Short communication

# Electrophoretic studies on mixed complexes
# Metal–methionine–penicillamine system

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## Abstract

Solution equilibria of binary [Fe(III)/Cr(III)–methionine] and mixed [Fe(III)/Cr(III)–methionine–penicillamine] complex systems are investigated by paper electrophoresis. Formation of 1:1:1 mixed ligand complexes is inferred and stability of these complexes were determined at 35°C and ionic strength=0.1 $M$/l. The stability constants of the complexes, [Fe(III)–methionine–penicillamine] and [Cr(III)–methionine–penicillamine] were found to be 6.80±0.09 and 4.60±0.16 (log $K$ values), respectively. © 1998 Elsevier Science B.V.

## 1. Introduction

Paper electrophoresis (PE) is being increasingly used for studies of metal complexes. Hurnick [1] studied tartrate complexes of Fe(II), Ce(II) and Ni(II) in aqueous media and determined stability constants. Soni and Bertusek [2] investigated Mo(II) complexes of *o*-diphenol and compared the stability constants with those obtained from spectrophotometric measurements. In the majority of the investigations reported, the studies are largely qualitative and did not throw light either on the nature of species or on their stabilities. Communications [3–5] from our laboratory described a new method for the study of mixed complexes in which nitrilotriacetate and amino acids act as primary and secondary ligand, respectively. Recently work reported [6,7] on mixed complexes in which sulphur containing amino acids act as primary and secondary ligand. The present work is an extension of this technique and reports observations on mixed systems, viz. $Fe^{3+}$/$Cr^{3+}$–methionine–penicillamine.

## 2. Experimental

Electrophoresis equipment, method, pH measurement and temperature control were as described earlier [3–7]. Solutions of perchlorates of $Fe^{3+}$ and $Cr^{3+}$ and also glucose (5 m$M$ in each case) were prepared as described earlier [3–7]. Stock solutions of 5.0 $M$ perchloric acid (SDS, AnalaR), 2.0 $M$ sodium hydroxide (AnalaR grade), 0.5 $M$ methionine and 0.5 $M$ penicillamine (BDH, Poole, UK) were prepared. Each solution was standardized using the appropriate method. Metal spots after electrophoresis were detected on paper using a 0.5% solution of potassium ferrocyanide (BDH) for $Fe^{3+}$ and 0.1%, 1-(2-pyridylazo)-2-napthol (PAN) (Merck, Darm-

stadt, Germany) in ethanol for $Cr^{3+}$. Glucose was detected by spraying with silver nitrate in acetone and then with 2% ethanolic sodium hydroxide.

## 3. Results and discussion

### 3.1. Metal–methionine binary system

The plot of overall electrophoretic mobility of metal spot against pH gives a curve with a number of plateaus shown in Fig. 1. Iron(III) and chromium(III) form two complexes step wise, both complexes being cationic in nature and so composition of these complexes should be 1:1 and 1:2. The concentration of the methionine anion is calculated at the given pH value using the protonation constants of the methionine ($pK_1 = 2.25$, $pK_2 = 9.00$) [8,9]. The stability constants of the binary complexes

Table 1
Stability constants of binary and mixed complexes of Fe(III)and Cr(III)

| Metal ions | Complexes | Log $K$ values |
|---|---|---|
| Fe(III) | ML | $7.95 \pm 0.04$ |
| | ML$_2$ | $12.65 \pm 0.07$ |
| | MLL$'$ | $6.80 \pm 0.09$ |
| Cr(III) | ML | $7.52 \pm 0.06$ |
| | ML$_2$ | $12.42 \pm 0.12$ |
| | MLL$'$ | $4.60 \pm 0.16$ |

Ionic strength=0.1 $M$; temperature=35°C; methionine anion= $[(CH_3)_2C(SCH_3)CH(NH_2)COO^-]$; penicillamine anion= $[(CH_3)_2C(S^-)CH(NH_2)COO^-]$.
M=Metal cations; L=primary ligand (methionine); L$'$=secondary ligand (penicillamine).

were calculated as described earlier [3–7]. The calculated values are given in Table 1.

As is evident from Table 1, Fe(III) has the stronger complexation tendency with chelating methionine. The higher stability of the Fe(III) com-
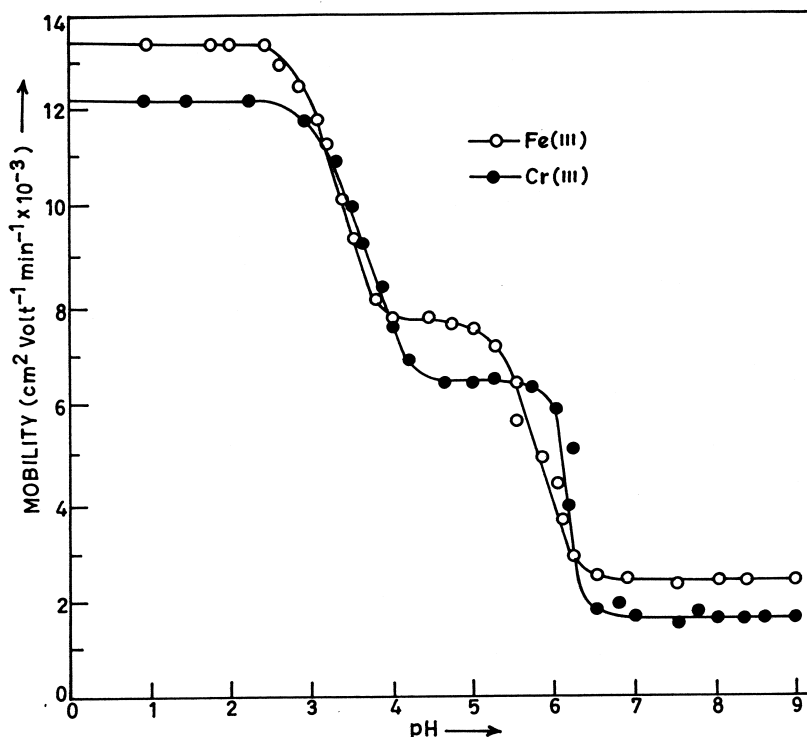


Fig. 1. Mobility curves for the M(III)–methionine systems. ○=Fe(III)–methionine; ●=Cr(III)–methionine. Background electrolytes: 0.1 $M$ perchloric acid and 0.01 $M$ methionine. The paper strips were spotted with 0.1 μl of sample solution and glucose (for making osmotic correction).

plex compared to that of Cr(III) may be ascribed to greater affinity for the oxygen donor ligands.

## 3.2. Metal–methionine–penicillamine mixed system

This system was studied at pH 8.5 for the same reason as given earlier [3–7]. The plot of mobility vs. log [penicillamine] gives the curve with two plateaus (Fig. 2). The mobility in the range of the first plateau corresponds to that of a 1:1 cation–methionine complex. The mobility of the second plateau does not agree with either of the methionine cationic complexes. The neutral value of mobility of the second plateau indicates the formation of uncharged complex. It is inferred that the complex moiety formed in the region of the second plateau is due to coordination of penicillamine anion to 1:1 cation methionine moiety resulting in 1:1:1 mixed complex (metal–methionine–penicillamine). The curves show the transformation of a simple complex to mixed complex. The concentration of penicillamine anion at pH 8.5 was calculated. $K_3$ is obviously equal to $1/[L^{2-}]$. All the values of $K_3$ (stability constants of mixed complexes) are given in Table 1.

It is clear from Table 1 that Fe(III) shows superior coordinating tendency in mixed complexes with

methionine and penicillamine as primary and secondary ligand, respectively.

Comparison of the log stability constants $K^{M}_{1, ML}$, $K^{M}_{2,ML2}$ and $K^{ML}_{3MLL'}$ showed that they remain the same in binary and mixed complexes, but the value is lower in mixed complexes. It is therefore inferred that the coordinating tendency of a ligand decreases with higher state of aggregation. In other words, the metal progressively lessens its tendency of linkage with a ligand on progressive filling of vacant orbitals. This conclusion is of universal validity as evident in chemical literature [10–12].

The precision of the method is limited to PE. However, uncertainty in the result is ±5%. No doubt it cannot replace the most reliable methods even though it is a new approach worth developing.
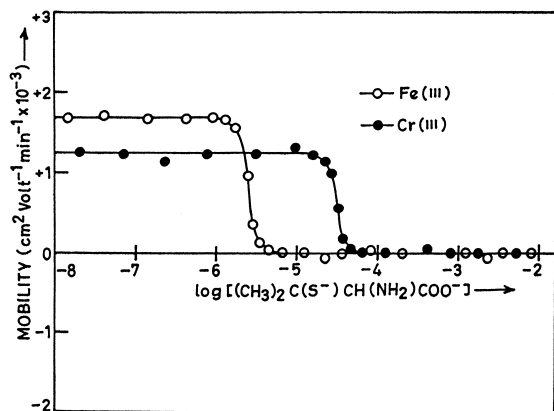
## Acknowledgements

Fig. 2. Mobility curves for M(III)–methionine–penicillamine systems. ○=Fe(III)–methionine–penicillamine; ●=Cr(III)–methionine–penicillamine. Background electrolytes: 0.1 *M* perchloric acid, 0.01 *M* methionine and 0.01 *M* penicillamine. pH: 8.5 (maintained by addition of sodium hydroxide). The paper strips were spotted with 0.1 μl of sample solution and glucose (for making osmotic correction).

## References

[1] B. Hurnick, Rocz. Chem. 39 (1965) 137.
[2] R.N. Soni, M. Bertusek, J. Inorg. Nucl. Chem. 33 (1971) 2557.
[3] B.B. Tewari, R.K.P. Singh, K.L. Yadava, J. Chromatogr. 542 (1991) 537.
[4] B.B. Tewari, S. Singh, R.K.P. Singh, K.L. Yadava, Bull. Soc. Chim. Fr. 127 (1990) 507.
[5] B.B. Tewari, A.K. Singh, V. Kumar, K.L. Yadava, Proc. Nat. Acad. Sci. India 61 (1991) 13.
[6] B.B. Tewari, R.K.P. Singh, K.L. Yadava, J. Electrochem. Soc., India 41 (1992) 203.
[7] B.B. Tewari, R. Chander, R.K.P. Singh, V. Kumar, K.L. Yadava, Proc. Nat. Acad. Sci., India 62 (1992) 521.
[8] D.D. Perrin, Stability Constants of Metal Ion Complexes, Part B (Organic Ligand), Pergamon Press, Oxford, 1979.
[9] A.E. Martell, R.M. Smith, Critical Stability Constants, Vol. 1 (Amino Acids), Plenum Press, New York, 1977.
[10] J.D. Joshi, Indian J. Chem. 21 (1982) 446.
[11] J.D. Joshi, P.K. Bhattacharya, J. Indian Chem. Soc. 57 (1980) 336.
[12] J.D. Joshi, P.K. Bhattacharya, J. Indian Chem. Soc. 50 (1973) 344.