

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 β_1 , β_2 and β_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 β_1 , β_2 , β_3 and β_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 β_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 π -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 Kabadi¹. Sun and Brewer² have evaluated the formation constants of Cu(II), Ni(II) and Ag(I) complexes of pyridine and its derivatives pH -metrically 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 Leden³. 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 Rossotti⁴.

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 Vogel⁵. 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-

solved. It was then gently boiled and filtered and the solution was made up to desired volume. Zinc was estimated quantitatively by the EDTA method of Schwarzenbach and Biedermann⁶.

The details on the preparation of sodium perchlorate and reagent solutions of required strength were the same as given in the previous publication⁷.

Zinc amalgam electrode (Zn-Hg) employed to measure the $[Zn^{2+}]$ in solution was prepared by adding specpure zinc (6 g) to triply distilled mercury (300 g) and about 10 ml of dilute perchloric acid. The contents were heated till it formed a homogeneous mixture and thereafter the liquid amalgam was cooled and washed with dilute perchloric acid.

The H-type titration cell (A) in which the middle compartment was separated by two sintered glass discs was employed.

Pt ⁺	Quinhydrone (saturated) + HClO ₄ (0.001M) NaClO ₄ (0.099M)	Agar-agar saturated with NaClO ₄	Zn(ClO ₄) ₂ + (1 mM) NaClO ₄ + reagent in water-ethanol solution. Total ionic strength=0.1	(Zn-Hg) ⁻
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(A)

Details of the experimental procedure used for the present study are the same as reported earlier⁷. A series of e.m.f. readings with the cell of the type (A) was taken on Pye potentiometer of sensitivity 0.1 mV at various [ligands], keeping $[Zn^{2+}]$ constant. To keep the total [metal ion] constant in the right-hand compartment of the cell (A), the ligand solution containing the same [metal ion] as that present initially in the right-hand compartment of the cell, was prepared. The [metal ion] employed was $10^{-3}M$ and the [ligand] was varied from 0 to 0.4 or 0.9M. The data were collected at a constant temperature of $30 \pm 0.1^\circ$. The e.m.f. of the cell is given by

$$E = E' - \frac{RT}{nF} \ln C_M$$

where E' includes the potential of reference electrode, the liquid junction potential and contribution due to activity of metal ions in amalgam electrode and activity coefficients. All these factors were assumed to remain constant throughout the measurements. In the above-mentioned relation, C_M is the total [metal ion] and other symbols have their usual significance⁸.

Metal-ligand stability constants — In absence and presence of the ligand, the e.m.f. of the cell is given by Eqs. (1) and (2) respectively.

$$E_1 = E' - \frac{RT}{nF} \ln C_M \quad \dots(1)$$

$$E_2 = E' - \frac{RT}{nF} \ln [M] \quad \dots(2)$$

where $[M]$ = free Zn^{2+} ion concentration in equilibrium. Hence

$$\Delta E = E_2 - E_1 = \frac{RT}{nF} \ln \phi = 0.03 \log \phi \text{ at } 30^\circ \text{ for } n = 2 \quad \dots(3)$$

TABLE 1 — PROTON- AND METAL-LIGAND STABILITY CONSTANTS

Ligand	$pK_{NH^+}^H$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
Pyridine	4.80	1.04	1.62	1.81
4-Ethylpyridine	5.69	1.31	2.15	2.63
3,5-Lutidine	5.77	1.35	2.32	2.63
3,4-Lutidine	6.17	1.46	2.53	3.32

In Eq. (3) ϕ is the degree of complex formation and is defined as the ratio of total concentration of metal ions added initially to the equilibrium concentration of free metal ions.

An expression for the function of ϕ in terms of free ligand concentration $[L]$ has been derived by Leden³. The free ligand concentration $[L]$ is found out using the formation function \bar{n} as proposed by Bjerrum⁹. The various equations and the method used for finding out the $[L]$ values are given in the previous publication⁷. From the data collected, the consecutive overall metal-ligand stability constants β_N were obtained using the graphical method of Leden³.

Proton-ligand stability constants — The experimental procedure adopted for the determination of proton association constants of the reagents was the Calvin-Bjerrum titration technique⁴. The details of the technique and the materials used are the same as given by Vartak and Menon¹⁰, except the solvent medium. The proton-ligand stability constants designated as $pK_{NH^+}^H$ and the metal stability constants of the reagents are recorded in Table 1.

The data in Table 1 indicate the formation of only 1:1, 1:2 and 1:3 (metal-ligand) complexes. The values of the stability constants of the complexes of Zn^{2+} with pyridine are observed to be in fair agreement with those reported earlier¹. The stability constants of the various Zn^{2+} complexes lie in the ligand order: 3,4-lutidine > 3,5-lutidine > 4-ethylpyridine > pyridine. This order compares well with that of their $pK_{NH^+}^H$ values as is generally expected on the basis of Lewis' definition of acids and bases. The increase in the values of stability constants of 4-ethylpyridine, 3,5-lutidine and 3,4-lutidine complexes of Zn^{2+} when compared to those of pyridine can be attributed to the electron-donating nature of the alkyl groups present in these reagents.

It was observed that the plot of $\log K_1$ ($\log \beta_1$) against $pK_{NH^+}^H$ was linear, but the slope of the line was only 0.3. Similar behaviour was exhibited by the Cd^{2+} complexes⁷ and Ag^+ complexes of the ligands. It has been reported^{1,2} that Cd^{2+} , Zn^{2+} and Ag^+ are capable of forming $d\pi-p\pi$ bonds with pyridine and substituted pyridines. The metal ions have their d -orbitals completely filled and hence $L \rightarrow M$, σ -bonding could take place by the acceptance of a lone pair of electrons from the nitrogen of the ligands. $M \rightarrow L$, π -bonding can occur by the partial transfer of electrons of the metal ions to the vacant p -orbitals of the nitrogen of the ligands.

The slope of the line is mainly influenced by the change in $M \rightarrow L$, π -strength because $L \rightarrow M$, σ -bonding, though weaker than that in the corresponding proton

complexes, is assumed to change in the similar way with change of substituent as the proton-ligand bonding. The observed low value of the slope from unity indicates a decrease of π -strength with increasing basicity due to the increase of electron density around the nitrogen of the pyridine. Thus, since π -strength is more significant in the bond formation of these metal complexes, the slope will be less than unity.

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Determination of Gallium in Bauxite & Silicate Rock Samples by Solvent Extraction-Atomic Absorption Spectrophotometry

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A solvent extraction-atomic absorption method for the determination of gallium in bauxite and silicate rock samples is described. The method involves decomposition of the sample with hydrofluoric-perchloric acid, separation of mixed oxide group metals by precipitation with excess sodium hydroxide, solvent extraction of gallium with cupferron-methyl isobutyl ketone and atomic absorption measurements for gallium in the organic phase. The method is free from interferences and it is very suitable for rapid and accurate determination of gallium in the range 5-100 ppm in many types of geological materials.

POLLOCK¹ has described an atomic absorption spectrophotometric method for the determination of gallium in limonite samples using methyl isobutyl ketone and titanium(III) chloride to extract gallium from hydrochloric acid solution of limonite for direct aspiration. The method of Lypka and Chow² for the determination of gallium in some ores and concentrates though similar requires gallium to be re-extracted from the solvent phase into aqueous phase before atomic absorption measure-

ments. In both the reports, however, samples containing moderately high concentrations of gallium have been chosen and the methods do not seem to be useful in cases of samples having much lower concentrations (10-100 ppm) of gallium as found in most geological samples. This difficulty has been overcome in the method described in this note. The method involves decomposition of the common geological sample by hydrofluoric-perchloric acid, separation of iron and titanium by precipitation with sodium hydroxide and solvent extraction of gallium with cupferron-methyl isobutyl ketone (MIBK) followed by atomic absorption measurements in the organic phase. The cupferron-MIBK extraction not only eliminates the undesirable background readings, it also increases the atomic absorption sensitivity of gallium by a factor of 2.5.

Gallium standards were prepared by dissolving pure metal (99.9% pure) in hydrochloric acid and diluting to a 1000 ppm solution. Further dilutions were made as necessary before use.

Cupferron-MIBK reagent was prepared by solvent extraction of acidified cupferron solution (3%) with equal volume of methyl isobutyl ketone³.

All other reagents were of AR quality except that the aluminium solution was prepared from specpure quality aluminium oxide.

A Perkin-Elmer 303 atomic absorption spectrophotometer was used with instrument settings as recommended in the instrument manual except that the acetylene flow rate was kept at 5 and air flow rate at 10 during aspiration of organic solvents. No scale expansion was used during the atomic absorption measurements.

The results of preliminary experiments have shown that gallium is quantitatively extracted at sulphuric acid concentration in the range 0.1-0.6N in the presence of 5% sodium sulphate and this agrees with previous work by Stary *et al.*⁴. Aluminium is not extracted under this condition but iron and titanium interfere. So it was decided to remove iron and titanium by hydroxide precipitation prior to application of cupferron-MIBK extraction. The possibility of loss of gallium by precipitation or adsorption with the mixed hydroxide precipitates were also studied. For this purpose mixtures of gallium (50 μ g) with iron(III) (200 mg), titanium(IV) (200 mg) and manganese(II) (200 mg) were heated to boiling with different amounts of sodium hydroxide (5N) solution, the hydroxide precipitates were centrifuged out and the amounts of gallium in the solution determined by cupferron-MIBK extraction and atomic absorption spectrophotometry as described above. It was observed that the hydroxide precipitates of Fe(III), Ti(IV) and Mn(II) retain significant amounts of gallium but this does not occur if some amount of Al(III) is added before hydroxide precipitation. Studies with varying amounts of NaOH and Al(III) suggests that the optimum concentration of NaOH should be about 1-2N and Al(III) concentration about 100 mg in the sample.

Recommended procedure — 0.50-1.00 g sample (100 mesh) was taken in a teflon beaker, mixed with 20 ml HF and 2 ml HClO₄ and slowly evaporated to