Asian Journal of Chemistry Vol. 15, Nos. 3 & 4 (2003), 1429–1434

Determination of Stability Constants of Some Transition Metal Complexes of 2-Hydroxybenzylidine-4-Toluidine

AMEYA RAUT, PULKESHI DESAI and KIRAN MANGAONKAR*

Department of Chemistry, Ramnarain Ruia College, Mumbai-400 019, India

Proton dissociation constants of the ligand 2-hydroxybenzylidine-4-toluidine and the stability constants of its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been determined potentiometrically at 30 ± 0.1°C and at ionic strength 0.1 M in 75 : 25 (v/v) dioxane-water medium. The values log K_1 and log K_2 have been determined. The stabilities of the chelates follow the order Cu > Zn > Co > Cd > Ni.

Key Words: Stability constant, Transition metal, Complexes, 2-Hydroxybenzylidine-4-toludine.

INTRODUCTION

In solution, metal-complexes result from the reversible association of one or more metal ions with the ligand molecules and laws of chemical equilibria are applicable to them. The stability denotes the extent of association in solutions containing two or more species in equilibrium, and greater the association, more stable is the complex. The term 'equilibrium constant', which is a more general one, assumes a new name and is referred to as 'stability constant'.

The successive stability constants of the complexes of 2-hydroxybenzylidine-4-toluidine with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been determined potentiometrically following the Calvin-Bjerrum pH titration technique adopted by Irving and Rossotti[1].

EXPERIMENTAL

The pH titrations were carried out on an expanded scale pH-meter model No. EQ-614 supplied by Equiptronics, a precision research pH-meter with a wide range glass electrode and a calomel reference electrode. The pH-meter has an arrangement for normal and expanded scale. The smallest scale division on the expanded scale is 0.01 pH unit.

The ligand 2-hydroxybenzylidine-4-toluidine was synthesized and crystallized to get an analytically pure sample.

The medium of titration was dioxane-water mixture 75 : 25 (v/v). The dioxane used for the experiments was purified by the method described by Vogel[2]. Distilled water, redistilled over alkaline potassium permanganate made free from carbon dioxide by boiling, used throughout the investigation. Sodium perchlorate (AR) salt was dried in a desiccator and requisite amount of it was dissolved in double distilled water to obtain 0.64 M solution. Metal perchlorates were prepared by dissolving a requisite amount of metal oxides or carbonates in perchloric acid (1.6 M), the final metal concentration being 0.08 M in 0.16 M perchloric acid. The concentrations of metal ions in solution were determined by complexometric titrations[3].

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1 M) [N′] solution keeping the total volume 40 mL [V_0].

(i) 5 mL of (0.16 M) $HClO_4$ + 5 mL of (0.64 M) $NaClO_4$ + 30 mL of dioxane [amount of NaOH required for titration = V′].

(ii) 5 mL of (0.16 M) $HClO_4$ + 5 mL of (0.64 M) $NaClO_4$ + requisite amount of the reagent accurately weighed to give 0.004 M [T_L^0] reagent concentration in the final solution + 30 mL of dioxane [amount of NaOH required for titration = V″].

(iii) 5 mL of (0.64 M) $NaClO_4$ + 5 mL of (0.001 M) metal salt solution in (0.16 M) $HClO_4$ + requisite amount of the reagent accurately weighed to give 0.004 M reagent concentration in the final solution + 30 mL of dioxane [amount of NaOH required for titration = V‴].

The method of Irving and Rossoti[1] was applied to find out the values of $\bar{n}$ and pL.

RESULTS AND DISCUSSION

In the ligand, the chelated phenolic 'OH' group takes part in the complex formation and the proton is replaced from it by metal ions during the formation of metal chelates. In the present investigation, 'Y', the total number of dissociable protons attached to a ligand molecule is one for the reagent.

nA is calculated by using the following form:

$$\bar{n}A = Y + \frac{(V' - V'')(N' + E^0)}{(V^0 + V')T_L^0}$$

From the titration curves using the solution (i) and (ii), $\bar{n}A$ values at various 'B' values (pH-meter readings) were calculated, and the curve between 'B' and the corresponding $\bar{n}A$ values was plotted (Fig. 1). The formation curve extends over a range $0.4 < \bar{n}A < 1.51$ and is wavelike. This indicates the formation of the species HL and H_2L, *i.e.*, the protonated nitrogen and the phenolic hydrogen are completely dissociable in steps, separable. In other words, in the case of these compounds the dissociation of phenolic hydrogen commences only after the protonated nitrogen is completely dissociated. The values of pK_1H and pK_2H could be evaluated from half integral point at $\bar{n}A = 0.5$ and 1.5 respectively.

A plot of log $[\bar{n}A/(1 - \bar{n}A)]$ against 'B' (Fig. 2) and log $[2 - nA/(nA - 1)]$ against 'B' (Fig. 3) were drawn. From these curves the values of pK_1H and pK_2H were evaluated. The two values agree fairly well.

From the plot of n against pL (Fig. 4), n values for Co(II), Cu(II), Zn(II) and Cd(II) metals extend over the range of $0.06 < \bar{n} < 1.8$ and hence log K_1 and log K_2 have been obtained by the half-integral method. For Ni(II) metal the $\bar{n}$ values obtained unto 0.91 and hence only log K_1 values have been obtained indicating the complete formation of 1 : 1 complex.

A plot of log $[\bar{n}/(1 - \bar{n})]$ against 'pL' (Fig. 5) and log $[2 - n/(n - 1)]$ against 'pL' (Fig. 6) were drawn. From these curves the values of log K_1 and log K_2 were evaluated. The two values agree fairly well (Table-1).

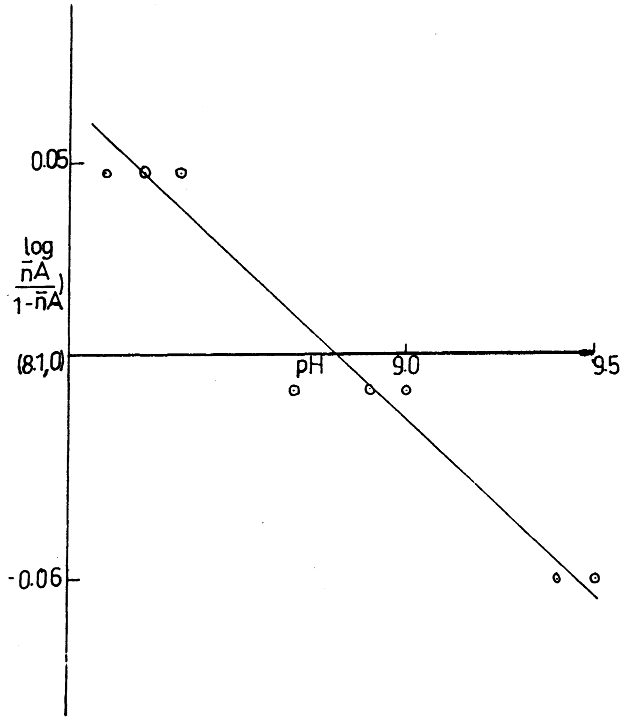

Fig. 1. Formation curve of 2-hydroxybenzylidine-N-4-toluidene

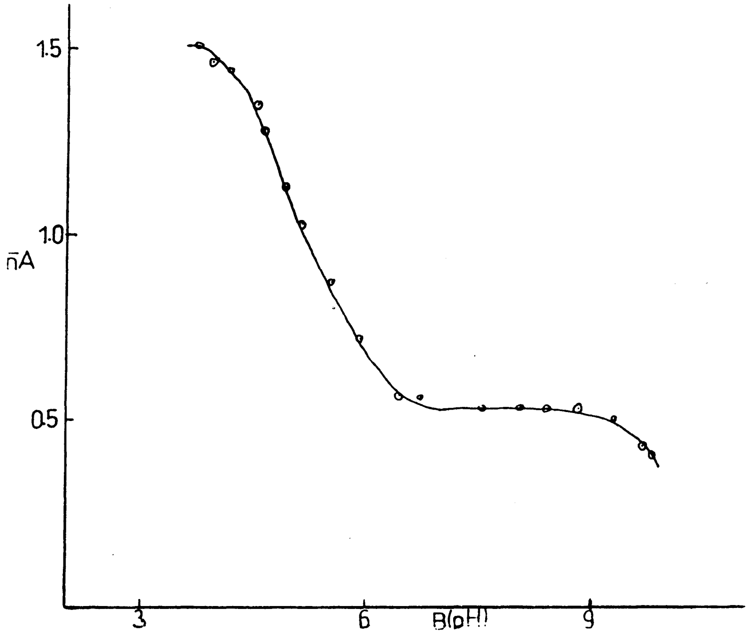

Fig. 2. A plot of log [$\bar{n}$A/1 – $\bar{n}$A] *vs.* B (pH-meter reading)

0.05 log ($\frac{\bar{n}A}{\quad}$) (8.1, 0 –0.06)

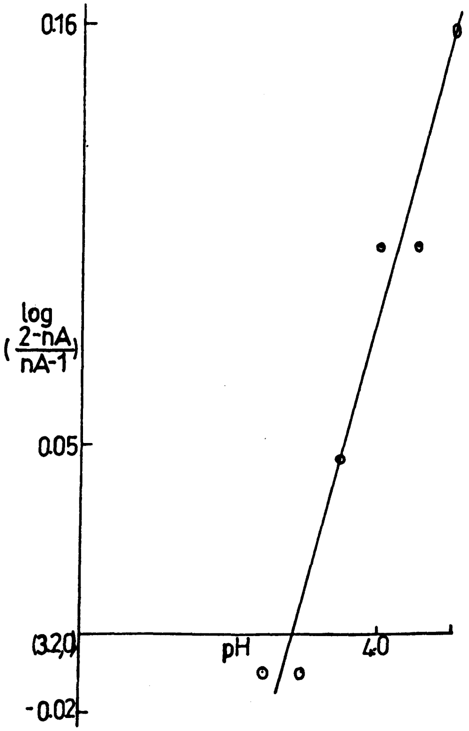

Fig. 3. Metal-ligand systems of 2-hydroxybenzylidine-N-4-toluidene formation curves

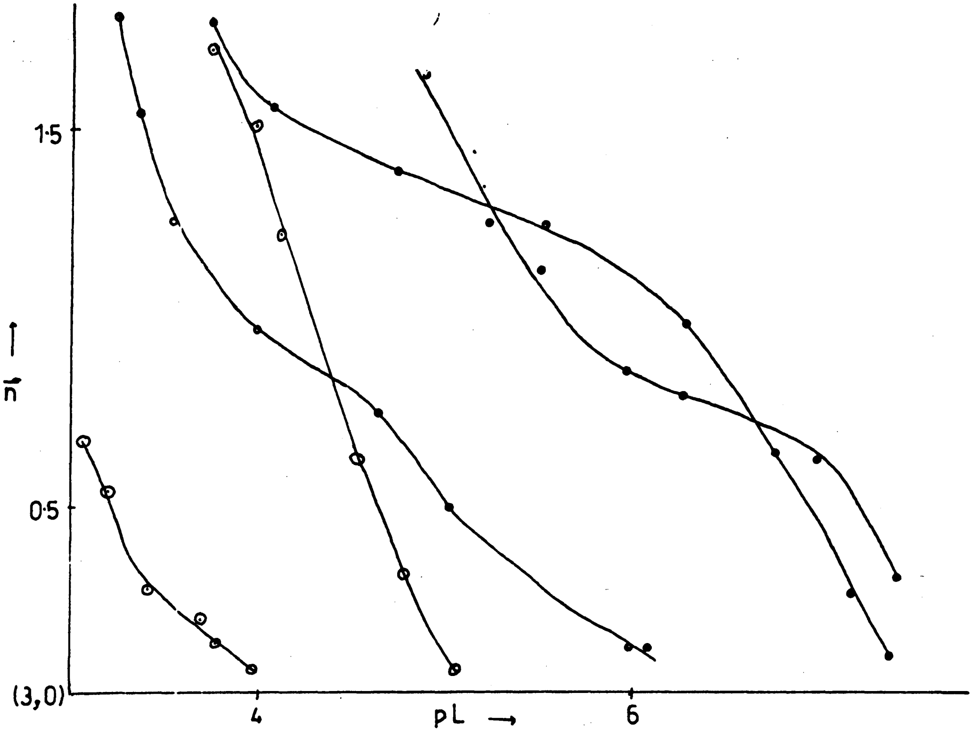

Fig. 4. Plot of n *vs.* pL for Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes

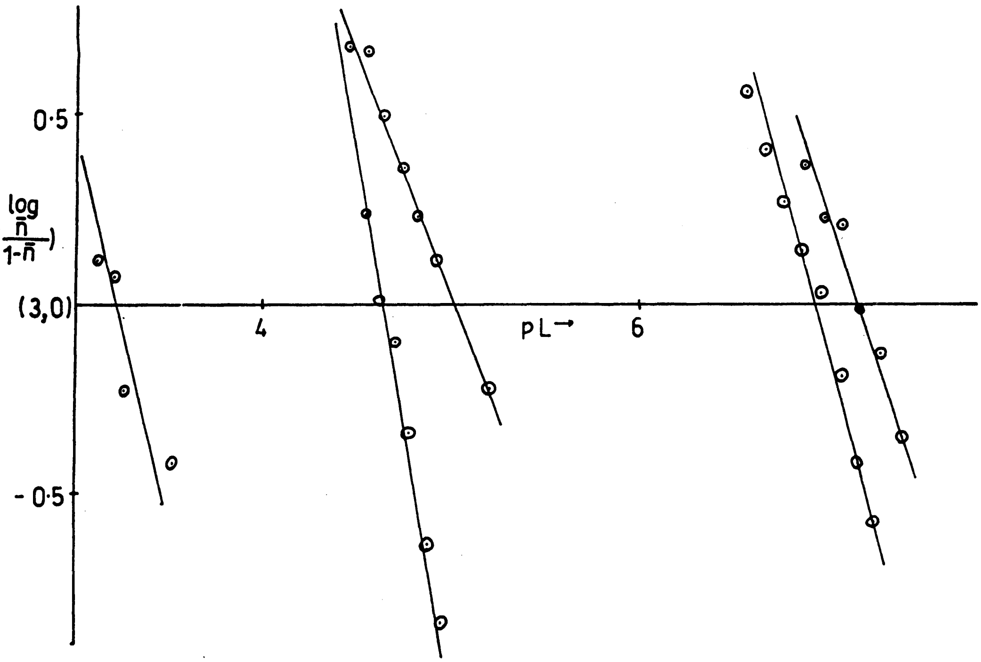

Fig. 5. Plot of log $\left[\frac{\bar{n}}{1}-\bar{n}\right]$ *vs.* pL for Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes

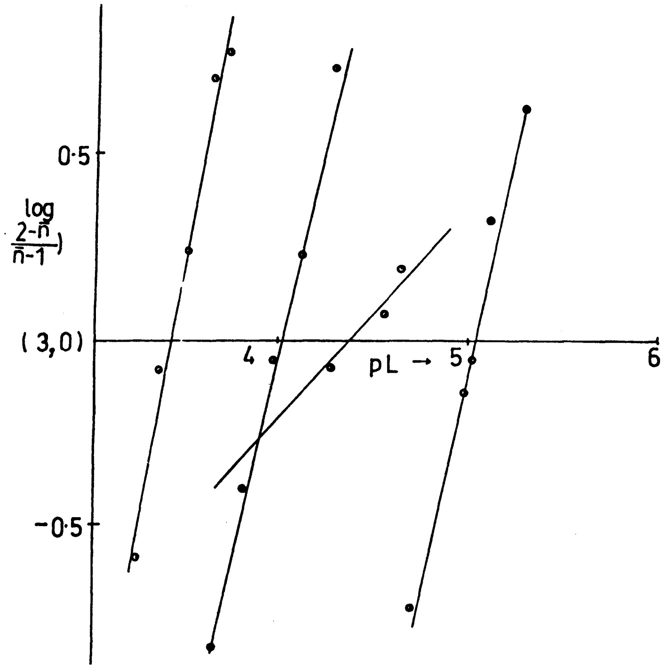

Fig. 6. Plot of log $\left[\frac{(2-n)}{(n-1)}\right]$ *vs.* pL for metal-complexes

TABLE–1
STEPWISE STABILITY CONSTANTS OF METAL-COMPLEXES OF 2-HYDROXYBENZALIDINE-4-TOLUIDINE

Temp. (t) = 30°C; Ionic strength (μ) = 0.1 M.

Cations	H^+	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
log K_1	9.14	5.02	3.25	7.20	6.94	4.64
log K_2	3.76	3.40	—	5.04	4.33	3.98

H^+ correspond to the species LH and LH_2 respectively, while for the metal ions K_1 and K_2 correspond to the species ML_1 and ML_2 respectively.

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(*Received*: 19 December 2002; *Accepted*: 9 April 2003) AJC–3142