LIGAND-PROTON STABILITY CONSTANT BY POLAROGRAPHIC TECHNIQUE

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A method for the determination of ligand - proton stability constant has been developed using polarographic half wave potentials at different pH. An attempt is made to evaluate proton-ligand stability constant of salicylaldehyde - trisbuffer (ST), anisaldehyde - ethylenediamine (AEN), ethylenediamine (EN) and thio-dipropionic acid (TDPA), these are compared with the potentiometric values. Dependence of the optical property of the ligand on pH is also shown.

In the determination of ligand–proton stability constants potentiometric method is widely used. A new method described in the present work is based on the dependence of $E_{\frac{1}{2}}$ of the complex on pH and was first set out by the authors while studying the complexation of Cd^{2+} with a Schiff base[1] at different pH.

EXPERIMENTAL DETAILS

All the chemicals used were of AR grade purity. The ligand, salicylaldehyde - trisbuffer (ST) was prepared by the method reported by Rustagi and Rao[2].

Polarograms were recorded manually on Toshniwal polarograph type CLO2A using 'Beltronix' microammeter and S.C.E. as a reference electrode. The test solution was deaerated just prior to analysis and inert atmosphere was maintained over it.

50% DMF - water mixture was utilized as a solvent. The final solution was 0.2mM in Cd^{2+}, 0.2 M in KNO_3, 0.04 M in ligand-ST and 0.005% in gelatin. The pH was adjusted with 0.2M HNO_3 and 0.2M KOH keeping ionic strength constant at $\mu = 0.2M$.

The $E_{\frac{1}{2}}$ vs pH plots are shown in Fig. 1, and the ligand–protonation constant was determined by the following equation.

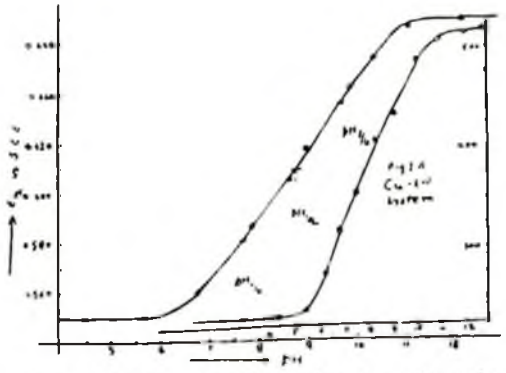


Fig. 1. $E_{\frac{1}{2}}$ of Cd^{2+}—ST Complex as a function of pH

$$pH = pH_{\frac{1}{2}} + A \log \left[\frac{E_{\frac{1}{2}}}{(E_{\frac{1}{2}})_L - E_{\frac{1}{2}}} \right] \quad \ldots \quad (1)$$

where $(E_{\frac{1}{2}})_L$ = limiting value of $E_{\frac{1}{2}}$ (i.e. beyond pH 11.0); $E_{\frac{1}{2}}$ = any value of $E_{\frac{1}{2}}$ on the graph, and $pH_{\frac{1}{2}}$ = the pH at the inflection point of the graph.

Plot of $\log \left[\frac{E_{\frac{1}{2}}}{(E_{\frac{1}{2}})_L - E_{\frac{1}{2}}} \right]$ vs. pH is a straight line (Fig. 2) indicating validity of eq. 1.

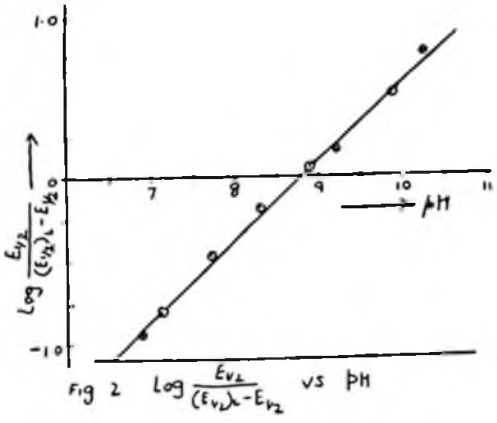


Fig 2 $\log \frac{E_{\frac{1}{2}}}{(E_{\frac{1}{2}})_L - E_{\frac{1}{2}}}$ vs pH

In order to determine the proton–ligand stability constant potentiometrically, Irving-Rossotti method[3,4] was applied.

The following two sets were titrated against 1.0M (carbondioxide free) NaOH on Systronics expanded-scale pH meter type 331 with Beckman electrodes: (1) 0.0.M HNO_3 + 0.1M KNO_3; final volume 60ml in 50% DMF; (2) 0.01M HNO_3 + 0.1M KNO_3 + 0.005M ligand ST; final volume 60ml in 50% DMF.

The formation curve for the ligand protonation was drawn which extended from 1 to 3 $\bar{n}_A$ value[5], based on structure of the ligand. The protonation constants were evaluated by half integer method[4].

Theory:

The dependence of $E_{\frac{1}{2}}$ of the complex on the pH of the solution is shown in Fig. 1. In the region between pH 6.0 and 11.0, $E_{\frac{1}{2}}$ is sharply affected by pH while for the remaining region it is virtually independent of pH. Hence it is clear that between pH 6.0 and 11.0 a varying degree of ligand protonation may be the cause of the shifting of $E_{\frac{1}{2}}$ because as per our expectation, at higher pH the concentration of protonated ligand is less and accordingly free ligand is more resulting in more

complexation. Hence Fig. 1 actually represents the equilibrium between a totally protonated ligand and a totally free ligand at various pH of the solution.

The probable Chemical Changes : The dependence of complex formation on pH is based on the nature of the ligand and can be explained as follows :

The structure of the ligand[2] is HO – ϕ – C = N – R.

Below pH 6.0, the ligand is totally protonated and has the form : HO–ϕ–C=$\overset{+}{N}$H–R (2) Between pH 6.0 and 8.8 (i.e. $pH_{\frac{1}{4}}$) the proton of =NH dissociates; at pH 7.7 (i.e., $pH_{\frac{1}{2}}$) the following equilibrium exists :

$$HO-\phi-C=\overset{+}{N}H-R \rightleftharpoons HO-\phi-C=N-R + H^+ \quad \ldots (3)$$

Now, beyond pH 8.8, the proton of —OH starts dissociating and we get at pH 9.7 (i.e., $pH_{\frac{3}{4}}$) the following equilibrium :

$$HO-\phi-C=N-R \rightleftharpoons \bar{O}-\phi-C=N-R + H^+ \quad \ldots (4)$$

The dissociation completes at pH 11.0 and therefore the change in pH beyond 11.0 has no effect on $E_{\frac{1}{2}}$, so that $(E_{\frac{1}{2}})_L$ is obtained.

The constants of each equilibrium in eq. (3) and (4) represent stepwise ligand - proton dissociation constant which can be expressed in general by the following relations :

$$LH_2^+ \rightleftharpoons LH + H^+ \quad \ldots (5)$$

and $LH \rightleftharpoons L^- + H^+ \quad \ldots (6)$

hence $k_1 = \{[LH]\,[H^+] / [LH_2^+]\} \quad \ldots (7)$

hence $k_2 = \{[L^-]\,[H^+] / [LH]\} \quad \ldots (8)$

From eq. (7) and (8)

$$pk_1 = pH - \log \{[LH] / [LH_2^+]\}$$

and $pk_2 = pH - \log \{[L^-] / [LH]\}$

from eq. (3) and 4, we deduce that at $pH_{\frac{1}{4}}$, [LH] = $[LH_2^+]$ and at $pH_{\frac{3}{4}}$, $[L^-]$ = [LH] respectively.

so, $pk_1 = pH_{\frac{1}{4}} \quad \ldots (9)$

and $pk_2 = pH_{\frac{3}{4}} \quad \ldots (10)$

RESULTS AND DISCUSSION

The stepwise proton dissociation constants for some ligands determined by polarography and potentiometry are given in Table - 1. The results are in good agreement with the Irving-Rossotti half integer method. The polarographic method is equally applicable to all the ligands of this type, e.g Cu - ethylenediamine (Cu - EN) complexation was studied employing 0.2mM Cu^{2+}, 0.1M KNO_3 and 0.67M EN. The same shape of curve (fig. 1A) was obtained for $E_{\frac{1}{2}}$ vs pH and pk_1 and pk_2 were evaluated, (table - 1). A schiff base derived from anisaldehyde and ethylenediamine was studied with Cd^{2+} at different pH, and the results were in agreement with that of potentiometry[1].

Several workers[6,7] have obtained the same shape of the graph of $E_{\frac{1}{2}}$ vs pH while studying metal comp'exes at different pH, but they have not interpreted it, and hence have failed to deduce anything from the results.

In the study of Pb-picolynic acid complex[6] at different pH, if some more points would have been taken for the curve of $E_{\frac{1}{2}}$ vs pH, the 'S' shaped curve was likely to occur, making possible to evaluate pk_1 and pk_2 for picolynic acid very near to 1.5 and 5.43 respectively. These values are actually the stepwise dissociation constants for picolynic acid as reported[8].

As per the method suggested, one can calculate stepwise proton dissociation constants, looking to the structure of the ligand, using graph of $E_{\frac{1}{2}}$ vs pH. Rawat and Gupta[7] while studying thiodipropionic acid complexes of Pb^{2+} and Zn^{2+} have obtained such graph. In this case as the ligand is an acid, $E_{\frac{1}{2}}$ is sharply affected between pH 4.1 and 6.0. The values for pk_1 ($= pk_{\frac{1}{4}}$) and pk_2 ($= pH_{\frac{3}{4}}$) are found as 4.75 and 5.60 respectively.

TABLE - 1. Comparison of Stability Constants

Ligand	Polarography		Potentiometry	
	pk_1	pk_2	pk_1	pk_2
ST (50% DMF)	7.7	9.7	7.9	9.2
AEN (40%DMF)	8.0	9.0	7.5	9.5
EN (aqueous)	6.75	9.3	7.49[8]	10.17[8]
TDPA	4.75	5.60	—	—

AEN : Anisaldehyde ethylenediamine

The ligand ST, in free state and in aqueous solution, is a yellow compound and absorbs light at 350 – 380 mμ range. It is observed that the absorbance of the 0.001M aqueous solution of ST at λ_{max} 380 mμ is a function of pH and the graph of absorbance vs pH has the same shape as that of $E_{\frac{1}{2}}$ vis pH (Fig. 3).

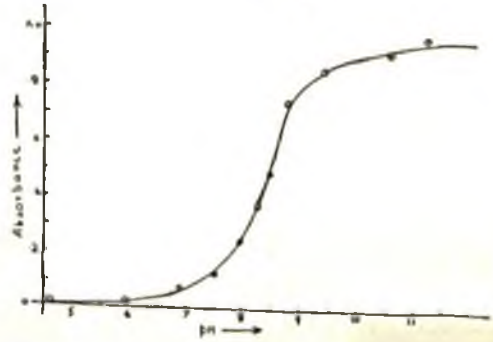


Fig. 3. Absorbance of ST (0.001M) as a function of pH

An attempt to calculate protonation constants from this graph gave the same value for pk_1 while the value of pk_2 is slightly different. A detailed study in this line is in progress.

The importance of polarographic method for evaluation of ligand-protonation constant lies in the fact that the constant can be obtained even when the ligand is not available in the free form, which is not possible for the potentiometric method. For any complex species which give the curve of the type shown in Fig. 1, proton – ligand stability constant can be determined by the method suggested.

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