Potentiometric Studies on the Complexes of Some Trivalent Metal ions with Schiff Bases

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The successive stability constants of the complexes of N-(2-hydroxy-5-phenylbenzylidene)-2' -methyl-aniline and N-(2-hydroxy-5-phenylbenzylidene) -2', 6'-dimethyl-aniline with Y^{3+}, Dy^{3+}, Pr^{3+}, Gd^{3+} and Sm^{3+} metal ions have been determined potentiometrically.

The present communication embodies the stability constants of Pr^{+3}, Dy^{+3}, Gd^{+3}, Y^{+3} and Sm^{+3} chelates of Schiff base N-(2-hydroxy-5-phenylbenzylidene)-2' -methylaniline and N-(2-hydroxy-5-phenylbenzylidene)-2',6'-dimethylaniline using pH titration techniques as adopted by Irving and Rossotti(1).

EXPERIMENTAL

The above title schiff bases were synthesized by condensing ethanolic solution of equimolar quantities of 4-hydroxy-3-aldehydobiphenyl and 2-methylaniline and 2,6-dimethylaniline respectively. The products obtained were repeatedly crystallised from appropriate solvents to obtain analytically pure samples. The purity was tested by TLC, IR, and elemental analysis

(i) Calculated for
$C_{20}H_{17}NO$: C, 83.62; H, 5.92; N, 4.88
Found : C, 82.58; H, 6.10; N, 4.74

(ii) Calculated for
$C_{21}H_{19}NO$: C, 83.72; H, 6.31; N, 4.65
Found : C, 82.73; H, 6.43; N, 4.64

All metal ion solutions were prepared from A.R. grade oxides or carbonates and were standardised by EDTA titrations(2). The strength of sodium hydroxide and perchloric acid were determined by usual methods.

TITRATION PROCEDURE:

Potentiometric titrations were carried out on an Elico Model LI-15 precision research pH meter (sensitive to 0.1 pH unit). All the titrations with (standard) sodium hydroxide were carried out in a specially designed cell maintained at the required temperature (30±0.1°C) by circulating water from a thermostatic bath. The details of the pH measurements are essentially the same as indicated by Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti(1).

The following solutions were titrated against standard carbonate free sodium hydroxide solution (1.067 M):

(i) the titration of the free acid (0.02 M $HClO_4$).

(ii) the titration of free perchloric acid + the reagent (L = 0.004 M), and

(iii) the titration of perchloric acid + the reagent and the metal perchlorate salt solution (M = 0.001M).

The ionic strength and composition of the mixture were maintained at 0.1 M ($NaClO_4$) and 75:25 v/v dioxan-water respectively. The titrations were performed in duplicate to ensure reproducibility.

RESULTS AND DISCUSSIONS

The $\bar{n}_A$ values were determined by the method of Irving and Mahnot and values were ploted to get the formation curves. The pK_1^H which corresponds to the association of proton to phenoxide ion of the reagent and the pK_2^H which corresponds to the association of proton to imino nitrogen were determined by half integral method. The plots of $\log [\bar{n}_A/(1-\bar{n}_A)]$ vs B and $\log [(2-\bar{n}_A)/(\bar{n}_A-1)]$ vs B (pH meter reading) were also drawn and from the former pK_1^H and from the latter pK_2^H values were determined. These values agree quite well with those obtained by half integral method.

Formation function $\bar{n}$ and pL were evaluated from the titration curves using standard expressions and $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of the metal complex ion equilibria (Fig.1 & 2). From the formation curves, the values of stability constants corresponding to 1:1 and 1:2 metal ligand complexes were determined from the value of pL at $\bar{n}$ = 0.5 and $\bar{n}$ = 1.5. These values further corroborated by plotting $\log [\bar{n}/(1-\bar{n})]$ and $\log [(2-\bar{n})/(\bar{n}-1)]$ vs pL.

These constants were also obtained by least square method. Limits of error(4) and standard deviation(5) for log K values were determined. The most representative values were recorded in Table 1. The order of stability constants was found to be $Dy^{+3} > Y^{+3} > Gd^{+3} > Sm^{+3} > Pr^{+3}$ for ligand N-(2-hydroxy-5-phenylbenzylidene)-2'-methylaniline. For the ligand N-(2-hydroxy-5-phenylbenzylidene)-2',6'-dimethlyaniline it was found to be $Dy^{+3} > Pr^{+3} > Y^{+3} > Gd^{+3} > Sm^{+3}$.

Plots of stability constants (log K_1) vs

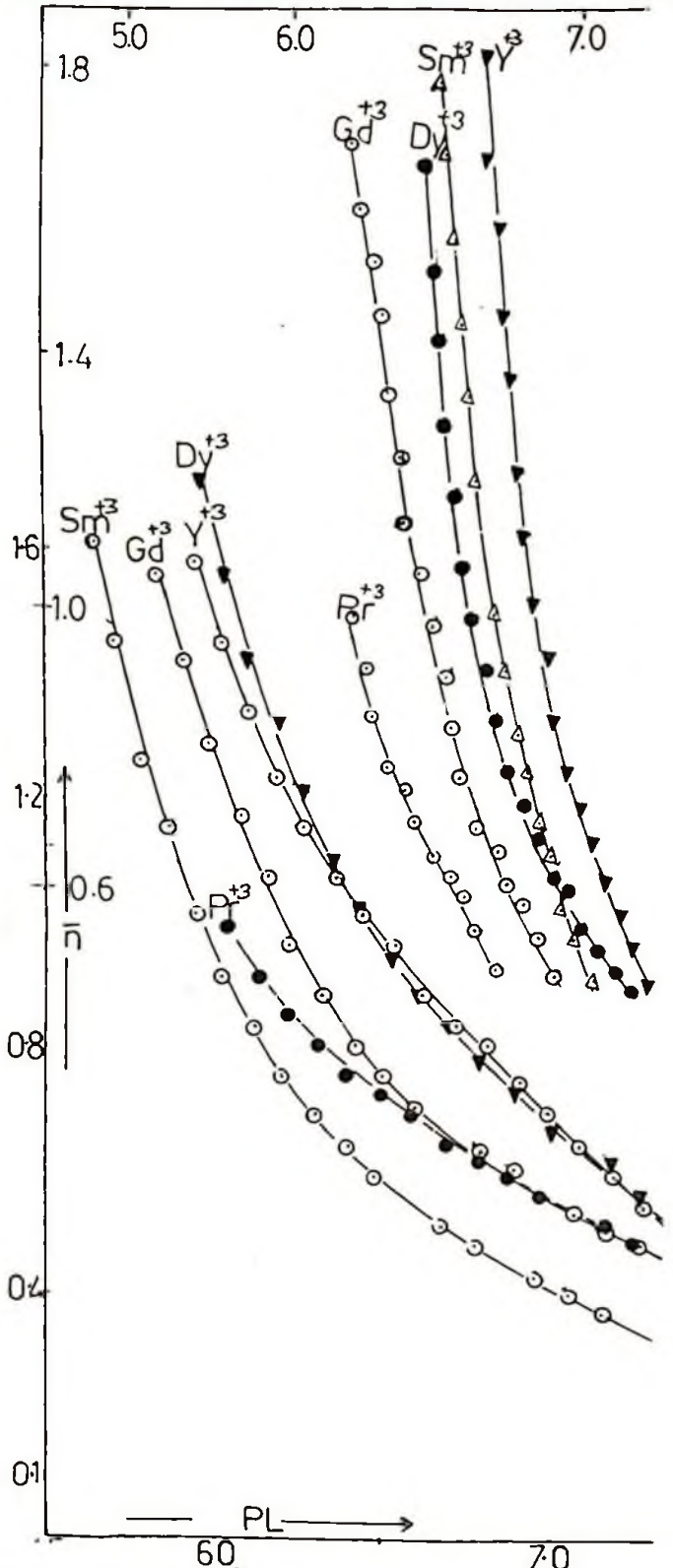


Fig. 1 Metal ligand systems-formation curves with

(A) ligand N-(2-hydroxy-5-phenylbenzyl-idine) -2'-methylaniline

(B) ligand N-(2-hydroxy-5-phenylbenzyl-idine) -2'-6'-dimethylaniline.

TABLE 1

VALUES OF PRACTICAL PROTON-LIGAND AND METAL—LIGAND STABILITY CONSTANTS.

t = 30±0.1°C Medium = Dioxan-Water (75:25 v/v) μ = 0.1 M

Metal ion	log K_1	log K_2	Standard deviation	Error
i) N-(2-hydroxy-5-phenylbenzylidene)-2'-Methylaniline.				
H^+	9.48 (pK^H_{OH})	2.78 (pK^H_{NH})		
Dy^{+3}	7.27±0.04	5.84±0.06	± 0.14	± 0.07
Pr^{+3}	6.66±0.04	5.14±0.07	± 0.12	± 0.07
Y^{+3}	7.02±0.03	5.73±0.06	± 0.08	± 0.05
Gd^{+3}	6.99±0.04	5.65±0.05	± 0.10	± 0.05
Sm^{+3}	6.72±0.02	5.65±0.01	± 0.05	± 0.03
ii) N-(2-hydroxy-5-phenylbenzylidene)-2', 6'-dimethylaniline				
H^+	9.31(pK^H_{OH})	2.29 (pK^H_{NH})		
Dy^{+3}	7.36±0.01	5.78±0.04	± 0.21	± 0.11
Pr^{+3}	6.93±0.04	4.91±0.09	± 0.14	± 0.06
Y^{+3}	6.92±0.04	6.01±0.02	± 0.16	± 0.07
Gd^{+3}	6.81±0.04	5.41±0.02	± 0.15	± 0.06
Sm^{+3}	6.67±0.05	5.46±0.05	± 0.14	± 0.08

ionization energies were drawn to explore any possible correlation. A straight line relationship was observed indicating ionization energies are parallel to log K values of the metal complexes (Fig.3).

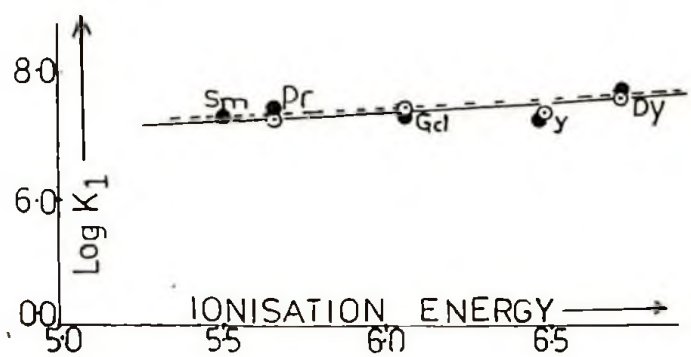


Fig. 3 Open circles and continous line refer to the ligand N-(2-hydroxy-5-phenyl-benzylidine)-2-methyl-aniline closed circles and dashed line refers to the ligand N-(2-hydroxy-5-phenylbenzylidine)-2',6'-dimethylaniline

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