

The construction of the model for the complexes indicates that the monomeric structure involves much steric hindrance as the ligand molecule has to attach itself to the one and the same metal ion through all its coordinating sites. The low solubility of the complexes in the common organic solvents may be due to an extended polymeric chain structure.

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POLAROGRAPHIC STUDY OF BIOLOGICALLY IMPORTANT COMPLEXES : Cd(II) AND Zn(II) COMPLEXES WITH CREATININE

S. W. RAJBHOJ* AND D. G. DHULEY

Department of Chemistry, Marathwada University, Aurangabad, Maharashtra,

ABSTRACT

Complexation of creatinine with cadmium and zinc has been studied in aqueous medium at $25 \pm 0.5^\circ \text{C}$. Creatinine formed three complexes with Cd (II) with their respective stability constants : $\log \beta_1 = 1.48 \pm 0.025$, $\log \beta_2 = 1.60 \pm 0.02$ and $\log \beta_3 = 2.07 \pm 0.035$. Two complex species were observed with Zn (II) with their respective stability constants : $\log \beta_1 = 0.60$ and $\log \beta_2 = 2.14$ (approx.). Zn(II)-creatinine system was examined by the method of Ringbom and Eriksson.

INTRODUCTION

CREATININE, an anhydride of creatine, represents a waste product of creatine metabolism in the body. Studies on the binding of metal ions with creatinine are of topical interest since they may be used as models for the study of metal-creatine interactions.

Literature survey revealed that there is no reported study on the polarographic determination of the nature and stability of metal complexes of creatinine except that of Pleticha's work on creatinine complexes with the iron group metals¹. This paper deals with the evaluation of the stability constants of Cd(II)-creatinine and Zn(II)-creatinine complexes.

EXPERIMENTAL

All chemicals used were of reagent grade. Sodium nitrate was used to maintain ionic strength constant at 1.0 M. All solutions were prepared in doubly distilled water. The dropping mercury electrode had the following characteristics:

$$t = 3.21 \text{ sec in } 0.1 \text{ M. NaNO}_3 \text{ (open circuit)}$$
$$\text{and}$$
$$m = 2.18 \text{ mg. sec.}^{-1}.$$

Measurements were made on Cambridge automatic recording polarograph. The half-wave potentials were obtained from the log-plots. Deoxygenation of the solutions to be polarographed was achieved by nitrogen gas. A saturated calomel electrode (SCE) was used as a reference electrode.

RESULTS AND DISCUSSION

Cd(II)-Creatinine System

A series of solutions of 1m M Cd(II) with various amounts of creatinine (0.08 to 0.40 M) and the requisite

* Chemistry Department, Milind College of Science, Aurangabad.

Address for Correspondence : Dr. D. G. Dhuley, Department of Chemistry, Marathwada University, Aurangabad, Maharashtra.

amount of supporting electrolyte were polarographed at $25 \pm 0.5^\circ \text{C}$. Maximum suppressor was not needed. Half-wave potentials and reversibility of the current-voltage curves were obtained from the plots of

$$-E_d, e. \text{ vs. } \log i/(id - i).$$

A plot of $-E_d$ vs. $\log C_L$ revealed the existence of three complexes. DeFord and Hume's method² was, therefore, applied to evaluate the stability constants (Fig. 1) of these complexes which are given below:

$\log \beta_1 = 1.48 \pm 0.025$, $\log \beta_2 = 1.60 \pm 0.02$ and $\log \beta_3 = 2.70 \pm 0.035$.

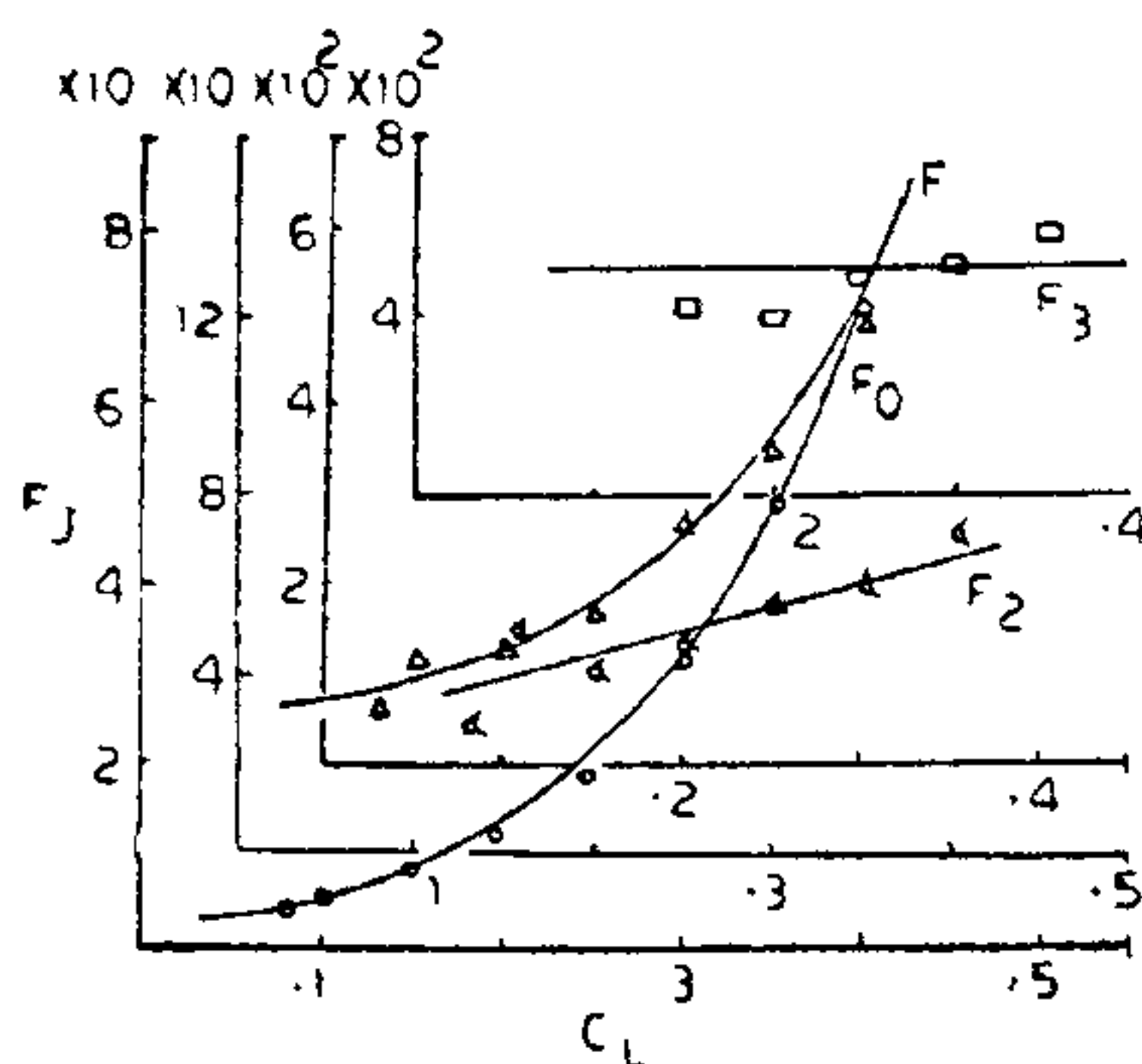


FIG. 1. Plots of F_j vs. C_L .

Zn(II)-Creatinine System:

The system was investigated by "indicator ion" method³. Cd(II), reducing at a potential more positive than that of Zn(II), was chosen as the indicator ion. As the half-wave potential for Cd(II) in presence of creatinine and at ionic strength of 1.0 M was required for comparison purposes under the present experimental conditions, to determine the shift in the presence of Zn(II), the half-wave potentials of Cd(II) in presence of different concentrations of creatinine were taken from the data of Cd(II)-Creatinine system.

These half-wave potentials are represented graphically in Fig. 2(a). The reversibility of the electrode reaction and the half-wave potentials were determined from the log-plots. The concentration of free ligand was taken to be the same as the total creatinine concentration, as Cd(II) formed rather weak complexes.

Polarograms of solutions containing 1m M Cd (II) and 0.14 M zinc were taken at different concentrations of creatinine. When zinc was added to a solution containing cadmium and creatinine, the half-wave potential of Cd (II) shifted to more positive potentials due to the decrease in free ligand concentrations as a result of the formation of zinc complexes. This is graphically represented in Fig. 2 (b).

The half-wave potentials were read from the smooth curve to obviate any experimental error in the individual measurements and are set out in Table I.

TABLE I
Free creatinine and \bar{n} values for Zn (II)-creatinine system

C_L M	$-E_d$ vs. S.C.E.	[L] M	\bar{n} exptl.
Zn(II) = 0.14 M			
0.025	0.601	0.010	0.11
0.040	0.603	0.020	0.13
0.050	0.603	0.025	0.18
0.070	0.605	0.030	0.28
0.100	0.607	0.046	0.43
0.125	0.609	0.050	0.53
0.150	0.610	0.055	0.68
0.175	0.612	0.070	0.75
0.200	0.613	0.075	0.89
0.225	0.614	0.080	1.04
0.250	0.615	0.085	1.18
0.275	0.616	0.090	1.32
0.300	0.616	0.090	1.50
Zn(II) = 0.22 M			
0.05	0.602	0.020	0.13
0.09	0.604	0.030	0.27
0.11	0.606	0.035	0.34
0.15	0.608	0.040	0.50
0.17	0.608	0.045	0.57
0.19	0.609	0.050	0.64
0.21	0.610	0.055	0.70
0.25	0.611	0.070	0.82
0.33	0.612	0.074	1.16

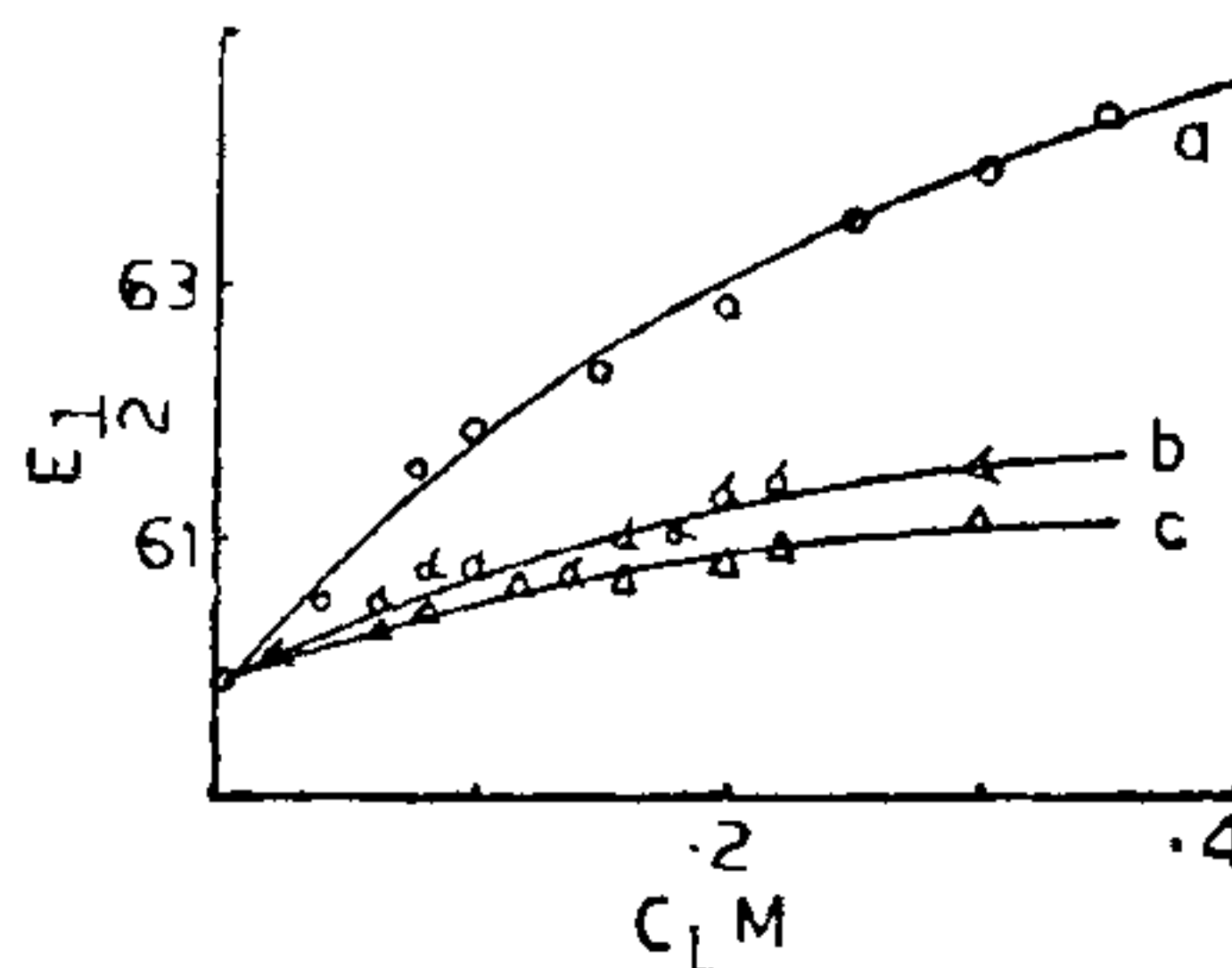


FIG. 2. Plot of $-E_d$ vs. C_L for Zn(II)-creatinine system; a—Cd(II), b—Cd(II) + 0.14 M Zn(II), c—0.22 M Zn(II).

The concentration of free ligand was calculated from these half-wave potentials using a plot of E_d vs. concentration of creatinine for Cd (II) by following the usual procedure (Fig. 2). These values are presented in Table I. The metal-ligand formation number \bar{n} is defined as:

$$\left(\frac{C_L - [L]}{C_{Zn}} \right)$$

Where C_L is initial concentration of creatinine, $[L]$ is the free ligand concentration and C_{Zn} is the amount

of zinc added. The values of \bar{n} thus calculated are plotted against [L].

TABLE II
Values for Rossotti Plot

[L] M	\bar{n} exptl.	\bar{n} (Calcd.)	$\frac{\bar{n}}{(1 - \bar{n}) [L]}$	$\frac{(2 - \bar{n})}{(1 - \bar{n})} [L]$
0.030	.26	.29	11.71	.070
.034	.33	.35	14.49	.085
.036	.37	.38	16.31	.093
.038	.40	.41	17.54	.101
.040	.43	.43	18.86	.110
.048	.54	.55	24.46	.152
.054	.62	.63	30.21	.196
.060	.70	.71	38.89	.260
.066	.74	.79	43.12	.320

These results were further confirmed by using a different concentration of zinc. Polarograms of solutions containing 1 mM Cd(II) and 0.22 M Zn(II) were taken at different concentrations of creatinine. The results are given in Table I and are represented graphically at *c* in Fig. 2. \bar{n} values calculated in the manner described above are also plotted with the previous set

of \bar{n} values. There is an excellent agreement between the values obtained for two concentrations of zinc. The values of \bar{n} obtained from the smooth curve of \bar{n} vs. [L] are solved for the overall stability constants by the method of Rossotti and Rossotti⁴ (Table II). The existence of two complexes was revealed from the Rossotti plot. The stability constants are found to be: $\log \beta_1 = 0.60$ and $\log \beta_2 = 2.14$ (Approx.).

By using these β values \bar{n} values were calculated from Rossotti's equation. The calculated \bar{n} values are presented along with experimental values in Table II. The agreement between two sets of \bar{n} values is fairly satisfactory.

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THE KIRLIAN PHANTOM LEAF

Y. T. THATHACHARI AND S. PUSHPA

Bio-Medical Engineering Division, Indian Institute of Technology, Madras 600 036

ABSTRACT

A leaf from which a small portion was excised was sandwiched between a pair of X-ray films and subject to AC pulses of about 10 KV and 20 KHz. The resultant Kirlian photographs contained, besides the expected images of the intact portion of the leaf, the 'Kirlian Phantom'—a luminous cap roughly of the same size and shape as the cut away portion of the leaf and occupying roughly the same area.

WHAT IS KIRLIAN PHOTOGRAPHY?

DURING the past three or four years there has been a considerable interest in an imaging technique known as Kirlian Photography—named after the Russian inventor Semyonof Kirlian¹⁻⁵. It is also referred to as Corona Discharge Photography and High Voltage Photography. In this technique, the object to be imaged is placed in a high voltage, high frequency electric field. The image is recorded either directly on a photographic film placed in the electric field or through a camera if transparent electrodes are used². The only source of illumination is provided by the electric fields. The Kirlian image resembles the conventional image—as regards the general shape and contours of the object, but, characteristically, is made up of a large number of luminous points or streaks referred to in popular

literature as 'balls of light' or 'aura'. The systematic studies of Professor Tiller and his associates at Stanford University attribute these luminous points to the streamers or coronas from the object points².

The recent interest in Kirlian photography has been triggered by the reports that the Russians have discovered some very strange—almost incredible—phenomena with the aid of this technique and that they have tremendous possibilities. The most talked about Kirlian phenomenon is the 'Phantom Leaf Effect'—the subject of this investigation. In the wake of the initial excitement, the systematic studies in U.S.A., notably by Tiller's group, seem to indicate that some of these popular claims may be rather exaggerated^{2,4,6}.

What kind of information can the Kirlian image of the object studied? Our systematic studies using