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SHORT COMMUNICATIONS

DETERMINATION OF STABILITY CONSTANT OF 1:1 LANTHANUM(III)-CHROMOTROPE-2B COMPLEX BY A GRAPHICAL METHOD USING NOVEL MEMBRANE AND COATED WIRE ELECTRODES

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ABSTRACT. A new approach for determining the stability constant of complexes using ion-selective electrode (ISE) as well as a coated wire ion-selective electrode (CWISE) as sensors has been developed. The membrane for ISE is based on the electroactive material using precipitated lanthanum cupferron complex. The CWISE is liquid ion exchanger based involving 20% Aliquot 336S in xylene hardened by PVC in THF. The characteristics of the two electrodes are reported. The stability constant (log K_1) of La(III) complex of *p*-nitrobenzeneazochromotropic acid (chromotrope-2B) using both the electrodes lie between 7.97 and 8.55 at 30°, at an ionic strength of 0.1 M.

INTRODUCTION

With increasing applications of ion-selective electrodes (ISEs) in equilibrium studies [1], it was considered to be of interest to develop graphical methods for the calculation of stability constants.

In this communication, we describe one such approach for determining the stability constant of 1:1 complex choosing lanthanum(III)-*p*-nitrobenzeneazochromotropic acid (chromotrope-2B, CTB) for study.

New electrodes for La(III) ion have been developed and their characteristics studied. An attempt has been also been made for the first time to use a coated wire ISE for the determination of metal-ligand stability constant, which has an added advantage that it requires very small volume of solutions for measurements.

Theory. For the following metal-ligand equilibrium

$$M + H_nL \rightleftharpoons ML + nH^+ \tag{1}$$

$$K_1 = K_1' \, \Phi \, F \quad where \; \Phi = \left(\frac{1 + [H^+]}{K_{d_1}}\right) \tag{2}$$

or

$$\Phi = \left(\frac{1 + [H^+]}{K_{d_1}} + \frac{[H^+]^2}{K_{d_1}K_{d_2}}\right) \tag{3}$$

depending, respectively, upon whether the number of dissociable protons of the ligand is one or two. K_1' is the conditional stability constant and is given by

$$K_1' = \frac{[ML]}{(M^{\circ} - [ML])\,(L^{\circ} - [ML])} \qquad (4)$$

where M° and L° are the total metal and ligand concentrations, respectively.

K_{d_1} and K_{d_2} are the first and second dissociation constants of the ligand, respectively. F is the correction factor for hydrolysis of metal ion, F is given by

$$9F = \frac{1 + K_h}{[H^+]} \qquad (5)$$

where K_h is the hydrolysis constant of the metal ion.

At constant pH. Equation (4) on rearrangement gives

$$\frac{[M]\,L^{\circ}}{M^{\circ} - [M]} = \frac{1}{K_1'} + [M] \qquad (6)$$

Hence a plot of $[M]L^{\circ} / (M^{\circ} - [M])$ against [M] would give a straight line with unit slope and intercept as $1/K_1$ where from K_1 can be calculated.

At varying pH. When the pH is varied, K_1' and F would vary and K_1' can be expressed as

$$K_1' = K_1 \,.\, \Phi \,.\, F \qquad (7)$$

from equation (4) and (7) one can arrive at equation (8)

$$\frac{[M]}{M^{\circ} - [M]} \cdot \frac{1}{\Phi F} = \frac{1}{K_1 L^{\circ}} + \frac{[M]}{\Phi F} \cdot \frac{1}{L^{\circ}} \qquad (8)$$

If total metal and ligand concentration are kept constant, a plot of $[M]/(M^{\circ} - [M]).\ 1/\Phi F$ against $[M]/\Phi F$ would give a straight line with slope equal to $1/L^{\circ}$ and intercept equal to $1/K_1L^{\circ}$ thus enabling the evaluation of the corrected values of stability constant of a 1:1 complex.

EXPERIMENTAL

Double distilled water was used throughout the experiments. A solution of lanthanum nitrate was prepared by dissolving 0.5 g of lanthanum nitrate in 100 ml water. Solution of Cupferron was prepared by dissolving 1.0 g cupferron in 100 ml of 20% ethanol.

Preparation of electrodes.

La(III) ion-selective membrane electrode. To a 20 ml aliquot of lanthanum nitrate solution cupferron solution was added drop-wise to obtain a light yellow precipitate [2] of $La(C_6H_5N.OH.ONH_4)$. The precipitate was washed thoroughly with 20% ethanol, followed by water. After air drying, the precipitate was powered and 0.4 g precipitate was mixed with 0.1 g PVC (dissolved in 6 ml of THF). To this 2-3 drops of plasticizer (dibutylphthalate) was added and the solution was allowed to evaporate over a dry glass plate, when a membrane was obtained. The membrane was then cut from the master disc and fixed at the end of a glass tube with the help of Araldite (Ciba-Giegy, India). The tube was filled with 0.01 M solution of La $(NO_3)_3$ which acted as an internal reference solution and a saturated calomel electrode was used as an internal reference electrode.

La(III) ion-selective coated wire electrode. Lanthanum nitrate solution (100 ml) was added to a 10 ml solution of 20% Aliquot 336S in xylene [3]. The acidity was adjusted to 0.1 M HNO_3. The resultant solution was shaken in a 250 ml separatory funnel for 4 h after which the organic phase separated [4] and was used as the electroactive material. A small amount of the electroactive material was mixed with (0.1 g) polyvinylchloride (PVC) in 6 ml THF and 0.5 g Araldite was added for hardness. A cleaned copper wire was dipped in the above solution several times for coating till a bead formed at the tip [5]. The electrode thus prepared was kept immersed overnight in 0.1 M lanthanum nitrate solution.

Instrument. A Phillips pH meter (Model PR 9405M) was used for potential measurements with a calomel electrode as reference electrode. All measurements were performed at a room temperature of 30 ± 1°. The cell assembly used for potential measurement using membrane electrode can be represented as: internal reference electrode (SCE)/La^{3+} (0.01 M), NO_3^-(0.03 M)/membrane/sample solution/external reference electrode (SCE). The cell assembly involving coated wire electrode can be represented as metal/membrane/sample solution/external reference electrode (SCE).

Stability Constants. In order to determine the stability constant of La(III)-CTB complex, two sets of solutions were prepared. In one set of solutions the metal ion and ligand concentrations were kept at 1×10^{-4} M and pH was varied in the range 5 to 6. An ionic strength of 0.1 M was maintained using sodium perchlorate. After allowing the solution to stand for one hour, the potential of each solution was measured with both the membrane as well as coated wire electrodes. Free metal ion concentration was then calculated [6].

In another set, the pH was kept constant at pH 6 and the total ligand concentration was varied in the range 1×10^{-4} to 4×10^{-4} M while maintaining the ionic strength at 0.1 M (sodium perchlorate). For each solution, the free metal ion concentration was determined from the potential measurements using the electrodes [6].

RESULTS AND DISCUSSIONS

The ISE for La(III) ion gave a linear response down to the concentration 1×10^{-6} M. The slope was found to be 20 mV per decade change in concentration which remained constant up to 14 weeks. In the case of CWISE for La(III) ion, the electrode gave a linear response and the slope was found to be 40 mV per decade change in concentration. The value of slope remained constant up to 8-10 weeks. The working pH range of the ISE is 3.9 to 9.5 and it was found to be selective in presence of

Be(II), Al(III), Ba(II), Th(IV) and Zr(IV) ions. While the working pH range of CWISE is 2.9 to 9.3 and it was found to be selective in presence of Ba(II), Be(II), Al(III), Cr(III) and Th(IV) ions. The response curves of CWISE and ISE are given in Figs. 1 and 2 and other characteristics of both the electrodes are summarised in Table 1 and 2.

Table 1. Characteristics of electrodes.

Electrode	Response time (sec)	Linear response range (M)	Slope per decade (mV)	Working pH range
ISE	40	1×10^{-1} - 1×10^{-6}	20	3.9 - 9.5
CWISE	28	1×10^{-1} - 5×10^{-5}	40	2.9 - 9.3

Table 2. Selectivity coefficient $K_{i,j}^{pot}$ in presence of different cations.

Electrode	$K_{i,j}^{pot}$					
	Ba^{2+}	Be^{2+}	Al^{3+}	Cr^{3+}	Th^{4+}	Zr^{4+}
ISE	--	0.001	0.01	0.2	0.18	0.87
CWISE	0.18	0.01	0.05	0.05	0.08	--

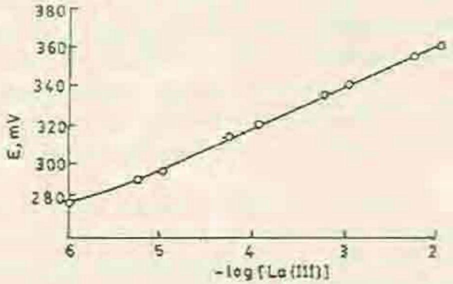

Figure 1 Response curve of ISE

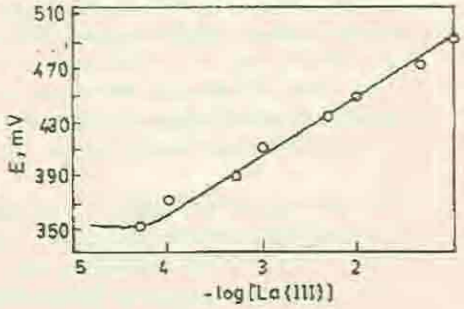

Figure 2 Response curve of CWISE

The 1:1 La(III)-CTB complex being stable between pH range 5.0 to 12.5, studies have been made at pH 6.0. The reported value [7] of stability constant of La(III)-Chromotrope-2B complex obtained by spectrophotometry varied considerably thus justifying the reinvestigation of the system and then ISE and CWISE were employed. With each electrode 5-6 determinations for the values of stability constants were made and the logarithm of average value of stability constant together with standard deviations were calculated (Table 3).

It may be observed that the two different electrodes yield results which are comparable, the small difference may be ascribed to the membrane electrode being more sensitive to lower concentrations than the coated wire electrode.

Table 3. Stability constant of La(III)-CTB 1:1 complex.

Electrode	By varying pH method log K_1 (mean ± SD)	By varying ligand at pH 6.0 log K_1 (mean ± SD)
ISE	8.15 ± 0.25	7.97 ± 0.29
CWISE	8.55 ± 0.38	8.26 ± 0.34

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REFERENCES

1. Moody, G.J.; Thomas, J.D.R. in *Ion-Selective Electrodes in Analytical Chemistry*, Freiser, H.; ed., Plenum : New York; **1978**; 1, 339.
2. Popov, A.I.; Wendlandt, W.W. *Anal. Chem.* **1954**, 26, 883.
3. (Mrs) Prabhu, A.R.; Khopkar, S.N. *J. Sci. Ind. Res.* **1971**, 30, 16.
4. Wheelwright, E.J.; Spedding, F.H.; Schwarzenbach, A. *J. Am. Chem. Soc.* **1953**, 75, 4196.
5. Cattrall, R.W.; Hamilton, I.C. *Ion Selective Electrode Review* **1984**, 6, 125.
6. Lal, U.S.; Chattopadhyaya, M.C.; Dey, A.K. *Electrochim. Acta* **1981**, 26, 283.
7. Sangal, S.P.; Srivastava, S.C.; Dey, A.K. *J. Indian Chem. Soc.* **1963**, 40, 275.