

STUDY OF MIXED COMPLEXES BY POLAROGRAPHY— COPPER-GLYCINE- α -ALANINE AND CADMIUM- AMMONIA-PYRIDINE COMPLEXES

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ABSTRACT

The method of DeFord and Hume for the study of complexes by polarography has been extended to the study of mixed complexes of copper-glycine- α -alanine and cadmium-ammonia-pyridine.

INTRODUCTION

ALTHOUGH the presence of mixed complexes in solution was recognised since long, systematic studies were made only recently to explain the formation of mixed complexes and to establish the composition and stability constants. Not much work is reported on the application of polarography to such systems with the exception of the study of cadmium-ethylenediamine-oxalate system by Schaap and McMasters.¹ It was, therefore, decided to investigate the suitability of the polarographic technique for the study of mixed complexes. This paper reports a polarographic study of copper-glycine- α -alanine and cadmium-ammonia-pyridine systems.

EXPERIMENTAL

Current-potential curves were obtained at $30 \pm 0.5^\circ \text{C}$ with a manual polarograph using a saturated calomel electrode (S.C.E.) as reference electrode. A Beckman Expandomatic-SS-2 pH-meter was used for pH measurements. The reported diffusion currents were corrected for residual currents.

Stock solutions of copper sulphate (B.D.H., AR) and cadmium sulphate (E. Merck, Pro Analysis) were estimated by standard methods. Potassium nitrate (E. Merck, Pro Analysis), sodium perchlorate (B.D.H., AR), glycine and α -alanine (B.D.H., L.R.) were used without further purification. Freshly prepared ammonia and pyridine (B.D.H., AR) were standardised by standard titration procedures.

RESULTS AND DISCUSSION

The stability constant of the mixed complex which characterises the equilibrium (charges omitted)



is given by

$$\beta_{ji} = \frac{[MX_jY_i]}{[M][X]^j[Y]^i} \quad (2)$$

The reproporationation or mixing constant, $K_{M(ji)}$, correlates the stability of the mixed complex species to that of the parent complexes and can be defined as the equilibrium constant of the reaction



by

$$K_{M(ji)} = \frac{[MX_jY_i]}{[MX_m]^{j/m} \cdot [MY_m]^{i/m}} \quad (4)$$

$$= \beta_{ji} \cdot \beta_{m0}^{-j/m} \cdot \beta_{0m}^{-i/m} \quad (5)$$

It is obvious that a major contribution to $K_{M(ji)}$ will arise from statistical factors. Hence, Marcus and Elizier² define another parameter called 'the stabilisation constant' which, for ligands of equal denticity, is given by

$$\log K_s = \log K_{M(ji)} - \log \left(\frac{n!}{i!j!} \right) \quad (6)$$

The stabilisation constant, therefore, gives a measure of the extra stability of the mixed complex due to electrostatic forces, geometric forces, solvent effect, etc., in addition to the statistical effect. The values of $K_{M(ji)}$ and K_s can be calculated from eqs. (5) and (6) respectively if the stability constants are known.

The polarographic method of studying the mixed complexes is essentially an extension of the method of DeFord and Hume,³ generally used for the study of complexes. The shift in the half-wave potential due to complex formation is related to a parameter, $F_{00}(X, Y)$, as

$$F_{00}(X, Y) = \text{antilog} \left[0.4343 \cdot \frac{nF}{RT} \{E_{\frac{1}{2}(s)} - E_{\frac{1}{2}(c)}\} + \log \frac{I_s}{I_c} \right] \quad (7)$$

where the subscripts s and c refer to the simple ion and complex ion respectively. This parameter is related to the stability constants of the different species by the expression

$$\begin{aligned}
 F_{00}(X, Y) = & \{1 + \beta_{10} [X] + \beta_{20} [X]^2 + \beta_{30} [X]^3 + \dots + \beta_{m0} [X]^m\} [Y]^0 \\
 & + \{\beta_{01} + \beta_{11} [X] + \beta_{21} [X]^2 + \dots \\
 & + \beta_{(m-1),1} [X]^{(m-1)}\} [Y]^1 + \{\beta_{02} + \beta_{12} [X] + \beta_{22} [X]^2 + \dots \\
 & + \beta_{(m-2),2} [X]^{(m-2)}\} [Y]^2 + \dots \\
 & + \{\beta_{0n} + \beta_{1n} [X] + \beta_{2n} [X]^2 + \dots \\
 & + \beta_{(m-n),n} [X]^{(m-n)}\} [Y]^n + \dots + \beta_{0,m} [Y]^m. \quad (8)
 \end{aligned}$$

This can be written in a simple form as

$$F_{00}(X, Y) = K + L(Y) + M(Y)^2 + N(Y)^3 + \dots \quad (9)$$

The constants K , L , M , etc., obtained either algebraically or graphically, can be solved for the individual stability constants.

COPPER- α -ALANINE-GLYCINE SYSTEM

Copper, with a maximum coordination number of four, forms complexes of the type CuA_2 , CuG_2 or a mixed complex, CuAG . The 'simple' complexes of copper with α -alanine (A) and glycine (G) were first studied from the polarograms of copper obtained at different concentrations of the ligand and pH. The concentration of the free ligand was calculated from the pH of the solution and the pK values of 9.87⁴ and 9.76⁵ for α -alanine and glycine respectively. The reduction was found to be reversible and the stability constants were evaluated from the shift in the half-wave potential (Fig. 1) by the method of DeFord and Hume (*loc. cit.*) as $\log \beta_{20} = 14.67$ and $\log \beta_{02} = 15.00$ for α -alanine and glycine respectively. The stability of the second species was much greater than that of the first in both the cases and hence the terms β_{10} and β_{01} as well as unity could be neglected. The F_{00} function at a fixed concentration of α -alanine can, therefore, be written as

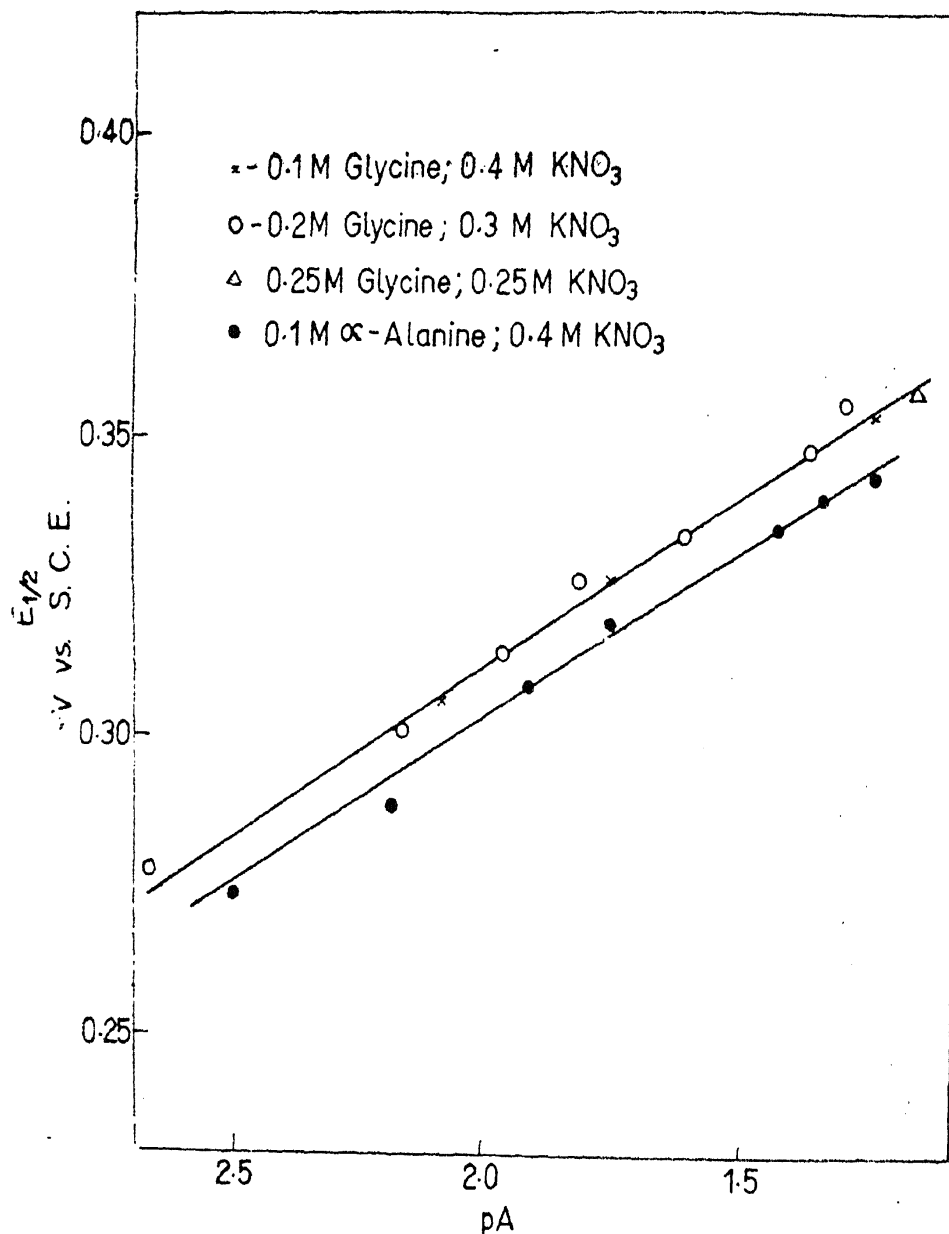
$$F_{00}(A, G) = \beta_{20} [A]^2 + \beta_{11} [A] [G] + \beta_{02} [G]^2. \quad (10)$$

At a constant concentration of glycine, eq. (10) can be expressed as a function of the varying concentration of α -alanine as

$$F_{00}(G, A) = \beta_{02} [G]^2 + \beta_{11} [A] [G] + \beta_{20} [A]^2. \quad (11)$$

Fig.1. COPPER - GLYCINE AND COPPER - α - ALANINE

$E_{1/2}$ vs. pA



Polarograms were obtained at different concentrations of either α -alanine or glycine, keeping the concentration of the other ligand constant. The F_{00} function was calculated from eq. (7) and the stability constants were obtained from eqs. (10) and (11) by a graphical extrapolation method. The data are presented in Tables I and II and Fig. 2 represents the graphical evaluation of the constants. The values of β_{11} from the two sets of data agree well

and there is also good agreement in the values of β_{20} and β_{02} obtained from the mixed complex and 'simple' systems.

TABLE I

Copper-glycine- α -alanine system

Cu = 4×10^{-4} M; Glycine = 0.1 M; pH = 11.4; Glycinate ion = 0.1 M; $\mu = 0.5$ (Potassium nitrate + glycine + α -alanine); $m = 1.51$ mg/sec., $t = 4.0$ sec. (0.5 M KNO₃, open circuit).

Alaninate concentration $\times 10^2$ M	$E_{\frac{1}{2}}$ -V vs. S.C.E.	i_d μ A	F_{00} (A, G) $\times 10^{-13}$	F_{10} (A, G) $\times 10^{-14}$	F_{20} (A, G) $\times 10^{-14}$
0	-0.0190	2.57
1.17	0.3675	2.47	0.75	2.17	..
3.87	0.3725	2.42	1.09	1.52	..
7.74	0.3800	2.41	1.94	1.86	9.6
11.9	0.3855	2.30	3.22	2.29	9.8
15.8	0.3905	2.29	4.56	2.57	9.2
19.8	0.3955	2.30	6.89	3.23	11.0
27.7	0.4010	2.14	11.2	3.86	9.9

$$K = 5.0 \times 10^{12}; \quad L = 1.12 \times 10^{14}; \quad M = 9.9 \times 10^{14}$$

$$\beta_{02} = 5.0 \times 10^{14}$$

$$\beta_{11} = 1.1 \times 10^{15} \quad \log K_M = 0.19$$

$$\beta_{20} = 9.9 \times 10^{14} \quad \log K_s = -0.11$$

Martin and Paris⁶ have studied this system by a pH-titration technique. They report 15.04, 15.01 and 15.18 (sodium perchlorate, $\mu = 0.35$) and 15.11, 15.04 and 15.27 ($\mu = 0.64$) for $\log \beta_{02}$, $\log \beta_{20}$ and $\log \beta_{11}$ respectively, and 0.15 and 0.19 for $\log K_M$ at the two ionic strengths. The values obtained from the present work compare favourably with these values.

CADMIUM-AMMONIA-PYRIDINE SYSTEM

The complexes that are formed in this system are of the composition CdA_iP_j, ($i + j$) varying from 1 to 4. Polarograms of cadmium were obtained

TABLE II

Copper-glycine- α -alanine system

Cu = 4×10^{-4} M; α -alanine = 0.1 M; pH = 9.90; Alaninate ion = 5.23×10^{-2} M; $\mu = 0.5$ (Potassium nitrate + glycine + α -alanine); $m = 1.51$ mg/sec.; $t = 4.0$ sec. (0.5 M KNO₃, open circuit).

Glycinate concentration $\times 10^2$ M	$E_{\frac{1}{2}}$ -V vs. S.C.E.	i_a μ A	F_{00} (A, G) $\times 10^{-12}$	F_{10} (A, G) $\times 10^{-13}$	F_{20} (A, G) $\times 10^{-14}$
0	-0.0190	2.60
0.278	0.3445	2.32	1.36
0.464	0.3445	2.36	1.36
2.274	0.3530	2.31	2.61	5.76	7.3
4.640	0.3605	2.40	4.46	6.82	5.9
9.281	0.3715	2.32	10.6	10.0	6.4
11.03	0.3755	2.30	14.4	11.9	7.1
13.06	0.3780	2.26	18.1	12.8	6.7
14.50	0.3800	2.27	20.6	13.3	6.3
15.78	0.3830	2.30	26.2	15.8	7.4

$$K = 1.3 \times 10^{12}; \quad L = 4.1 \times 10^{13}; \quad M = 6.7 \times 10^{14}$$

$$\beta_{20} = 4.8 \times 10^{14}$$

$$\beta_{11} = 7.8 \times 10^{14}$$

$$\beta_{02} = 6.7 \times 10^{14}$$

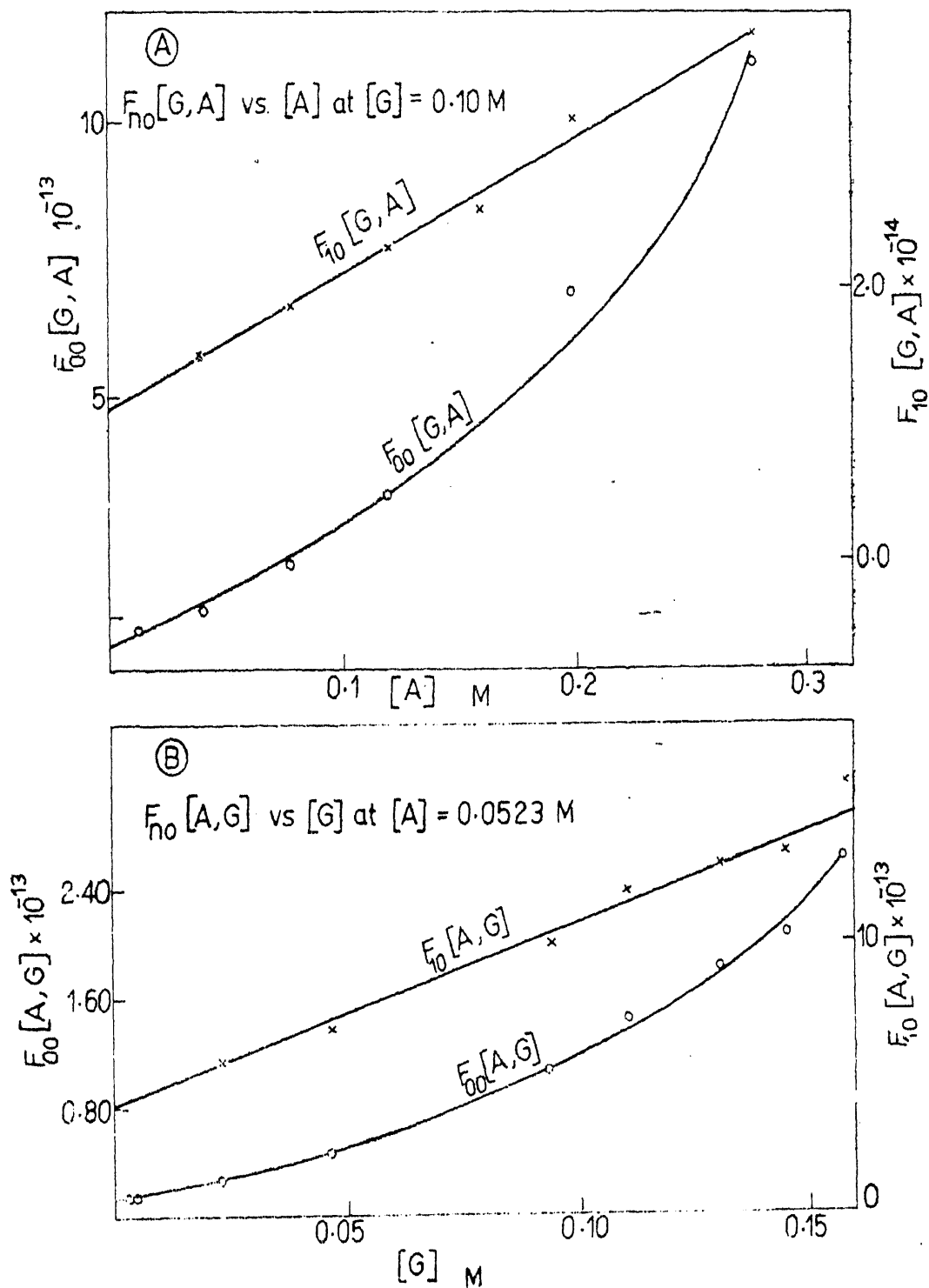
$$\log K_m = 0.14$$

$$\log K_s = -0.16$$

at different concentrations of ammonia varying from 0.04 to 0.74 M. The reduction was found to be reversible. The stability constants of the lower complexes could not be calculated from these data because the higher complexes predominate in solution even at low concentrations of ammonia. It was, however, found that the half-wave potentials calculated from the reported values of the stability constants⁷ agreed well with the present data. The data obtained from the polarograms of cadmium in the presence of pyridine were utilised for the calculation of the stability constants of

cadmium-pyridine complexes (Table III). These values which differed from the literature values^{7, 8} were used in subsequent calculations of the stability constants of the mixed complexes.

Fig.2. COPPER - GLYCINE - α - ALANINE: F_{n0} FUNCTIONS.



At a constant concentration of ammonia, the $F_{00}(A, P)$ function for the mixed complexes of cadmium with ammonia and pyridine can be written as

$$F_{00}(A, P) = K + L [P] + M [P]^2 + N [P]^3 + Q [P]^4 \quad (12)$$

TABLE III

Cadmium-pyridine system

Cd = 4×10^{-4} M; $\mu = 1.0$ (Sodium perchlorate); $m = 1.55$ mg/sec.; $t = 3.8$ sec
(1.0 M NaClO₄, open circuit).

(Py) M	$-\log(\text{Py})$ pA	$E_{1/2}$ $-V$ vs. S.C.E.	i_a μA	Slope mV
0	..	0.5490	2.82	33.0
0.04420	1.35	0.5615	2.49	33.5
0.07368	1.13	0.5650	2.48	32.5
0.2210	0.66	0.5840	2.30	32.0
0.3684	0.43	0.6020	2.23	32.0
0.5894	0.23	0.6170	1.92	32.0
0.8105	0.09	0.6285	1.66	32.0
1.032	-0.01	0.6375	1.50	32.0
1.326	-0.12	0.6500	1.57	32.0
1.842	-0.27	0.6645	1.53	33.0

$\beta_1 = 35; \beta_2 = 155; \beta_3 = 510; \beta_4 = 780$

where

$$\begin{aligned}
 K &= 1 + \beta_{10} [A] + \beta_{20} [A]^2 + \beta_{30} [A]^3 + \beta_{40} [A]^4 \\
 L &= \beta_{01} + \beta_{11} [A] + \beta_{21} [A]^2 + \beta_{31} [A]^3 \\
 M &= \beta_{02} + \beta_{12} [A] + \beta_{22} [A]^2 \\
 N &= \beta_{03} + \beta_{13} [A]
 \end{aligned}
 \tag{13}$$

and

$$Q = \beta_{04}$$

Polarograms of cadmium were obtained at varying concentrations of pyridine, keeping the concentration of ammonia constant (Table IV). The $F_{70}(A, P)$ values, obtained from the smooth curve of the plot of $F_{00}(A, P)$

TABLE IV

Cadmium-ammonia-pyridine system

Cd = 4×10^{-4} M; $\mu = 1.0$ (Sodium perchlorate and ammonium hydroxide); $m = 1.55$ mg/sec.; $t = 3.8$ sec. (1.0 M NaClO₄, open circuit).

(Py) M	$E_{\frac{1}{2}}$ -V vs. S.C.E.	i_a μA	F_{00} (A, P)
$C_{NH_3} = 3.06 \times 10^{-2}$ M			
0	0.5490	2.75	91
0.231	0.6145	1.72	242
0.346	0.6250	2.27	408
0.462	0.6285	2.31	525
0.577	0.6330	2.08	826
0.633	0.6385	2.09	1251
0.808	0.6400	1.82	1612
K = 91; L = 500; M = 830; N = 630; Q = 760			
$C_{NH_3} = 6.11 \times 10^{-2}$ M			
0	0.5490	2.75	558
0.0706	0.6350	2.66	753
0.141	0.6375	2.66	910
0.289	0.6410	2.45	1291
0.427	0.6460	2.55	1823
0.565	0.6500	2.51	2511
0.706	0.6530	2.38	3181
K = 558; L = 1860; M = 1860; N = 820; Q = 800.			
$C_{NH_3} = 9.17 \times 10^{-2}$ M			
0	0.5490	2.75	1907
0.2887	0.6540	2.66	3221
0.3532	0.6560	2.59	3856
0.5651	0.6610	2.50	5866
K = 1910; L = 4200; M = 3170; N = 1420; Q = 840.			

TABLE V

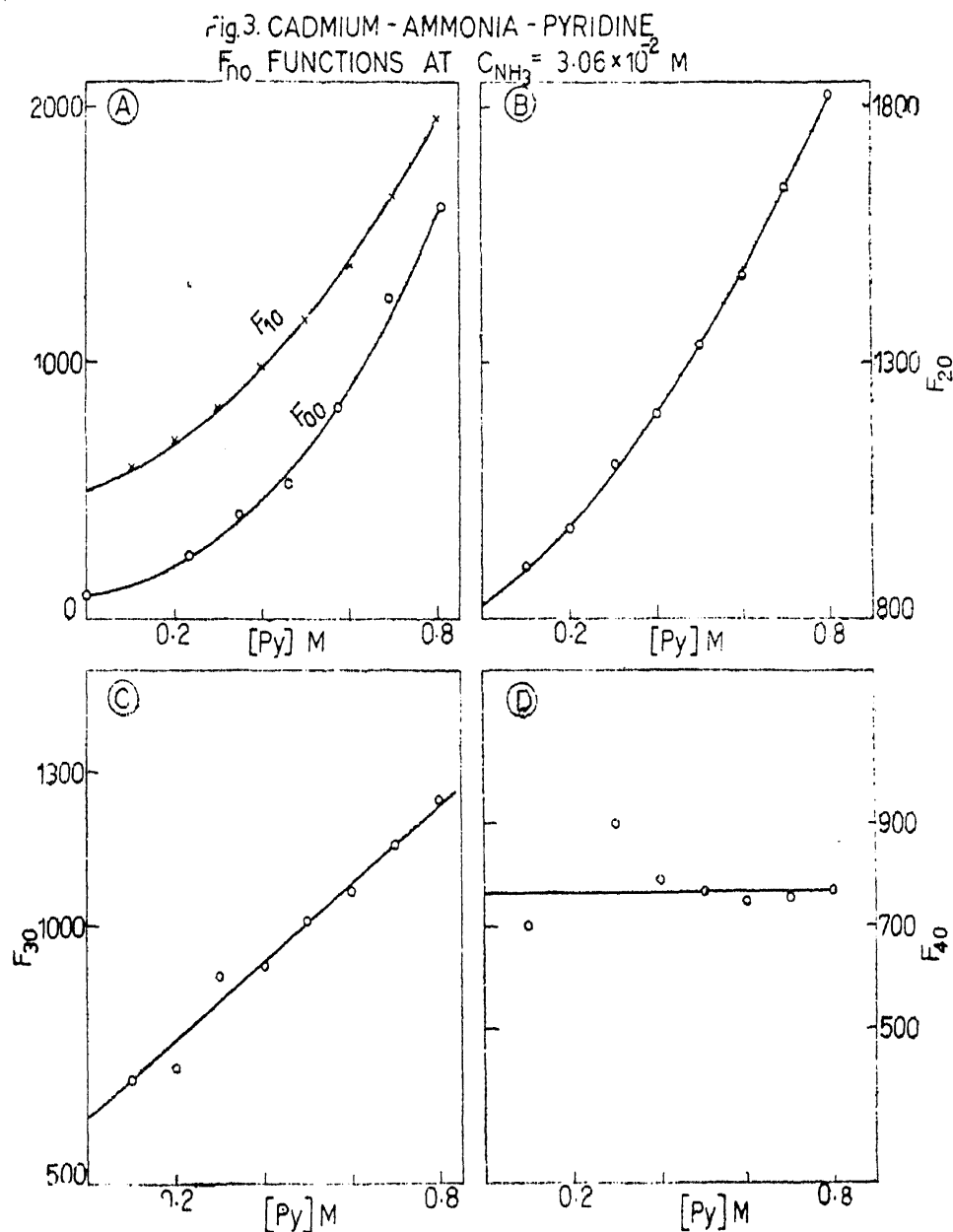
Cadmium-ammonia-pyridine system

Species	log β		log K_M		log K_s	
	This work	Ref. 7	This work	Ref. 7	This work	Ref. 7
Cd (NH ₃)	2.70
Cd (Py) ..	1.54	1.51
Cd (NH ₃) ₂	4.60
Cd (NH ₃) (Py)	3.18	3.25	-0.32	-0.28	-0.62	-0.58
Cd (Py) ₂ ..	2.19	2.46
Cd (NH ₃) ₃	6.00
Cd (NH ₃) ₂ (Py)	5.64	5.60	0.74	0.80	0.26	0.32
Cd (NH ₃) (Py) ₂	4.30	4.04	0.49	0.44	0.01	-0.04
Cd (Py) ₃ ..	2.71
Cd (NH ₃) ₄	7.03
Cd (NH ₃) ₃ (Py)	5.70	6.69	-0.29	0.78	-0.89	0.18
Cd (NH ₃) ₂ (Py) ₂	5.18	5.90	0.21	1.23	-0.57	0.45
Cd (NH ₃) (Py) ₃	3.71	4.08	-0.22	0.44	-0.82	-0.16
Cd (Py) ₄ ..	2.89	2.50

vs. (P), were then solved graphically to obtain the values of the constants K, L, M, etc. A typical plot is shown in Fig. 3. These constants obtained at different concentrations of ammonia were solved algebraically for the individual stability constants listed in Table V. The values of the mixing constants and the stabilisation constants for the different species are also reported in the same table.

Fridman and Levina⁷ have studied this system by solvent extraction. The present results broadly agree with theirs though some differences are

observed in the values of the stabilities of a few species. This may be due to the discrepancies in the values for the cadmium-pyridine complexes.



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