

**INFLUENCE OF TEMPERATURE AND IONIC STRENGTH ON THE
COMPLEXATION PARAMETERS OF THE SYSTEM CU(II)-FULVIC ACID**

M. Teresa S. D. Vasconcelos, Adélio A. S. C. Machado and Francisco Rey L. *

Departamento de Química, Faculdade de Ciências, P4000 Porto

*Departamento de Química Pura e Aplicada, Universidade de Vigo, E36208 Espanha

Ionic strength and temperature play an important role in complexation processes, specially when the ligand contains a large number of complexation sites, like for instance in fulvic acids (H_nFA). Although the complexation of fulvic acids with metals has deserved much attention, as far as we know no systematic study of the influence of those two variables on the complexation parameters of this type of systems has been described. As an extension of previous work in the field¹⁻³, we developed such a study for the Cu(II)- H_nFA system, whose results are reported here. Values of the the mean equivalent weight (EW) of the ligand and of the stoichiometric stability constants of its 1:1 complexes with Cu(II) at ionic strengths in the range 0.01-0.1 M and temperatures between 288 and 303 K, as well as thermodynamic parameters, are presented.

EXPERIMENTAL

A sample of H_nFA was isolated by the procedure recommended by the IHSS⁴ from a portuguese forest soil collected at Ermesinde (near Oporto).

Deionised water with resistivity > 4 MΩ cm was used. All reagents were p. a. or of similar grade and were used without further purification. Cu(II) solutions were prepared from a $Cu(NO_3)_2$ standard solution (Radiometer S-3546). $NaClO_4$ was used to adjust the ionic strength.

A Radiometer Selectrode F-3012 activated⁵ with a mixture of Ag_2S and CuS and a Philips GAH110 glass electrode were used. An Orion 90-02-00 double-junction reference electrode (outer solution KNO_3 0.1 M) and an Orion 811 pHmeter (\pm 0.1 mV) with an Orion 605 manual electrode switch were used to complete the potentiometric assembly.

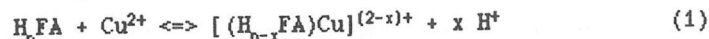
Electrodes were calibrated (potential vs. concentration) before each experiment by titrations of background electrolyte solution (Cu(II) electrode: 20.0 mL of solution with a 5×10^{-3} M Cu(II) solution, pCu range 4.6 to 3.6; glass electrode: 50.0 mL of solution with a HCl standard solution, pH range

2.9 to 3.3).

pH and pCu potentiometric titrations of 20.0 mL of a 100.0 mg/L H_nFA solution with Cu(II) in the range 10⁻⁵ - 1.2 x 10⁻⁴ M at temperatures and ionic strengths indicated in Table 1, were made under nitrogen as before²⁻³. The pH varied less than 1.3 units in the range 5.5 to 7.3.

CALCULATIONS

For a 1:1 complexation reaction



the following expression (where t and f stand for total and free and {H_nFA}_t is expressed in g/L) can be obtained⁶

$$\frac{\{H_nFA\}_t}{(|Cu^{2+}|_t - |Cu^{2+}|_f)} = EW + \frac{EW}{\beta_1} |H^+|^x / |Cu^{2+}|_f \quad (2)$$

At constant pH and for metal to ligand ratios such as 1:1 complexation predominates, a plot of {H_nFA}_t / (|Cu²⁺|_t - |Cu²⁺|_f) vs. 1/|Cu²⁺|_f is linear. EW can be obtained from the intercept and the conditional stability constant β₁' = β₁ / |H⁺|^x from the slope and the determined EW value. If experiments are repeated at several constant pH values, the stoichiometric parameter x (eq.1), and β₁ can be obtained⁶ from a plot of log β₁' vs. pH:

$$\log \beta_1' = \log \beta_1 + x \text{ pH} \quad (3)$$

Alternatively, we have recently shown² that EW and β₁ can be obtained by an iterative calculation from experiments without fixing the pH to constant values, which can be performed more easily. For this purpose, from the plot of {H_nFA}_t / (|Cu²⁺|_t - |Cu²⁺|_f) vs. |H⁺|^x / |Cu²⁺|_f with a value for x near the expected, a new value for x is obtained from the plot of

$$\log \{ [(1/n)-1] |Cu^{2+}|_f \} = - \log \beta_1 - x \text{ pH} \quad (4)$$

where

$$n = (|Cu^{2+}|_t - |Cu^{2+}|_f) / \{H_nFA\}_t \quad (5)$$

Table 1 - Complexation Parameters

I(M)	x				10 ³ EW (g/mol)				β ₁			
	288	293	298	303	288	293	298	303	288	293	298	303
0.00*									689	56.1	4.95	1.38
0.01	0.79	0.91	1.05	1.13	1.82	1.46	1.48	1.40	103	10.7	2.14	0.62
0.02	0.79	0.93	1.06	1.12	1.70	1.37	1.25	1.20	79	10.0	1.04	0.53
0.04	0.79	0.93	1.07	1.12	1.65	1.34	1.27	1.14	18	4.6	0.96	0.39
0.06	0.82	0.92	1.06	1.12	1.49	1.16	1.19	1.10	10	3.0	0.52	0.25
0.10	ND	0.96	1.06	1.12	ND	1.09	1.14	1.07	ND	0.6	0.25	0.14

*) Extrapolated values (see text)

ND) Not determined (stabilization time was > 2 h).

This new value of x is used in another plot of the first type and so on until the difference between successive x values is less than 0.01. From the last x value, β₁ is calculated by standard procedures⁶.

RESULTS AND DISCUSSION

Results for the complexation parameters (x, EW and β₁) are presented in Table 1. Values of β₁ for I = 0 were obtained by extrapolating log β₁ vs. √I.

Values in Table 1 show that the stoichiometric parameter x is practically not influenced by ionic strength but increases markedly with temperature. As β₁ decreases with temperature, this suggests that the acid-base constant (ionization constant) of the ligand increases with the temperature, a point still to be studied.

The mean equivalent weight, EW, decreases both with temperature and ionic strength. This suggests structural modifications in the ligand induced by counterions and temperature, as already shown in previous work¹ with respect to ionic strength. As EW depends on the metal ion which coordinates the fulvic acid, another point to be investigated is how the nature of the metal ion affects the temperature and ionic strength dependence of the equivalent weight

Table 2 - Thermodynamic Parameters

I(M)	ΔH (kJ/mol)	ΔS (J/mol K)
0.01	-246	-819
0.02	-251	-839
0.04	-189	-634
0.06	-187	-629
0.10	-105	-363

of the ligand.

The stability constant β_1 follows the same pattern as EW, but the relative ranges of variation are much larger. The decrease of β_1 with increasing ionic strength follows roughly a linear $\log \beta_1$ vs. \sqrt{I} relationship.

Values of the thermodynamic parameters ΔH and ΔS were obtained from the values of β_1 at different temperatures for each value of ionic strength (Table 2). The large negative values for ΔS suggest that complexation is accompanied by an ordering arrangement of the fulvic acid molecule. Besides both $|\Delta H|$ and $|\Delta S|$ decrease markedly with increasing ionic strength, showing that at high ionic strength Cu(II)-H_nFA interactions are much weaker than in conditions found in natural waters. The results also show that the extent of such interactions depends very much on the water temperature in the environmental temperature range.

Acknowledgements: F.Rey acknowledges a grant for residence in Oporto to the University of Vigo (Spain). Financial support was received from INIC through Research Line 4A of CIQ(UP). We thank A.J.T.Sousa for routine work.

1. Vasconcelos, Santos and Machado, *Sci.Tot. Environ*, **81/2**, 489 (1989)
2. Vasconcelos, Machado, Santos and Rey, XI Reunion del Grupo de Electroquímica de la RSEQ, Valladolid, 1989, Comunicação PT3.20
3. Vasconcelos, Machado and Rey, Resumos das Comunicações ao IV Encontro Luso-Galego de Química, Porto, 1990, p.109, Comunicação 04.3
4. Thurman, 'Isolation of soil and aquatic humic substances', em Frimmel and Christaman (eds.), 'Humic substances and their role in the environment', Wiley, 1988, p.31
5. Hansen, Lamm and Ruzicka, *Anal.Chim.Acta*, **59**, 403 (1972)
6. Brady and Pagenkopf, *Can.J.Chem.*, **56**, 2331 (1978)

CONDUCTIVITY STUDIES OF A NOVEL POLYMER ELECTROLYTE BASED ON EUROPIUM TRIFLUOROMETHANESULPHONATE

Michael Smith, Carlos Silva

Centro de Química Pura e Aplicada da Universidade do Minho,
Av. João XXI, 4700 Braga, Portugal.

Summary

In this article conductivity results obtained with a new member of the class of polymer electrolytes are presented. The electrolyte, prepared from europium (III) trifluoromethanesulphonate and a poly(ethylene oxide) host polymer, shows ionic conductivity levels comparable with divalent and trivalent systems previously reported.

Introduction

During the last decade a remarkable number of papers have been published describing the preparation and properties of polymer electrolytes based on monovalent cations with several different anions in a variety of host polymers [1]. The most obvious application of these materials, and until recently the principle motivation for the continuing research effort in this field, is in electrochemical power sources. Already several laboratories have produced prototype cells [2-5] and reported very encouraging results.

More recently attention has turned to the investigation of the properties of divalent [6-8] and trivalent [9-12] salts which form complexes with the donor ether oxygen atoms present in the extended macromolecular chains of poly(ethylene oxide), PEO. Preliminary results from studies of these materials suggest that the range of applications may be significantly greater than that of monovalent electrolytes. Devices which have been proposed as possible