Electrophoretic Determination of Stability Constants of Some Mixed Complexes of Th(IV), Cr(III) and Al(III)

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The study of binary complexes of metals Th(IV) Cr(III) & Al(III) with NTA and valine was carried out using electrophoresis. The stability constants of the complexes, metal-nitrilotriacetate-valinate have also been found. The log K values are 6.65, 5.65 and 5.25 for Th(IV), Cr(III) and Al(III) complexes respectively at μ = 0.1 and temperature 35°C.

Publication from our laboratories described a new method for study of mixed complexes [1]. The present work is an extension of the technique and reports our observation on the mixed system viz. Th (IV)/Cr(III)/Al(III)-nitrilotriacetate-valinate.

EXPERIMENTAL

The instrument and method are as given in ref. 1.

Chemicals

Th(IV), Cr(III) and Al(III) perchlorates were prepared via carbonates and solutions were standardized w.r to the metal. Final concentration was kept at 5.0×10^{-3} M.

1-(2-Pyridylazo)-2-naphthol (PAN), 0.1% (w/v) in ethanol was used for detecting the Th(IV) and Cr(III) ions. Aluminon-ammonium acetate mixture in water was used for detecting the Al(III) ion. Glucose was detected by spraying with silver nitrate in acetone and then with 2% ethanolic sodium hydroxide.

Stock solutions of 9.0 M perchloric acid, 2.0 M sodium hydroxide, 0.5 M valine, and 0.01 M nitrilotriacetic acid (NTA) were prepared and standardized.

Procedure

For Binary Complexes

The background electrolyte was 0.1 M $HClO_4$, and 1×10^{-2} M valine or 1.0×10^{-3} M NTA. The mobility was determined at different pH values as described in ref. [1].

For Ternary Complexes

The background electrolyte consisting of 0.1 M $NaClO_4$, 1.0×10^{-3} M NTA, and varying amounts of valine. The solution was maintained at pH 8.5 by addition of $NaClO_4$. Mobility of different metals were determined at pH 8.5 as a function of valine concentration. A plot of mobility against log [valine] was made.

RESULTS AND DISCUSSION

Metal-valinate Binary Systems

The plot of overall electrophoretic mobility of metal spot against pH gives a curve with a number of plateaus shown in Figure 1.

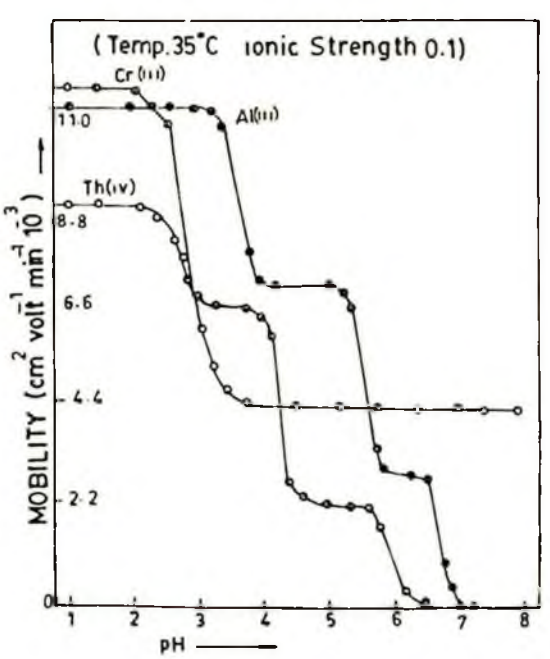


Fig.1 Mobility Curve [M-Valine] System

Thorium is known to form cationic complex only. Cr(III) and Al(III) form 3 complexes step wise, the highest complex being electroneutral in nature and so compostion of this complexes should be 1:3.

The lower complexes should consequently be 1:1 and 1:2 with respect to metal and ligand.

The concentration of valinate anion is calculated at the given pH value using the dissociation constants of the amino acid [2] [log K_1 = 2.20 log K_2 = 9.59]. The stability constants of the complex metal ion are calculated as described earlier. The calculated values are given in Table 1.

TABLB 1

STABILITY CONSTANTS OF Th(IV), Cr(III) AND Al (III) COMPLEXES

μ = 0.1 Temperature 35°

Valiate ion L^- NTA anion A^{-3}

Metal ion	Complex	Log K values of Present study	Literature
Th(IV)	ML	8.50	8.58 [7]
	ML_2	-	-
	ML_3	-	-
	MA	11.64	8.6 [6] 13.3 [7], 8.6 [7] 16.9 [8], 13.3 [8]
	MAL	6.65	--
Cr(III)	ML	8.35	8.30 [7]
	ML_2	6.74	6.40 [7]
	ML_3	5.10	6.10 [7]
	MA	11.58	5.87 [6], 8.74 [6] 11.81 [6], 6.23 [6] 8.45 [7]
	MAL	5.65	-
Al(III)	ML	7.69	-
	ML_2	6.00	-
	ML_3	4.80	-
	MA	9.13	11.4 [7], 5.09 [7] 5.35 [7], 8.28 [7] 8.81 [7] 11.37 [8], 9.5 [8]
	ML	5.25	--

Metal-NTA-Binary Systems

The observation on overall mobility of metal spots in presence of NTA at different pH values are represented in Figure 2.

As it is evident from figure that with all three metal ions two plateaus are formed. The mobility of last plateau in case of Th(IV) is positive, while it is zero in case of Cr(III) and Al(III), showing cationic nature of Th(IV) - complex and electrically neutral nature of Cr(III)/Al(III)-NTA complex. Hence only one NTA anion (NTA^{3-}) is assumed to combine with metal ions to give 1:1

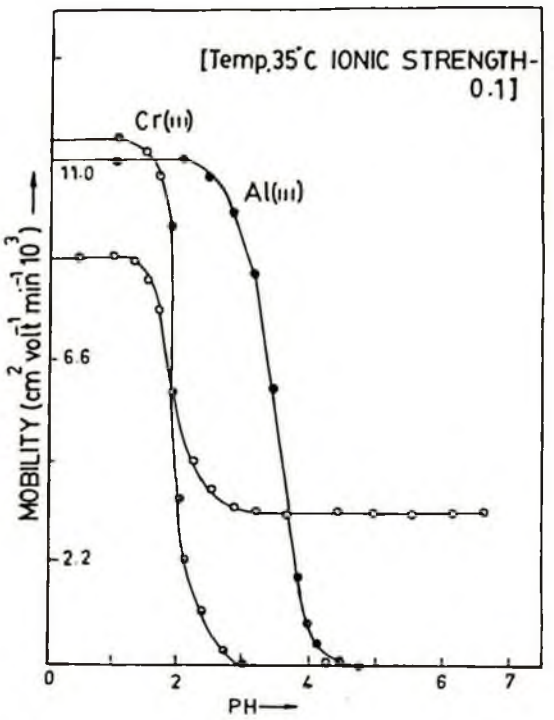


Fig.2 Mobility Curve [M-NTA] System

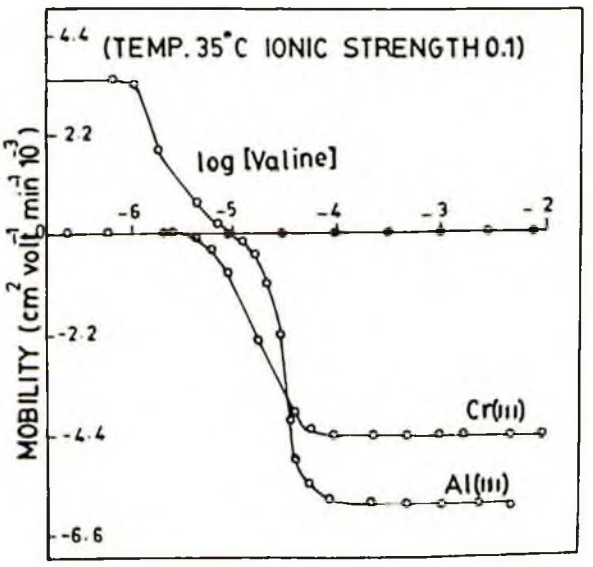


Fig.3 Mobility Curve [M-NTA-Valine] System

complex which is in conformity with finding of others [3,4,5]. The stability constants of complex with NTA are calculated in a manner described in preceding paragraph. The calculated values are given in Table 1.

Metal-nitrilotriacetate-valinate ternary systems

Study of this system has been done at pH 8.5 for the same reason as given in the preceeding paper.

The plot of mobility against logarithm of concentration of added valine gives a curve (Figure 3) containing two plateaus. The mobility in the range of first plateau corresponds to mobilities of 1:1 M-NTA complexes as also observed in the study of M-NTA complexes. It is inferred that the complex moiety formed in the region of last plateau is due to co-ordination of valinate anion to 1:1 M-NTA moiety resulting in the formation of 1:1:1 mixed complex (M-NTA-valinate).

The stability constants are calculated. All these calculated values of K's are given in Table 1.

In literature no mention has been made about valinate complexes except that of Cr(III). The literature values are quite in agreement with our values for K_1 , K_2 and K_3 of Cr(III) complexes.

The precision of the method is limited to that of paper electrophoresis i.e. the order of uncertainity is 1 %. Obviously this method cannot be intended to replace more reliable methods, but it certainly provides a new technique worthdeveloping, and perhaps with future refinements the method may prove valuable.

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