TABLE 1 — IRREVERSIBILITY AND KINETIC PARAMETER DATA

| [Tryptophan] (m$M$) | $E_{3/4}-E_{1/4}$ | By Meites and Israel treatment | | |
|---|---|---|---|---|
| | | $\alpha n_a$ | $\Delta G^\ddagger$ (kcal) | $k^\circ_{fh}$ |
| 1 | 0·130 | 0·57 | 28·90 | $2{\cdot}3\times10^{-11}$ |
| 2 | 0·100 | 0·56 | 29·49 | $2{\cdot}5\times10^{-11}$ |
| 3 | 0·100 | 0·57 | 31·34 | $2{\cdot}6\times10^{-12}$ |
| 4 | 0·120 | 0·55 | 27·57 | $2{\cdot}0\times10^{-10}$ |
| 5 | 0·110 | 0·54 | 30·45 | $8{\cdot}0\times10^{-12}$ |
| 6 | 0·095 | 0·53 | 29·86 | $1{\cdot}6\times10^{-11}$ |
| 7 | 0·090 | 0·60 | 31·31 | $5{\cdot}6\times10^{-12}$ |
| 8 | 0·090 | 0·61 | 31·63 | $3{\cdot}9\times10^{-12}$ |
| 9 | 0·090 | 0·58 | 30·61 | $1{\cdot}3\times10^{-11}$ |
| 10 | 0·090 | 0·56 | 31·43 | $4{\cdot}2\times10^{-11}$ |
| 15 | 0·090 | 0·60 | 31·46 | $4{\cdot}3\times10^{-12}$ |
| 20 | 0·090 | 0·53 | 29·23 | $4{\cdot}6\times10^{-11}$ |

*$\alpha$ is derived from the relation $E_{3/4}-E_{1/4} = 0{\cdot}0564/\alpha n$ and $\alpha<0{\cdot}5$ at $n=2$ is regarded as a condition for total irreversibility[11].

that the slope increased significantly rendering the electrode process from near reversible to totally irreversible (Table 1), indicated a change in basic nature of the reaction and in analogy with Ni(II)-tryptophan system it can be concluded that the first wave corresponds to an irreversible reduction of Zn(II)-tryptophan complex. Similar to Ni(II)-tryptophan system reported by Lal and Christian[4] there is a second wave also but it is masked by a maximum at lower [tryptophan]. The role of amino acids as maximium suppressors[2] is already known and as the [tryptophan] is increased in the present study the maximium gradually disappears and the second wave can be observed. However, the concentration of the maximium suppressor (i.e. tryptophan) at this stage is rather high ($7\times10^{-3}M$) and possibly because of this the height of the second wave is very much reduced rendering a reliable quantitative study of this second wave at this stage doubtful. At 20 m$M$ tryptophan it is completely eliminated. Studies regarding the origin, nature and kinetics of this wave under alternative experimental conditions are in progress.

The positive shift of the $E_{\frac{1}{2}}$ (first wave) at [tryptophan] >6 m$M$ may be attributed to the double layer effect[10] due to high [tryptophan]. Tryptophan being charged species in solution (due to zwitterion formation) and also surface-active is quite likely to bring changes in double layer structure which may lead to a positive shift in $E_{\frac{1}{2}}$.

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# Thermodynamic Functions & Stability Constants of Some Rare Earths with Phloroglucinol

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**Stability constants of the complexes of phloroglucinol with Sc(III), Y(III), La(III), Ce(III), Pr(III) and Nd(III) have been evaluated in aqueous medium at $\mu$=0·02$M$ (NaClO$_4$), employing Bjerrum-Calvin $p$H-titration technique, as used by Irving and Rossotti. The values of overall changes in free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) accompanying the complex formation have been reported. The order of stability constant is Sc(III)>Y(III)>La(III) and La(III)<Ce(III)<Pr(III)<Nd(III).**

IN this note the thermodynamic functions and stability constants of some rare earths with phloroglucinol have been evaluated in aqueous medium.

The methods used were the same as described in previous communications[1,2]. The practical proton-ligand stability constants and metal-ligand stability constants at various temperatures were obtained employing Bjerrum-Calvin $p$H-titration technique[3,4], as used by Irving and Rossotti[5].

All the chemicals used were of AR grade. The stock solution (0·01$M$) of phloroglucinol (E. Merck) was prepared in CO$_2$-free doubly distilled water. All other solutions were prepared as described in previous papers[1,2]. Titrations were carried out under N$_2$ atmosphere and temperature was maintained with an accuracy of $\pm0{\cdot}1$°C.

Titrations were carried out with 0·909$M$ NaOH as in previous papers[1,2] at $\mu = 0{\cdot}02M$ (NaClO$_4$); total volume was 100 ml.

The proton-ligand and metal-ligand stability constants were calculated as described in previous papers[1,2]. The values of stability constants obtained by interpolation at half $\bar{n}$-values[5] method are given in Table 1.

The temperature coefficient and Gibbs-Helmholtz equation were used to determine the overall changes in free energy ($\Delta G$), enthalpy ($\Delta H$), and entropy ($\Delta S$). The total free energy change was obtained from the equation $\Delta G = -RT \ln \beta$, where $\beta$ is the

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TABLE 1 — PROTON-LIGAND AND METAL-LIGAND STABILITY CONSTANTS AT VARIOUS TEMPERATURES
[$\mu=0.02M$ (NaClO$_4$)]

| Metal | | Temp. (°C) | | |
|---|---|---|---|---|
| | | 20 | 30 | 40 |
| | log $K_1^H$ | 11·54 | 11·12 | 10·75 |
| | log $K_2^H$ | 9·17 | 8·94 | 8·74 |
| | log $K_3^H$ | 8·41 | 8·17 | 7·97 |
| Sc(III) | log $K_1$ | 15·07 | 15·27 | 15·50 |
| Y(III) | log $K_1$ | 7·92 | 8·10 | 8·30 |
| La(III) | log $K_1$ | 6·08 | 6·25 | 6·40 |
| Ce(III) | log $K_1$ | 6·20 | 6·37 | 6·52 |
| Pr(III) | log $K_1$ | 6·68 | 6·85 | 7·10 |
| Nd(III) | log $K_1$ | 6·92 | 7·12 | 7·25 |

TABLE 2 — VALUES OF THERMODYNAMIC PARAMETERS OF COMPLEXATION REACTIONS
[$\mu=0.02M$ (NaClO$_4$)]

| Metal | Temp. °C | $\Delta G$ kcal mole$^{-1}$ | $\Delta H$ kcal mole$^{-1}$ | $\Delta S$ cal deg$^{-1}$. mole$^{-1}$ |
|---|---|---|---|---|
| Sc(III) | 20 | −20·338 | | |
| | 30 | −21·311 | +5·027 | +86·924 |
| | 40 | −22·346 | | |
| Y(III) | 20 | −10·689 | | |
| | 30 | −11·304 | +5·112 | +54·178 |
| | 40 | −11·966 | | |
| La(III) | 20 | −8·206 | | |
| | 30 | −8·723 | +7·321 | +51·259 |
| | 40 | −9·227 | | |
| Ce(III) | 20 | −8·368 | | |
| | 30 | −8·890 | +7·370 | +53·663 |
| | 40 | −9·400 | | |
| Pr(III) | 20 | −9·018 | | |
| | 30 | −9·546 | +5·973 | +51·218 |
| | 40 | −10·236 | | |
| Nd(III) | 20 | −9·339 | | |
| | 30 | −9·937 | +7·925 | +58·950 |
| | 40 | −10·596 | | |

overall stability constant. The values of enthalpy changes ($\Delta H$) were obtained by plotting log $\beta$ against $1/T$, and equating slope of the linear plot to $-\Delta H/4.57$. Overall entropy changes ($\Delta S$) of the reactions were evaluated from the equation $\Delta S = (\Delta H - \Delta G)/T$.

All the thermodynamic parameters so obtained are given in Table 2.

The proton-ligand stability constants decrease as the temperature increases. The values of $\bar{n}$ in all the cases were found to be less than 1 which shows that only 1:1 complex is formed.

The data in Table 1 show that as the temperature increases, metal-ligand stability constant increases and also stability decreases as the ionic radii increase. The order of stability constants in Sc(III) > Y(III) > La(III) and La(III) < Ce(III) < Pr(III) < Nd(III).

Although $\Delta H$ values in all the cases are positive, the larger positive entropy changes make the complexes stable.

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# Ternary Cu(II) & Ni(II) Complexes Containing Aromatic Aldimines

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**Reactions of aromatic amines with the mixed Schiff base complexes of the type MLL′, where M = Cu(II) or Ni(II); L = salicylaldimine and L′ = 2-hydroxy-1-naphthaldimine, have been carried out. The new mixed Schiff base complexes (I-III) have also been synthesized by treating the equivalent amounts of preformed Schiff bases of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with aromatic amines with an equivalent amount of the metal salt solution. The complexes of the type $[M(A(N-N)]^+ClO_4^-$, where M = Cu(II), A = Schiff base of salicyldehyde with aniline and N,N-dipyridyl or *o*-phenanthroline, have also been prepared. The complexes have been characterized on the basis of elemental and TLC analyses, conductance, magnetic moment and spectral data.**

WE have recently reported[1] the formation of mixed ligand complexes of the type MLL′, where M = Cu(II) or Ni(II), L = salicylaldimine, and L′ = 2-hydroxy-1-naphthaldimine. In the present investigation, transamination reactions were carried out by reacting such mixed Schiff base complexes with aromatic amines. The mixed Schiff base complexes were also prepared by treating Cu(II) or Ni(II) salts with preformed Schiff bases derived from salicylaldehyde and 2-hydroxy-1-naphthaldehyde with aromatic amines.

The mixed Schiff base complexes of Cu(II) or Ni(II) containing one mole each of salicylaldimine and 2-hydroxy-1-naphthaldimine were prepared as reported earlier[1]. Other chemicals, namely aniline, *o*-, *m*- and *p*-toluidines used were of analar grade. UV (CHCl$_3$) and IR (nujol) data of the complexes were recorded on Beckmann DUZ and Beckmann IR-20 spectrophotometers, respectively. Conductivity measurements were carried out in CHCl$_3$ and H$_2$O on a Toshniwal conductivity bridge type CLO/01A. Except for the two Cu(II) complexes (IVa, b) where ClO$_4^-$ happens to be in the outer sphere, the molar conductances of all other complexes showed them to be non-electrolytes.

The UV absorbance of (N-phenyl-salicylaldiminato) (4′-methyl-N-phenylsalicylaldiminato)Cu(II) (IIa) was found to lie between those of bis(N-phenyl-salicyl-