

the wave mixes with the hydrogen wave but the  $E_{1/2}$  remains constant in the pH range 7.5-9. So all the polarograms were recorded at pH 8.2. The polarograms for the solutions containing unknown amounts of the metal ions were recorded under identical conditions and the values of the diffusion current referred to the calibration graph and the concentration of the metal ions determined. For the mixture the mixed polarograms were recorded and the  $i_d$  values obtained for the unknown were compared with the known for the determination. This method gave the results with an error within 0.5%.

The metal ions like Bi, Sn, Th, U(VI), Au, Ag (precipitated), Se(IV), Ce(IV) and W(VI) do not undergo reduction while thallium (0.475 V), In (0.575 V), Pb (0.43 V), Cu (0.08 V) and Mo (0.595 V) do not interfere. However, cobalt, Cr, Sb and Te cause interference in the determination of Ni(II) and Zn(II).

The advantage of sodium crotonate as base electrolyte over others is that it can be used without the addition of any other auxiliary electrolyte and results are reproducible and accurate.

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#### Electrochemical Behaviour of Pb(II) & Cd(II) in Presence of 6-Aminohexanoate Ions at d.m.e.

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The electrochemical behaviour of Pb(II) and Cd(II) has been studied in the presence of 6-aminohexanoate ions at 30° and 40° and  $\mu = 1.0$ . The electrode process was diffusion-controlled and reversible for two-electron transfer. The composition and formation constants of the complexes formed have been calculated by DeFord and Hume's method. Cd(II) forms three complex species having  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  values of 4.5, 50 and 92.5 at 30° and 10, 93 and 107 at 40°. Pb(II) forms four complex species having  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$  and  $\beta_4$  values of 90, 410, 165 and 1000 at 30° and 120, 620, 340 and 1040 at 40°.

COMPLEXES of Cd(II) and Pb(II) with some aliphatic acids<sup>1</sup> and hydroxy acids<sup>2-3</sup> have already been reported by us. The present note deals with the composition and formation constants of the Pb(II) and Cd(II) complexes with 6-aminohexanoate ions in aqueous medium at 30° and 40°.

The d.m.e. had the following characteristics:  $m = 1.7645$  mg/sec and  $t = 3.46$  sec (open circuit). Sodium salt of 6-aminohexanoic acid was used as the complexing agent. The pH was maintained at  $6.8 \pm 0.1$  and was measured by a Toshniwal pH meter.

For all the solutions, a single well-defined diffusion-controlled wave appeared whose half-wave potential shifted towards more negative values and the diffusion current decreased with increasing ligand concentration indicating the complex formation. The plots of  $E_{1/2}$  versus  $\log C_X$  were found to be smooth curves, showing the formation of two or more complexes which are in equilibrium. The classical method due to Lingane<sup>4</sup> could not be applied. Thus the formation constants and the composition of the complexes formed have been calculated by the method of DeFord and Hume<sup>5</sup>.

*Cd(II)-6-aminohexanoate system* — The values of overall formation constants were calculated using the graphical extrapolation. The polarographic characteristics together with the  $F_0([X])$  values calculated at both the temperatures are summarized in Table 1.

6-Aminohexanoate ions form three complexes with Cd(II) corresponding to the composition  $MX_1$ ,  $MX_2$  and  $MX_3$  at both the temperatures (30° and

TABLE 1 — POLAROGRAPHIC CHARACTERISTICS OF Cd(II)-6-AMINOHEXANOATE COMPLEXES

$C_X$ (M)	$E_{1/2}$ (-V vs SCE)	$i_d$ (divisions)	$F_0([X])$	[ $\mu = 1.0$ ; Cd <sup>2+</sup> = 1.0 mM]			
				TEMP. = 30°			
0.00	0.5765	90.0	—				
0.05	0.5795	80.5	1.407				
0.10	0.5850	79.0	2.041				
0.20	0.5935	71.5	4.640				
0.30	0.6020	67.5	9.439				
0.40	0.6090	64.5	16.900				
0.50	0.6150	63.0	27.430				
0.60	0.6200	61.5	41.240				
0.70	0.6245	60.0	59.710				
0.80	0.6290	66.0	89.950				
				TEMP. = 40°			
0.00	0.5745	101.5	—				
0.05	0.5775	90.0	1.406				
0.10	0.5875	87.5	3.047				
0.20	0.5990	82.0	7.638				
0.30	0.6075	77.5	15.20				
0.40	0.6145	73.0	27.12				
0.50	0.6195	73.0	40.81				
0.60	0.6255	69.0	64.97				
0.70	0.6300	69.0	90.76				
0.80	0.6340	65.0	129.60				

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TABLE 2 — POLAROGRAPHIC CHARACTERISTICS OF Pb(II)-6-AMINOHEXANOATE COMPLEXES

[ $\mu = 1.0$ ;  $Pb^{2+} = 1.0 \text{ mM}$ ]

$C_X$ (M)	$E_{1/2}$ (-V vs SCE)	$i_d$ (divisions)	$F_0([X])$
TEMP. = 30°			
0.00	0.3945	81.0	—
0.05	0.4165	66.5	6.592
0.10	0.4260	66.5	13.670
0.20	0.4395	66.0	38.820
0.30	0.4490	66.0	77.450
0.40	0.4550	61.0	138.000
0.50	0.4610	58.5	228.000
0.60	0.4670	57.5	367.700
0.70	0.4725	57.0	565.700
0.80	0.4780	54.5	862.800
TEMP. = 40°			
0.00	0.3875	96.0	—
0.05	0.4110	86.0	6.390
0.10	0.4240	84.5	17.09
0.20	0.4385	74.0	55.78
0.30	0.4470	72.0	110.50
0.40	0.4545	70.0	198.7
0.50	0.4610	69.5	324.4
0.60	0.4670	69.5	506.8
0.70	0.4720	68.0	750.9
0.80	0.4765	65.5	1088.0

40°) with  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  values equal to 4.5, 50 and 92.5 at 30° and 10, 93 and 107 at 40° respectively.

**Pb(II)-6-aminohexanoate system** — Similar results were obtained with Pb(II)-6-aminohexanoate system where four complex species  $MX_1$ ,  $MX_2$ ,  $MX_3$  and  $MX_4$  are formed. The values of  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$  and  $\beta_4$  are 90, 410, 165 and 1000 at 30° and 120, 620, 340 and 1040 at 40°. The polarographic characteristics along with the  $F_0([X])$  values are presented in Table 2. It has been observed that at higher temperature (40°) the values of  $\beta_i$  increase suggesting higher stability of the complexes. This might be due to the fact that at higher temperature the dissociation of ligand, which is a weak acid, is facilitated and hence more ligand ions are available for coordination with metal ions.

On comparing the values of stability constants for the highest complex  $MX_4$ , it can be concluded that the complexes formed by Pb(II) are stronger than those by Cd(II).

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## Studies on Zn(II) Complexes of Pyridine, 4-Ethylpyridine, 3,5-Lutidine & 3,4-Lutidine

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Stability constants of Zn(II) complexes of pyridine, 4-ethylpyridine, 3,4-lutidine and 3,5-lutidine have been determined potentiometrically in ethanol-water medium containing 25% (v/v) ethanol at 30° and at an ionic strength of 0.1M ( $NaClO_4$ ) using graphical method of Leden. Only three complexes 1:1, 1:2 and 1:3 are formed in each case in the range of reagent concentrations employed ( $Zn^{2+} = 10^{-3}M$  and reagent = 0 to 0.4M or 0.9M). The values of metal-ligand stability constants are in the sequence expected from the reagent affinities for hydrogen ion. The plot of metal-ligand stability constant ( $\log K_1$ ) against the proton association constant ( $pK_{NH^+}^H$ ) of the reagent is linear; but the slope of the plot is less than unity. The deviation from the unit slope is attributed to the  $\pi$ -bond formation between the metal ion and the donor atom of the reagent. Proton association constants of the reagents have also been determined in ethanol-water (25%, v/v) medium at 30° and at an ionic strength  $\mu = 0.1M$  ( $NaClO_4$ ) using Calvin-Bjerrum pH titration technique.

**STEPWISE** stability constants of pyridine and some of its derivatives with Cd(II) and Zn(II) have been determined in aqueous medium potentiometrically by Desai and Kabadi<sup>1</sup>. Sun and Brewer<sup>2</sup> have evaluated the formation constants of Cu(II), Ni(II) and Ag(I) complexes of pyridine and its derivatives potentiometrically in aqueous medium. However, the stepwise stability constants of Zn(II) complexes of 4-ethylpyridine, 3,4-lutidine and 3,5-lutidine have not been determined so far. This study has been carried out potentiometrically in ethanol-water medium (25:75, v/v) at 30° utilizing the method suggested by Leden<sup>3</sup>. Ethanol-water medium has been used because of the poor solubility of these reagents in water. For comparison, the stability constants of Zn(II) complexes of pyridine in aqueous medium have also been evaluated under the same experimental conditions. Proton association constants of the reagents have been determined in the same mixed solvent medium at 30° using Calvin-Bjerrum pH titration technique as applied by Irving and Rossotti<sup>4</sup>.

All the chemicals except the ligands were of AR grade. In the preparation of different solutions, freshly prepared doubly distilled  $CO_2$ -free water was used. The ethanol used for the experiments was purified by the method described by Vogel<sup>5</sup>. The reagents were distilled under reduced pressure before use. Zinc perchlorate solution of known strength (0.1M) was prepared by dissolving zinc oxide in equivalent quantity of perchloric acid solution till excess of zinc oxide remained undis-