

POLAROGRAPHIC STUDY OF Cd(II)-PYRIDINE SYSTEM IN WATER-METHANOL MIXTURES

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ABSTRACT

The Cd(II)-pyridine system has been studied in (i) 0, 10, 20, 40, 50 and 70% (v/v) methanol-water mixtures and (ii) in 20% (v/v) DMF-water mixture. The coordination number (p) calculated from the slopes of the plot of $(-E_{1/2})_c$ vs $\log C_L$ gave three segments which showed the existence of 1:1, 1:2 and 1:3 complex species. The value of p increased with the increase in concentration of the ligand. The method of DeFord and Hume was adopted for the calculations of the formation constants.

It was observed that (i) three complex species are formed in all the solvent mixtures and (ii) the $\log \beta$ values remain nearly constant with the increase in the percentage of methanol from 10 to 70%. The experimentally determined $\log \beta$ values were utilised to understand the chemical specificity of the solvent mixtures.

INTRODUCTION

THE stability constants of metal complexes of pyridine have been the subject of study by many workers. Metal ions such as copper¹, zinc²⁻⁶, cobalt⁶⁻⁹, nickel^{6-8,10-12} and palladium¹³ were investigated by some workers to examine their interactions with pyridine in aqueous as well as in non-aqueous media using different electrolytes. Cd(II)-pyridine system has been investigated in aqueous^{3,4,14,15}, in DMF-water mixtures¹⁶, in 50% (v/v) ethanol-water mixture⁵ and in ethylene glycol medium¹⁷.

Despite the fact that the Cd(II)-pyridine system was investigated in certain non-aqueous media, a systematic study covering a wide range of solvent mixtures is still lacking. Such a study will help us to understand the nature of binding between the metal ion and pyridine. This work was, therefore, undertaken to investigate this aspect.

EXPERIMENTAL

Cambridge Pen Recording type polarograph with the necessary accessories was used for the measurement of half-wave potentials and the diffusion currents. All potentials were measured against the S.C.E. The capillary electrode used had the following characteristics:

$t = 3.0$ sec in 0.5 M KCl (open circuit)

$m = 2.21$ mg sec⁻¹ and $m^{1/2} = 1.56$ mg^{1/2}sec^{-1/2}

Decameter DK 03 supplied by Wissenschaftlich-Technische Werkstätten GmbH, Weilheim/Obb-Germany was used for the measurement of dielectric constants of the different solvent mixtures.

Cadmium (BDH, AnalaR), was used as its nitrate. Methanol (AnalaR) was purified by the method of Lund and Bjerrum¹⁸. N,N-Dimethylformamide (L.R. Merck) was purified as described by Wawzonek *et al.*¹⁹. The mercury was purified by treatment with dilute nitric acid,

degassed with 0.1 N sodium hydroxide solution and then distilled thrice. Potassium nitrate (AnalaR, BDH) was used without any further purification. The measurements were taken in an airconditioned room where the temperature was maintained at $25 \pm 0.5^\circ$ C.

All the solutions contained 1 mM cadmium nitrate and 0.004% Triton X-100 as a maximum suppressor. The concentration of pyridine varied from 0.103 M to 2.131 M and the ionic strength was maintained at 0.1 M by the addition of an appropriate amount of 2.0 M potassium nitrate solution. Dissolved oxygen was removed by bubbling purified nitrogen.

RESULTS AND DISCUSSION

Though negligibly small, the iR drop corrections were taken into account and the values of $-E_{1/2}$ were modified. These values along with the ligand concentrations are listed in Table I. The half-wave potentials were obtained from the log plots. The diffusion currents, i_d , were corrected for the residual current. The shift in half-wave potentials of cadmium(II) towards more negative values in the presence of pyridine in aqueous as well as in non-aqueous media indicated complex formation between cadmium(II) and pyridine.

The slopes value of the straight lines of the log plots were in the range of 30 to 34 mV indicating that the reduction of cadmium(II) ion in the absence and in the presence of pyridine is reversible and involves two electrons. This was found to be true in every methanol-water and DMF-water mixtures. The reduction could be represented as:



The values of $(-E_{1/2})_c$ were plotted against $\log C_L$ for all sets of experiments (Fig. 1) where C_L is the molar concentration of the ligand. The relationships were not linear but were represented by smooth curves with three distinct segments.

TABLE I

Analysis of $-E_1$ of Cd(II)-pyridine in methanol-water mixtures and 20% DMF-water mixture

c_{pyr}	0%	10%	20%	40%	50%	70%	20% DMF
0.000	0.580	0.580	0.578	0.576	0.572	0.570	0.586
0.103	0.598	0.597	0.595	0.595	0.590	0.585	0.600
0.206	0.607	0.607	0.608	0.604	0.601	0.596	0.614
0.309	0.617	0.615	0.615	0.610	0.609	0.602	0.621
0.412	0.622	0.622	0.620	0.618	0.614	0.607	0.628
0.515	0.627	0.626	0.626	0.623	0.622	0.612	0.603
0.618	0.634	0.631	0.630	0.628	0.627	0.616	—
0.824	0.642	0.640	0.640	0.635	0.632	0.625	0.644
0.927	0.644	0.643	0.643	0.637	0.635	0.628	0.646
1.030	—	0.645	0.645	0.646	0.638	0.630	0.649
1.133	0.650	0.648	0.647	0.644	0.640	0.633	0.651
1.236	0.653	0.650	0.650	0.648	0.643	0.635	0.652
1.442	0.658	0.655	0.656	0.652	0.646	0.639	0.656
1.545	0.658	0.659	0.658	0.655	0.648	0.642	0.659
1.648	0.660	—	0.660	0.657	0.650	0.645	0.661
1.854	0.665	0.663	0.663	0.660	—	0.648	0.664
1.880	—	—	—	—	0.656	0.650	—
2.061	0.668	0.666	—	—	—	—	—
2.131	—	—	—	—	0.660	—	—

The coordination numbers (p) calculated from the slopes of these segments were about 1, 2 and 3 which showed the existence of 1:1, 1:2 and 1:3 complex species respectively. The value of p increased with the increase in concentration of the ligand.

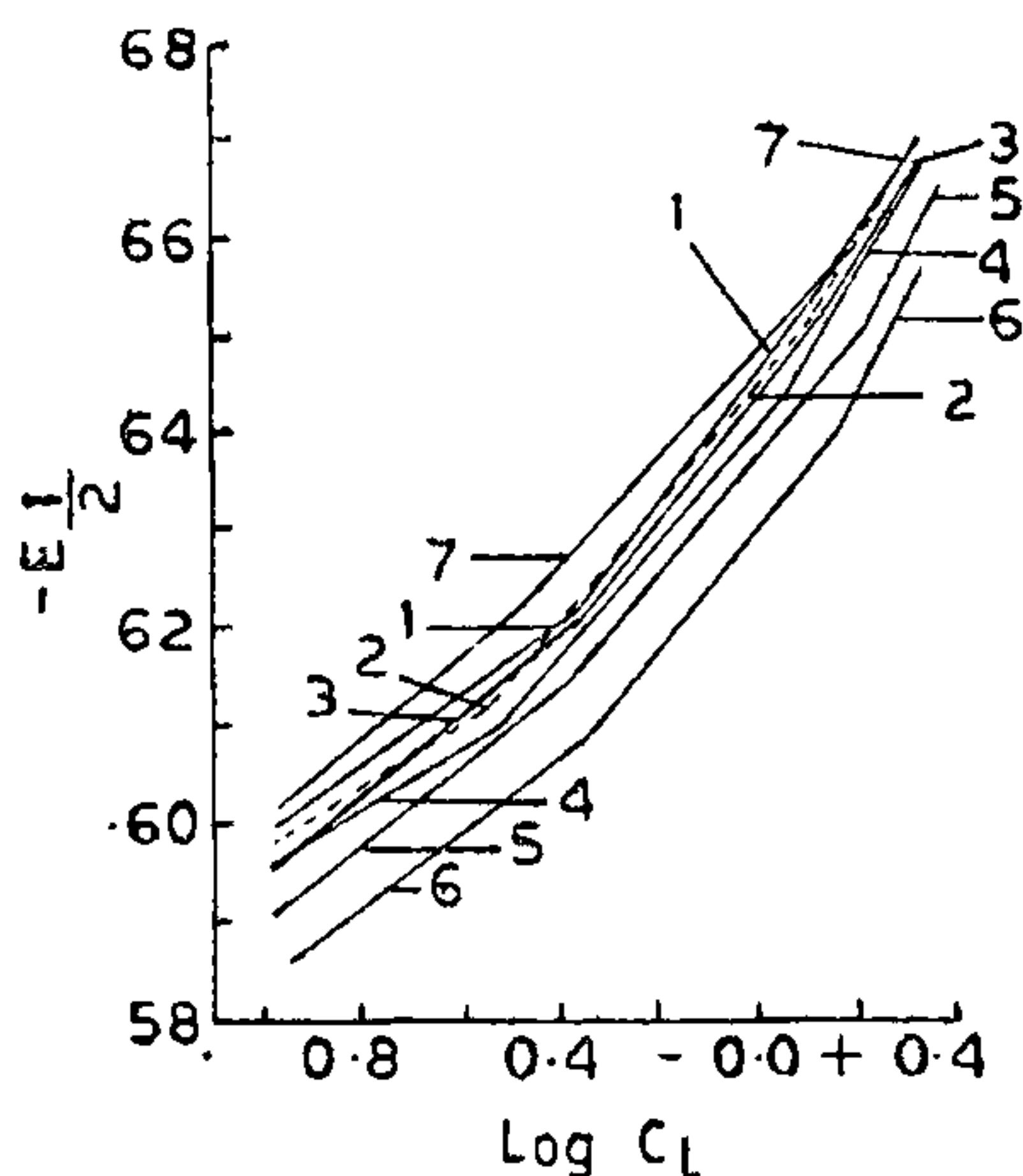


FIG. 1. Plots of $-E$ vs $\log C$ in various methanol-water mixtures: 0% methanol (1), 10% methanol (2), 20% methanol (3), 40% methanol (4), 50% methanol (5), 70% methanol (6) and 20% DMF (7).

The method of DeFord and Hume²⁰ was adopted for the calculations of the formation constants. The formation constants were obtained by plotting the $F_j(L)$ functions against the ligand concentrations and extrapolating the respective curves to zero concentration of the ligand for the system in aqueous medium (Fig. 2). Similar plots have been obtained in the other cases.

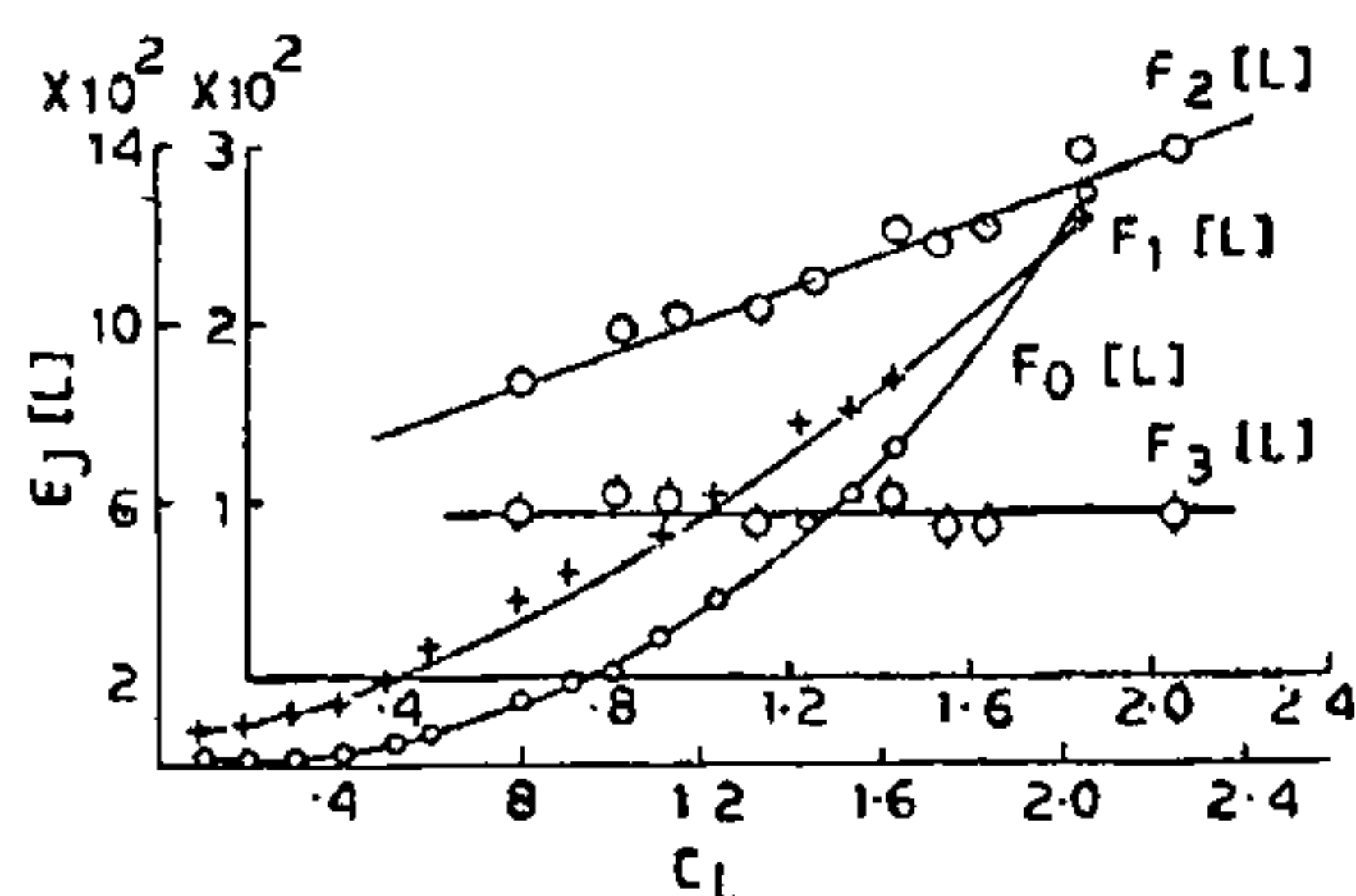


FIG. 2. Plots of $F_j[L]$ in 0% methanol.

The $\log \beta$ values for Cd(II)-pyridine systems in various solvent mixtures are presented in Table II. The accuracy of the β values in both aqueous and non-aqueous media was observed to be of the order of ± 2 for β_1 , ± 5 for β_2 and ± 4 for β_3 . The literature values, wherever available, at an ionic strength of 0.1 M (KNO_3) are also given in the same table. It could be seen from the

TABLE II
Cd(II)-pyridine system in water and methanol-water mixture
 $\mu = 0.1$ (KNO₃) Temp. = $25 \pm 0.5^\circ$ C

Mol. fraction of methanol %	0	10	20	40	50	20% DMF
Wt. fraction of methanol %	—	7.91	15.82	31.67	39.57	55.40
$1/\epsilon \times 10^{-3}$	12.73	13.51	14.38	16.67	18.01	21.74
$\log \beta_1$	1.48 1.40 ⁽¹⁴⁾ 1.36 ⁽⁴⁾	1.48	1.48	1.54	1.54	1.48
$\log \beta_2$	2.04 1.95 ⁽¹⁴⁾ 1.86 ⁽⁴⁾ 2.14 ⁽¹⁸⁾	1.90	1.90	1.70	1.85	1.30
$\log \beta_3$	1.95 2.27 ⁽¹⁴⁾ 1.90 ⁽⁴⁾	2.00	2.00	1.98	1.90	1.74

literature values that the agreement between our β_1 and β_2 values and those reported by Morinaga¹⁴ and Sharma and Gaur⁴ is satisfactory. Our value of β_3 is closer to that reported by Sharma and Gaur⁴ than that of Morinaga¹⁴. β_1 value for Cd(II)-pyridine system obtained by EMF measurements is 17.8 as reported by Desai and Kabadi²¹. The polarographic values are, however, higher than the EMF values.

Pyridine is a very weak base, since it derives its basicity from the unshared electrons of the nitrogen atoms in a plane trigonal sp^2 orbital. Considering its low basicity, however, it is capable of forming a stable complex with Cd(II). This is probably due to the additional π -bonds ($M \rightarrow L$) between the completely filled d orbitals of Cd(II) and the π -electron sextet of pyridine.

$M \rightarrow L$ π -bonding could be examined by comparing the β values of Cd(II) and Zn(II) (literature values 4) with pyridine. These values at 0.1 M (KNO₃) ionic strength are $\log \beta_1 = 0.90$ and $\log \beta_2 = 1.53$. The β values for Cd(II)-pyridine system are higher than those of Zn(II)-pyridine system. The stability of these complexes depends on the relative effects of both σ - and π -bonds. The strength of $M \rightarrow L$ π -bond is governed by the mobility of the free d_e electrons of the central atom. The π -bonds in the Cd(II)-complexes are stronger than those in Zn(II) complexes since ionisation potential of cadmium is lower than that of zinc if as a first approximation the mobility of the electrons in the ions is a measure of ionization potential of the metals.

EFFECT OF DIELECTRIC CONSTANT ON β VALUES

The $\log \beta$ values remain nearly constant with the increase in the percentage of methanol from

10% to 70%. The plots of $\log \beta_i$ vs $1/\epsilon$ (Fig. 3) show :

- a straight line relationships for $\log \beta_1$,
- that $\log \beta_2$ values remain nearly constant upto 50% of methanol-water mixture and then register a fall, and
- that in the case of $\log \beta_3$ values a near linearity is observed with respect to $1/\epsilon$ values over the entire range of solvent mixtures investigated in the present work.

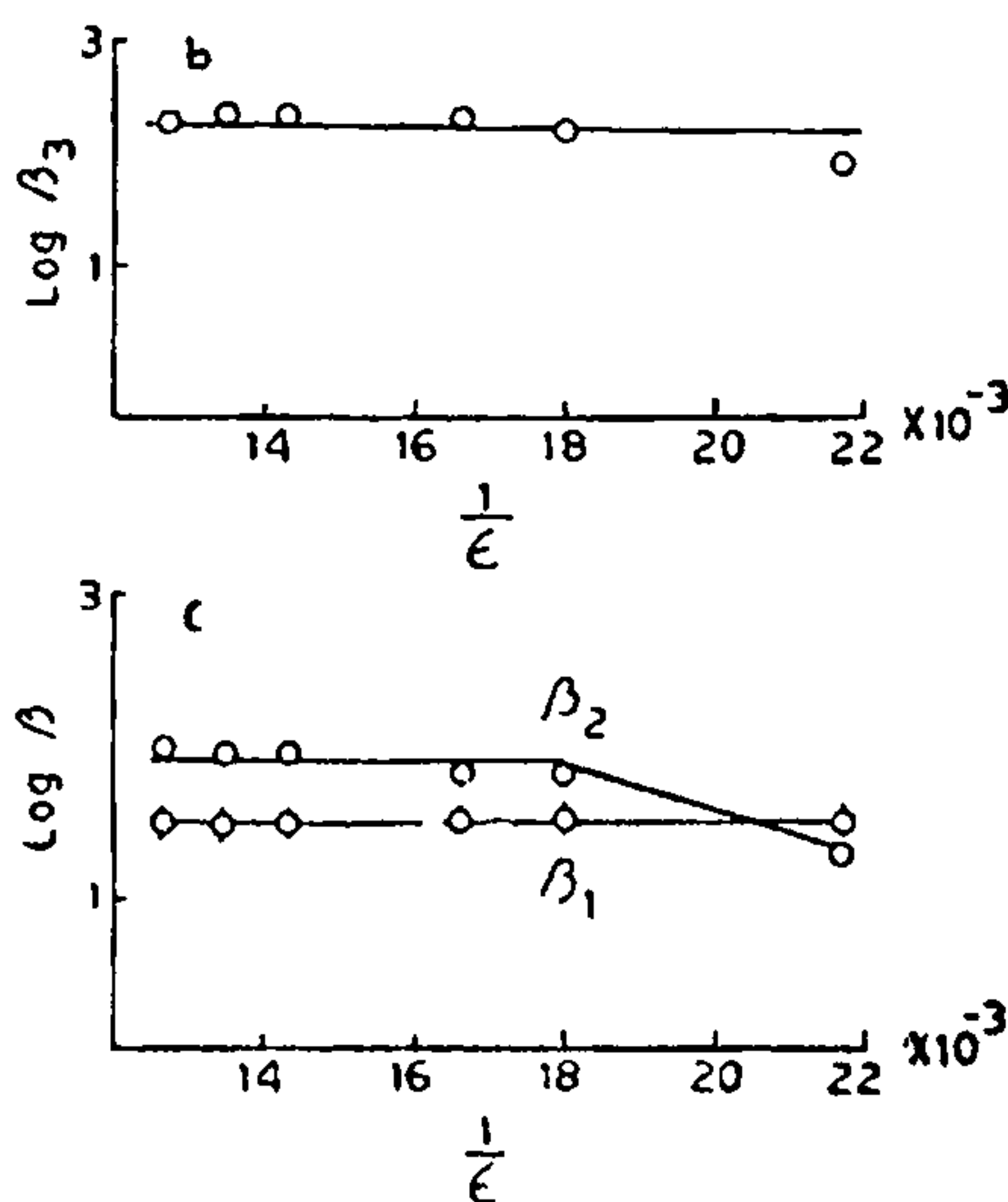


FIG. 3. Plots of $\log \beta_1$, $\log \beta_2$, and $\log \beta_3$ vs $1/\epsilon$ in various methanol-water mixtures.

The near constancy of $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$ values with the sole exception of one $\log \beta_2$ value supports the argument put forward regarding the back donation of electrons from the metal to the pyridinium nucleus. The predominance of the covalent nature of the metal-ligand bond in the 1:1 complex will not show any significant change in the $\log \beta_1$ values with respect to changes in dielectric constant.

The constancy of the $\log \beta$ values at various percentages of methanol shows that the solvent methanol as such is not playing any part in the reaction by which complexation occurs. This may be due to the fact that pyridine is a stronger base than methanol. Further, the mixtures of pyridine, water and methanol are a complex system due to the possibility of hydrogen bonding between water and pyridine and also between methanol and pyridine. Adam²² has reported that: (i) the water molecules approach the nitrogen lone pair of electrons in such a way that the hydrogen bonded system O—H...N is linear and (ii) the results of methanol-pyridine system are parallel to those of water pyridine system, the only difference being in the orientation of the methyl groups. Either the carbon atom of the methyl group is in the plane of pyridine ring or perpendicular to it. Since it is not possible to know the concentration of water molecules and methanol molecules, hydrogen bonded to pyridine separately, no quantitative conclusions can be drawn from the observed results.

The system was also investigated in 20% (v/v) DMF-water mixture, the $1/\epsilon$ value of which is 13.52×10^{-3} . The $\log \beta$ values in methanol-water mixture corresponding to $1/\epsilon$ values of 13.52×10^{-3} were obtained from the plots of $\log \beta_i$ vs $1/\epsilon$ (Fig. 3). The comparative data are given in Table III. In this case a discrepancy

TABLE III

$\log \beta_i$ values in 20% (v/v) DMF-water mixture having $1/\epsilon = 13.52 \times 10^{-3}$	$\log \beta_i$ values in methanol-water mixture having $1/\epsilon = 13.52 \times 10^{-3}$
$\beta_1 = 1.30$	1.50
$\beta_2 = 2.00$	1.90
$\beta_3 = 1.60$	2.00

between the two sets of values was observed. The difference in specific chemical effects of the two organic solvents despite identical dielectric constant of their mixtures is probably responsible for the observed discrepancy. The possibility of hydrogen bonding will be greater at the higher concentrations

of pyridine ions which may have resulted in the large discrepancy in $\log \beta_3$ as compared to $\log \beta_1$ and $\log \beta_2$.

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1. Korshunov, I. A. and Malyugina, N. T., *Zhur. Obshchei Khim.*, 1950, 20, 402.
2. Nyman, C. J., *J. Am. Chem. Soc.*, 1953, 75, 3575.
3. Popel, A. A. and Marunina, A. T., *Teroriya i Praktika Poliarograf. Analiza, Akad. Nauk Moldavsk. SSR. Materialy Pervoga Vses. Soreshch.*, 1963, p. 139.
4. Sharma, V. K. and Gaur, J. N., *J. Electroanal. Chem.*, 1965, 9 (4), 321.
5. Popel, A. A. and Belozerskaya, V. V., *Uch. Zap., Kagansk. Gos. Univ.*, 1964, 124 (3), 135.
6. Robert Lee, *J. Chem. Soc. D.*, 1970, 23, 1594.
7. Turlyan, Ya. I. and Serova, G. F., *Zhur. Fiz. Khim.*, 1957, 31, 1976.
8. Fiha, J., *Electrochim. Acta*, 1962, 6, 75.
9. Sundaresan, R., Saraiya, S. C. and Sundaram, A. K., *Proc. Ind. Acad. Sci.*, 1967, 66 A, 246.
10. Mark, H. B., *Anal. Chem.*, 1963, 35, 195.
11. Turlyan, Y. I., *Dokl. Acad. Nauk. SSSR*, 1962, 146, 848.
12. — and Malyavinskaya, O. N., *Elektrokhimiya*, 1967, 3 (6), 773.
13. Woodeburn, S. I., Blackmore, M. W. and Robert Magee, J., *Anal. Chim. Acta*, 1970, 49 (2), 279.
14. Morinaga, K., *Nippon Kagaku Zasshi*, 1956, 77, 865.
15. Douglas B. E., Laitinen, H. A. and Baillar, J. C. Jr., *J. Am. Chem. Soc.*, 1950, 72, 2484.
16. Gaur, J. N. and Sharma, V. K., *Rev. Polarogr.*, 1967, 13 (3-6), 287.
17. Shrivastava, O. N., Gupta, I. K. and Gupta, C. M., *Ind. J. Chem.*, 1970, 8 (3), 302.
18. Vogel, A. I., *A Text-Book of Practical Organic Chemistry*, 3rd Edition, Longmans, 1959, p. 167.
19. Wawzonek, S., Berkey, R., Blaha, E. H. and Runner, M. E., *J. Electrochem. Soc.*, 1956, 103, 456.
20. DeFord, D. D. and Hume, D. N., *J. Am. Chem. Soc.*, 1951, 73, 5321.
21. Desai, A. G. and Kadi, M. B., *J. Ind. Chem. Soc.*, 1961, 38, 805.
22. Adam, W., Grimson, A., Hoffmann, R. and Conchita Zanzaga de Ortiz, *J. Am. Chem. Soc.*, 1968, 90, 1509.