The complexation of Cu(II) and Zn(II) with DL-serine has been investigated polarographically in aqueous medium at 25° and 35°. The composition and stability constants have been calculated by the methods of DeFord and Hume, and Mihailov. Complexes with metal to ligand ratios of 1:1 and 1:2 for Cu(II)-DL-serine and 1:1, 1:2 and 1:3 for Zn(II)-DL-serine are indicated. Thermodynamic parameters, ΔG, ΔH and ΔS have also been calculated.

EXCEPT for the work of Li and Doody, the complexation of Cu(II)-serine complex. The polarographic determination of the stabilities of complexes of Cu(II) and Zn(II) with DL-serine in aqueous media at 25° ± 0.1° and 35° ± 0.1° is reported in this note.

All the chemicals used were of AR grade. The solutions were prepared in doubly distilled water. Experiments were performed with 0.5mM of metal ions. The ionic strength, 2μ, was maintained constant at 0.5M with KNO3. Gelatin (0.005%) was used as a suppressor. Polargrams were recorded for deaerated solutions using a manual polargraph. The dropping mercury electrode had the following characteristics in 0.5M KNO3 in open circuit: m = 1.52 mg/sec; t = 4.48 sec; and h eff = 45 cm.

Cu(II) and Zn(II) in the presence of serine gave a well-defined wave in each case. The wave has been found to be diffusion-controlled and reversible as revealed by the linear plots of √h eff versus t 0.5 passing through the origin and slopes of the plots of E 1/2 versus log i /i0. The effect of pH on the complexation has been studied in the range 3.9-9.5 for Cu(II)-serine system and 3.8-9.7 for Zn(II)-serine system. At pH > 9.5 or 9.7 turbidity appears. For Cu(II)-serine system, the half-wave potential increased sharply to negative potentials between pH 3.9 and 4.95 and then less sharply up to pH 9.5. But for Zn(II)-serine system, the cathodic shift in half-wave potential increased slightly between pH 3.8 and 6.1 and then sharply up to 9.05, above which there appeared no shift. The half-wave potentials show a gradual cathodic shift with increasing serine concentration. The concentration of serinate ion, [X], was calculated from the pH of the solution and the pH value of serine, determined separately, as 9.10 and 8.90, by the pH-titration technique of Irving and Rossotti at 25° ± 0.1° and 35° ± 0.1° respectively. These values agree with the literature. The corresponding plots of E 1/2 versus pH were smooth curves indicating successive complexation. The data regarding metal-ligand ratios and overall stability constants of the complexes were, therefore, analyzed by the methods of DeFord and Hume as improved by Irving, and of Mihailov. The plots of F 2/[X] and F 3/[X] were horizontal to the [X]-axis for Cu(II)-serine and Zn(II)-serine systems respectively indicating the formation of two complexes in the case of Cu(II)-serine system with metal to ligand ratios of 1:1 and 1:2 and three for Zn(II)-serine system having metal to ligand ratios of 1:1, 1:2, and 1:3.

The values of overall stability constants g obtained are given in Table 1, which are in good agreement with those obtained by the other methods. The changes in free energy, enthalpy and entropy have been calculated using appropriate standard equations and their values are given in Table 2.

### Table 2 — Thermodynamic Parameters of the Complexes of Cu(II) and Zn(II) with DL-Serine

<table>
<thead>
<tr>
<th>System</th>
<th>pH</th>
<th>ΔG (kcal)</th>
<th>ΔH (kcal)</th>
<th>ΔS (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II) complexes</td>
<td>25°</td>
<td>10.74</td>
<td>21.13</td>
<td>17.73</td>
</tr>
<tr>
<td></td>
<td>35°</td>
<td>10.92</td>
<td>21.39</td>
<td>17.73</td>
</tr>
<tr>
<td>Zn(II) complexes</td>
<td>25°</td>
<td>6.27</td>
<td>11.32</td>
<td>9.77</td>
</tr>
<tr>
<td></td>
<td>35°</td>
<td>6.37</td>
<td>11.46</td>
<td>9.77</td>
</tr>
</tbody>
</table>
A comparison of the overall stability constant values of Cu(II)- and Zn(II)-serine complexes with those of other amino acids\textsuperscript{1,4,8,14} indicates that the coordination is through the amino group and the carboxylic group without any significant role being played by the hydroxyl group in the β-position. Thus a five-membered ring must be present in the above complexes, and these complexes are highly stable due to this ring\textsuperscript{15} and the nitrogen as a member of the same\textsuperscript{16}. The authors are grateful to Prof. J. P. Tandon for laboratory facilities. Two of the authors (N. P. S. and S. K. S.) acknowledge the support of the UGC, New Delhi, and the University of Rajasthan, Jaipur, for the grant of teacher fellowships.

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Formation Constants & Thermodynamic Functions of Cr(III), Al(III) & Be(II) Chelates with Oxydiacetic Acid

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The proton-ligand stability constants and stepwise formation constants of Cr(III), Al(III) and Be(II) chelates with oxydiacetic acid (ODAA) have been determined potentiometrically in aqueous medium at different ionic strengths (0-1M, 0-2M, 0-3M and 0-4M) and temperatures (25°C, 35°C and 45°C) using Calvini-Bjerrum pH-titration technique, as modified by Irving and Rossotti. Thermodynamic formation constants and thermodynamic parameters of complexation reactions have also been evaluated. The stability of the metal chelates follows the order Cr(III) > Al(III) > Be(II).

Complexation reactions of oxydiacetic acid with bivalent metal ions\textsuperscript{1-3} and also with lanthanide elements\textsuperscript{4,5} have been studied. However, no attempt has been made to determine the proton-ligand stability constant of oxydiacetic acid (ODAA) and formation constants of its chelates with Cr(III), Al(III) and Be(II). The present note reports the results of potentiometric determination of formation constants of the chelates of ODAA with Cr(III), Al(III) and Be(II).

The metal ion solution of chromic nitrate (Orianal Schiaparelli Torino, Italy), aluminium nitrate (E. Merck) and erbium sulphate (Reachin, USSR) were prepared in doubly distilled CO\textsubscript{2}-free, water and were standardized by conventional methods.\textsuperscript{4} The stock solutions of ODAA (John Baker, USA) and sodium perchorlate (Riedel) were prepared in conductivity water.

The titrations of following three solutions (total vol. 50 ml) were carried out against CO\textsubscript{2}-free NaOH under N\textsubscript{2} atmosphere in a specially designed double-walled beaker employing Bjerrum-Calvin pH-titration technique\textsuperscript{4,5} as used by Irving and Rossotti:\textsuperscript{\textsuperscript{5}} (i) 4 x 10\textsuperscript{-3}M perchloric acid (ii) 4 x 10\textsuperscript{-3}M perchloric acid + 3 x 10\textsuperscript{-3}M ligand and (iii) 4 x 10\textsuperscript{-3}M perchloric acid + 3 x 10\textsuperscript{-3}M ligand + 5 x 10\textsuperscript{-3}M metal ion solution. In these solutions the concentration of the common ingredients were identical. An appropriate quantity of sodium perchorlate (2-0M) was added to maintain the desired ionic strength.

The proton-ligand stability constants and stepwise formation constants were determined as follows:

The values of $\theta$ were evaluated at various $pH$ values from acid and ligand titration curves using the formula of Irving and Rossotti\textsuperscript{5}. The values of $\theta$ were plotted against the $pH$. From the plot the values of proton-ligand stability constants were computed using different computational techniques.\textsuperscript{8} The mean values are given in Table 1.

The stepwise stability constants of the metal complexes were determined with the help of formation curves ($\theta$ versus $\Delta L$) using various computational methods\textsuperscript{8}. The values of $\theta$, the average number of ligands attached per metal ion, and the free-ligand exponent $\Delta L$ were calculated from ligand and complex titration curves using the formula of Irving and Rossotti\textsuperscript{5}. The mean values are given in Table 1.

Thermodynamic stability constants were obtained by extrapolation of experimentally determined formation constants to zero ionic strength and the values for Cr(III), Al(III) and Be(II) are 3-69, 3-15, 3-52, 3-05 and 2-63 respectively.

The values of the overall changes in free energy ($\Delta G^{\circ}$) and entropy ($\Delta S^{\circ}$) for the complexes, given in Table 2, were calculated using the temperature coefficient and Gibbs-Helmholtz equation.\textsuperscript{10} The values of $\Delta H^{\circ}$ were calculated graphically by plotting log $\theta$ values at different temperatures as a function of $1/T$ and equating the gradient of this plot with $-\Delta H^{\circ}/4\cdot576$. The values are given in Table 2.

A comparison of the stepwise formation constants indicates that the stability increases with the increase in temperature, i.e. higher temperature is