

## Graphical methods of determination of stability constants of metal complexes using spectrophotometric and ion-selective electrode measurement data : cobalt(II)-PAR complex

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A new heterogeneous Co<sup>II</sup>-ion selective electrode has been developed and its characteristics have been studied. Using the electrode the stability constant of the complexes formed by Co<sup>II</sup>-ion with 4-(2-pyridylazo)resorcinol (PAR) has been determined ( $\log \beta_2 = 19.75$ ) involving a graphical method. Stability constant of 1 : 2 complexes, determined by the ion-selective electrode ( $\log \beta_2 = 19.75$ ) agrees well with the value ( $\log \beta_2 = 19.6$ ) determined by spectrophotometric method.

4-(2-Pyridylazo)resorcinol (PAR) has been found useful as a colorimetric reagent, as amperometric reagent for trace determination. Metal complexes of PAR have been studied in water as well as in dioxane-water mixture by pH-titration technique. Several workers have also studied the stability constant of the metal complexes spectrophotometrically.

However, the stability constant data available in the literature either have incomplete information (do not incorporate the dissociation of ligand) or not consistent with each other. With this in view the Co<sup>II</sup>-PAR system was reinvestigated using two different techniques, spectrophotometry and potentiometry. The potentiometric study has been carried out using new Co<sup>II</sup>-ion-selective electrode, which is found to be a improved electrode over those reported in the literature<sup>5</sup>.

For calculation of stability constant of the complex using spectrophotometric data, the graphical method of calculations developed in this laboratory for 1 : 1 complex<sup>6</sup> has been modified for higher complexes and the results of the stability constants determined by the two techniques are compared.

### Results and Discussion

#### (a) Spectrophotometric technique :

Job's method of continuous variations at wavelength of 510 nm revealed that Co<sup>II</sup> forms a 1 : 2 complex with PAR in the pH range 4–7.

**Stability constant :** A series of solutions were prepared by mixing cobalt chloride and PAR in 1 : 2 ratio. The absor-

bance of each solution was recorded at 510 nm. For the determination of molar absorptivity and the apparent stability constant using the eqn. (4), given in the section calculations, in a computer based program, the first trial value of  $\epsilon$  was taken as  $1 \times 10^5$  and using the data and eqn. (4) a plot was constructed by the method of least-squares. From the slope of linear graph new value of  $\epsilon$  was obtained. This new value of  $\epsilon$  was used as trial in next iteration to get a fresh value of  $\epsilon$ . The process was continued till two successive values were the same. From the final value of  $\epsilon$  and the intercept of linear equation,  $\beta'_2$  was calculated. If one chooses the trial value less than in subsequent iterations the value of  $\epsilon$  increases and  $\beta'_2$  decreases. In order to calculate the stability constant, the value of  $\beta'_2$  has to be multiplied by  $\phi = 1 + \frac{[H]}{K_{d1}} + \frac{[H]^2}{K_{d1}K_{d2}}$  where  $K_{d1}$  and  $K_{d2}$  are the respective dissociation constant of PAR, taken from the literature<sup>7</sup>. The value of stability constant ( $\log \beta_2$ ) was found to be 19.6.

**(b) Ion-selective electrode method : Characteristics of electrode. Electrode response :** The electrode was first conditioned in 0.1 mol dm<sup>-3</sup> solution of Co<sup>II</sup> ion till it attained stable equilibrium after which it was used for determination of the characteristics of the electrode. The electrode potentials for a series of standard solutions of Co<sup>II</sup> ion were measured. The electrode gave a linear response to Co<sup>II</sup> ion in the concentration range  $1.0 \times 10^{-1}$  to  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup>. The slope was found to be 27 mV/decade change in Co<sup>II</sup>-ion concentration.

**Response time :** The electrode was first dipped in 0.01

mol dm<sup>-3</sup> of Co<sup>II</sup> ion solution and suddenly the concentration of solution was changed to 0.001 mol dm<sup>-3</sup>. It took 35 s to give a constant potential. Hence 35 s may be regarded as the response time of the electrode.

**Effect of pH :** A series of solutions containing 0.01 mol dm<sup>-3</sup> Co<sup>II</sup> solution was prepared in which the pH was varied by the addition of a dilute solution of NaOH or HCl. It was found that the potential remained unchanged within the pH range 2.0–8.0, which is the working range of pH for the electrode.

**Interference by different cations :** The cationic interference due to other ions were studied by the determination of selectivity coefficients by mixed solution method<sup>7</sup>. The electrode potentials were recorded in mixed solutions having a fixed concentration of interferent ion, B, (1 × 10<sup>-3</sup> mol dm<sup>-3</sup>) and varying concentrations (1 × 10<sup>-1</sup> to 1.0 × 10<sup>-6</sup> mol dm<sup>-3</sup>) of solutions of Co<sup>II</sup> ion. The selectivity coefficients were calculated from the plot of potential of electrode system vs concentration in the usual manner. The selectivity coefficients determined for several cations are as follows : Mg<sup>II</sup>–0.08, Mn<sup>II</sup> and Zn<sup>II</sup>–0.20, Cu<sup>II</sup>–0.10, Ni<sup>II</sup>–0.40, Al<sup>III</sup>–0.07.

**Stability constant :** A series of solutions were prepared in which the concentrations of the metal and ligand were kept constant, but pH was varied in the range 6.38–6.99. The electrode potentials of each solution was measured and the corresponding values of concentration of Co<sup>II</sup> ion were obtained from the calibration curve. The dissociation constant being known<sup>8</sup>, the free ligand concentration and therefore, the value of stability constant (log β<sub>2</sub>) was calculated to be 19.75.

Thus we see that the stability constant value obtained from the graphical method using the spectrophotometric data agrees quite well with the value obtained by another graphical method using the data obtained with Co<sup>II</sup> ion selective electrode.

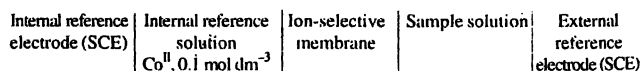
## Experimental

The stock solutions of Co<sup>II</sup> were prepared by dissolving CoCl<sub>2</sub>·6H<sub>2</sub>O (Sarabhai Chemicals) in double-distilled water. The stock solution of the ligand PAR (E. Merck) was prepared in double-distilled water. Solutions of required concentrations were obtained by appropriate dilution of the stock solutions.

**Preparation of membrane and electrode :** Thiopentone [sodium-5-ethyl-5-(1-methylbutyl)-2-thiobarbiturate] was chosen as the ligand for the preparation of Co<sup>II</sup>-thiopentone complex. To a solution of thiopentone (Abbot Lab. (India);

0.528 g) CoCl<sub>2</sub>·6H<sub>2</sub>O (0.238 g) solution was added, when a light purple coloured precipitate was obtained. The solution was allowed to evaporate at room temperature (~30°) for a few days. The resulting solid was washed with double-distilled water, dried and used as an electroactive material for the electrode.

The electroactive material (150 mg) was mixed with 600 mg of Araldite (Ciba-Geigy) and the paste was applied on Whatman filter paper (No. 42). It was spread uniformly over the filter paper to obtain a 0.1 mm thick layer of the electroactive material with matrix and left in air to dry for 48 h. To prepare the electrode, the filter paper was separated from the membrane by dipping it in a solution of Ni<sup>II</sup> ion. Any portion of the filter paper adhering to the surface of the membrane was removed to obtain a disc. A small portion was cut out from the disc, fixed with Araldite to one end of a glass tube (dia. 1 cm × 15 cm) and allowed to dry for 24 h. The tube was then filled with 0.1 mol dm<sup>-3</sup> Co<sup>II</sup>-ion solution and kept immersed in a solution of 0.1 mol dm<sup>-3</sup> Co<sup>II</sup>-ion solution for 7 days. The internal and external reference electrodes were saturated calomel electrodes. The entire electrode system for the measurement can be represented as



The pH was measured on Orion Research Ionalyzer-901 and a combined glass electrode. A Sicospec 200 GL spectrophotometer was used. A Philips PR 9405 pH meter with a saturated calomel electrode was used. All measurements were made at room temperature (25 ± 2°). Double-distilled water was used in all experiments.

## Calculations :

(a) **Spectrophotometric method :** Chattopadhyaya<sup>6</sup> developed a graphical method which does not employ an excess of ligand and also does not neglect any term for determination of 1 : 1 complex. The same approach was extended in present work for higher complexes.

Considering the formation of 1 : 2 species,



the stability constant can be expressed as

$$\beta'_2 = \frac{[ML_2]}{(M^0 - [ML_2])(L^0 - 2[ML_2])^2} \quad (2)$$

If metal ion, ligand and complex absorb light in the spectral region of study of absorbance (A) for unit path-length, it can be expressed as

$$A = (M^0 - [ML_2])\epsilon_M + (L^0 - 2[ML_2])\epsilon_L + [ML_2]\epsilon_{ML_2} \quad (3)$$

where  $\epsilon_M$ ,  $\epsilon_L$  and  $\epsilon_{ML_2}$  are the molar absorptivity of the species M, L and  $ML_2$ , respectively. On combining eqn. (2) with (3) and rearranging, we get,

$$\frac{M^0(L^0)^2}{A - \epsilon} - \frac{4(A - \epsilon)^2}{\epsilon_p^3} + \frac{4(A - \epsilon)(M^0 + L^0)}{\epsilon_p^2} = \frac{[4M^0L^0 + (L^0)^2]}{\epsilon_p} + \frac{1}{\epsilon_2\epsilon_p} \quad (4)$$

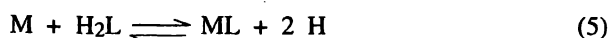
where,  $\epsilon_p = \epsilon_{ML_2} - 2\epsilon_L - \epsilon_M$

and  $\epsilon = M^0\epsilon_M + L^0\epsilon_L$

Now, if the left-hand-side of eqn. (4) is plotted against  $[4M^0L^0 + (L^0)^2]$ , a straight line of gradient  $1/\epsilon_p$  and intercept  $1/\beta_2\epsilon_p$ , will be obtained.

(b) Ion-selective electrode method :

Consider the following metal-ligand equilibria,



$$K_1'' = \frac{[ML][H]^2}{[M][H_2L]} \quad (6)$$

where  $K_1''$  is conditional stability constant at a defined ionic strength. If  $K_1''$  is determined at constant pH, a new expression for the stability constant can be written as

$$K_1' = \frac{[ML]}{[M][H_2L]} \quad (7)$$

But, the stability constant for 1 : 1 complex is given as

$$K_1 = \frac{[ML]}{[M][L]} \quad (8)$$

For a ligand with two dissociable protons, one can write,



Charges are omitted for simplicity,

$$K_{d1} = \frac{[HL][H]}{H_2L} \quad (11)$$

and

$$K_{d2} = \frac{[L][H]}{[HL]} \quad (12)$$

From eqns. (11) and (12),

$$[H_2L] = \frac{[L][H]^2}{K_{d1}K_{d2}} \quad (13)$$

Thus, total free ligand concentration,

$$\begin{aligned} L^0 &= [H_2L] + [HL] + [L] \\ &= \frac{[L][H]^2}{K_{d1}K_{d2}} + \frac{[L][H]}{K_{d2}} + [L] \\ &= \left( \frac{[H]^2}{K_{d1}K_{d2}} + \frac{[H]}{K_{d2}} + 1 \right) [L] \end{aligned} \quad (14)$$

If, we write,

$$\phi = \frac{[H]^2}{K_{d1}K_{d2}} + \frac{[H]}{K_{d2}} + 1 \quad (15)$$

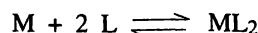
then,  $L^0 = [L]\phi$

$$\text{or } [L] = \frac{L^0}{\phi} \quad (16)$$

$$K_1 = \frac{[ML]}{[M][L]} = \frac{[ML]}{[M][H_2L]}\phi$$

$$\text{or } K_1 = K_1'\phi \quad (17)$$

Similarly, for 1 : 2 complex,



$$\beta_2 = \frac{[ML_2]}{[M][L]^2}\phi^2 \quad (18)$$

$$\text{or } \beta_2' = \frac{[ML_2]}{[M][L]^2} \quad (19)$$

where  $\beta_2'$  is conditional stability constant whose value is determined at constant pH and  $\beta_2$  is stability constant. The relation between the two constants are given by

$$\beta_2 = \beta_2'\phi^2 \quad (20)$$

Eqns. (17) and (18) can be multiplied by correction factor  $F$  to take into account the hydrolysis of the metal ions.

$$\text{where, } F = 1 + \frac{k_{h1}}{[H^+]} + \frac{k_{h1}k_{h2}}{[H^+]^2} \quad (21)$$

where  $k_{h1}$  and  $k_{h2}$  are hydrolysis constants of metal ions and  $[H^+]$  is hydrogen ion concentration.

Under the experimental conditions, if the pH is varied,  $K_1'\phi$  and  $F$  would vary and  $K_1'$  can be expressed as

$$K_1' = \frac{K_1(\text{True})}{\phi F} \quad (22)$$

Eqn. (7) could be written as

$$K_1' = \frac{[ML]}{(M^0 - [ML])(L^0 - [ML])} \quad (23)$$

and rearranging the same we get,

$$\frac{[M]L^0}{M^0 - [M]} = \frac{1}{K_1'} \quad (24)$$

From eqns. (23) and (24), we obtain eqn. (25),

$$\frac{[M]}{(M^0 - [M])}\frac{1}{\phi F} = \frac{1}{K_1(\text{True})L^0} + \frac{[M]}{\phi F}\frac{1}{L^0} \quad (25)$$

If total metal and ligand concentrations are kept constant, a plot of  $\frac{[M]}{(M^0 - [M])}\frac{1}{\phi F}$  against  $\frac{[M]}{\phi F}$  will give a straight-line

with slope equal to  $1/L^0$  and intercept equal to  $1/K_{1(\text{True})}L^0$ , thus, true value of stability constant of 1 : 1 complex can be obtained.

The stability constant for 1 : 2 complex can be shown to be related to other parameters as follows :

$$\frac{[M]L^0}{(M^0 - [M])\phi^2} = \frac{1}{\beta_2 L^0} + \frac{4[M]\{L^0(M^0 - [M])\}}{\phi^2 L^0} \quad (26)$$

If total metal and ligand concentrations are kept constants, a plot of  $\frac{[M]L^0}{(M^0 - [M])\phi}$  against  $\frac{[M]L^0 - (M^0 - [M])}{\phi^2 L^0}$  will give a straight-line with an intercept equal to  $1/\beta_2 L^0$ , thus enabling one to calculate the true value of stability constant of 1 : 2 complex<sup>9</sup>. If, however, the hydrolysis constant of the metal has to be taken into account to calculate the true value of the stability constant then the graph can be constructed from a plot of  $\frac{[M]L^0}{(M^0 - [M])\phi^2 F}$  versus  $\frac{[M](L^0 - (M^0 - [M]))}{\phi^2 F L^0}$ .

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9. The relationship between free metal ion concentration and the electrode potential is given by Nernst equation. In the present case, the slope of the Nernst relation is 27 mV per decade change in  $\text{Co}^{\text{II}}$  ion concentration. From the calibration curve and using the electrode potential the free metal ion concentration was determined, which was substituted in eqn. (26) to evaluate the value of stability constant,  $\beta_2$ .