^{2-} \overset{pK_3}{\rightleftharpoons} HL^{3-} \overset{pK_4}{\rightleftharpoons} L^{4-}$$

$$Tl^+ + H_2L^{2-} \rightleftharpoons TlHL^{2-} \rightleftharpoons TlL^{3-}$$

and inserting for pK_3 6.12 and pK_4 12.3.

New calculations show that in the solutions at lower pH, between 5 and 8, also $TlHL^{2-}$ is formed, being its maximal concentration always lower than 10% of the total amount of the metal ion. The values given in the table are calculated using differents titration curves. As found by K. and T. Tl^+ forms with CyDTA also an hydrogen complex $TlHL^{2-}$, with a limited pH range of existence (pK of $TlHL^{2-}=7.32$).

References

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TABLE 1. STABILITY CONSTANTS OF SOME Tl(I) COMPLEXES[a]

		$\log \frac{[ML]}{[M][L]}$	$\log \frac{[MHL]}{[M][HL]}$	pK of MHL	Ionic medium
DTPA	K. and T.	5.45	4.24	8.8	$I=0.4$ ($NaClO_4$)
	A. and B.	5.97±0.05	4.2±0.1	8.8±0.1	$I=0.1$ (KNO_3)
CyDTA	K. and T.	3.85	3.71	11.29	$I=0.3$ ($NaClO_4$)
	A. and B.	6.7±0.05	1.7±0.2	7.3±0.2	$I=0.1$ (KNO_3)

a) Unit of concentration used is mol dm^{-3}.