

Potentiometric Estimation of Metal Ions Using Membrane as Indicator Electrodes

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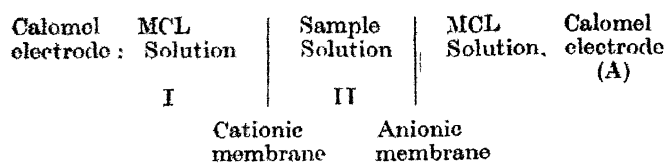
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Metal ions e.g., Ag⁺, Ba⁺⁺, Ca⁺⁺ and Mg⁺⁺ present singly or in their mixture were estimated potentiometrically by an assembly of two membrane electrodes, one cationic and the other anionic. This method avoids the disturbance of reference electrodes due to adherence of precipitates on them, if a precipitation occurs during titration.

MEMBRANE electrodes can be used as indicator electrodes in potentiometric titrations.¹⁻⁶ Membranes prepared from simple inorganic compounds like barium arsenate, have been used for acid-base titrations. In this investigation membranes prepared from ion-exchange resin, simple inorganic compounds, and complexes embedded on a resin bed have been used as indicator electrodes in the estimation of metal ions (Ag⁺, Ba⁺⁺, Ca⁺⁺, Mg⁺⁺) potentiometrically by precipitation or complexometric titration.

Materials used for the preparation of cationic membranes were Dowex 50WX8 cation exchanger resin, Dowex 50WX8 impregnated with copper-dipyridyl complex (mentioned as R_D^{Cu}), and calcium oxalate (cationic exchanger⁸). For anionic membranes, Dowex 1×8 anion exchange resin and calcium fluoride anion exchanger⁸ were used.

The following electrochemical cell was set up :



Experimental

Barium was titrated with potassium chromate, silver with potassium chloride, and calcium and magnesium with EDTA. All the reagents used were of analytical reagent grade (B.D.H. or E. Merck).

Apparatus : A Leeds-Northrup K₂ type potentiometer and galvanometer was used.

Procedure : R_D^{Cu} was prepared by treating the Dowex 50W×8 resin powder (<200 mesh) with CuCl₂ solution and refluxing the copper resin thus obtained with dipyridyl solution (20%) in alcohol.

The resultant material was then vacuum dried. Calcium oxalate and calcium fluoride were prepared in the usual way (Vogel⁹ and Macdonald¹⁰).

The membranes were prepared by vigorously shaking 0.4 gm membrane material (<200 mesh) with a solution of 0.6 g polystyrene in 10 ml of toluene containing 0.05 ml dibutyl phthalate. The suspension was poured over a stainless steel plate and allowed to dry slowly. The solid membranes were cut into suitable sizes with a sharp blade and fixed on the end of pyrex tubes of internal diameter 5.6mm. The adhesive used was polystyrene dissolved in toluene. The membranes, after being tested for leaks, were soaked both inside and out with approximately N/20 aqueous potassium chloride. After 24 hr, the membranes were thoroughly washed with distilled water, then a dilute potassium chloride solution was placed on both sides of the membrane and two tiny calomel electrodes, with KCl-agar agar tips, were dipped into the solutions on each side. The membranes, which showed zero asymmetry potential, were acceptable.

For exchanging two sides of a membrane with two different ions, the procedure followed was similar to that just mentioned, except that the two solutions used on the two sides were of two different electrolytes having the ions concerned.

For the estimation of a metal ion, a known volume of sample solution was taken in compartment II of cell (A) and then diluted to 100 ml. The cationic and anionic membrane tubes were then dipped in the solution. Both the tubes contained the same dilute BaCl₂ solution in case of the Ba⁺⁺ estimation and the same dilute KCl solution for the rest of the titrations. The inside and outside of the cationic membranes were exchanged previously with Ba⁺⁺ and K⁺, K⁺ and Ag⁺, K⁺ and Ca⁺⁺, K⁺ and Mg⁺⁺ for Ba⁺⁺, Ag⁺, Ca⁺⁺ and Mg⁺⁺ estimations respectively. The inside and outside of the anionic membranes were exchanged previously with Cl⁻ and CrO₄²⁻ for Ba⁺⁺ estimation, Cl⁻ and NO₃⁻ for Ag⁺ estimation, and Cl⁻ on both

sides for Ca^{++} or Mg^{++} estimation. Only membranes giving reproducible potentials were used.

Table 1. Membranes used for determinations

Species estimated	Cationic membrane	Anionic membrane
Ba^{++}	Dowex 50W \times 8	Dowex 1 \times 8
Ag^+	R_DCu	Dowex 1 \times 8
Ca^{++}	Calcium oxalate	Calcium fluoride
Mg^{++}	"	"
Ca^{++} and Mg^{++} in a mixture	"	"

corresponded to a barium concentration of 0.0775M while the strength of this solution estimated iodometrically was 0.0771M.

In the titration of silver, the potential increased steadily with steeper slope after the end-point (Fig Ib). The strength of Ag^+ was found to be 0.0102M using 1 ml of AgNO_3 solution and KCl of 0.1M as titrant. From volumetric estimation of this AgNO_3 solution with K_2CrO_4 as internal indicator the strength was 0.0105M.

In case of Ca^{++} , with the gradual addition of EDTA there was an increase in the e.m.f. The rate of increase of e.m.f. was initially constant (0.30 mV to 0.35 mV per ml of EDTA added), but afterwards the rate of increase was much reduced showing a

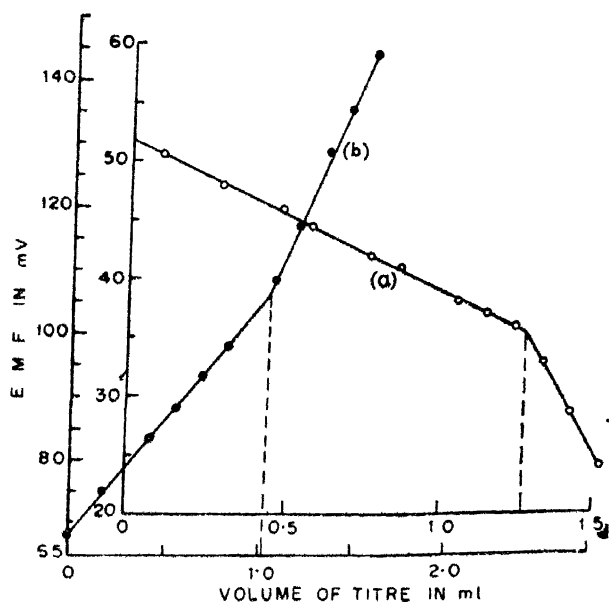
Table 2

Species estimated	Ba^{++}	Ag^+	Ca^{++}	Mg^{++}	Ca^{++} in mixture	Mg^{++} in a mixture
Expected molarity	7.71×10^{-2}	1.05×10^{-2}	1.225×10^{-3}	9.0×10^{-4}	6.125×10^{-4}	4.5×10^{-4}
Found molarity	7.753×10^{-2}	1.02×10^{-2}	1.205×10^{-3}	8.25×10^{-4}	6.025×10^{-4}	4.6×10^{-4}
Deviation	4.3×10^{-4}	3×10^{-4}	0.2×10^{-4}	0.75×10^{-4}	0.1×10^{-4}	0.1×10^{-4}

Two tiny calomel electrodes with KCl-agar agar tips were dipped into the membrane tubes. After each addition of titrant, the solution was well stirred and the cell potential was measured. A time of 5-15 min was necessary for equilibrium to be established, before making the e.m.f. measurements.

Results and Discussion

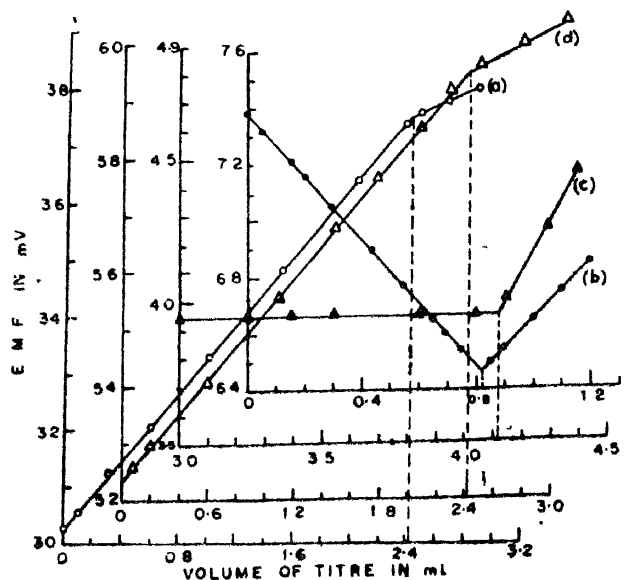
Figure Ia shows the curve obtained when titrating barium with chromate. A break was obtained which corresponded to end-point. The end-point



Figs. I a, b.

- 1a : Estimation of Ba^{2+}
1.27 ml K_2CrO_4 solution required for 1 ml Ba^{2+} solution
1b : Estimation of Ag^+
1.02 ml KCl solution required for 1 ml Ag^+ solution

break in the curve (Fig. IIa) thereby indicating the end-point. For 2 ml of CaCl_2 solution 2.41 ml of 0.001M EDTA was necessary for complete complexation of Ca^{++} but in the case of volumetric titration with calcon C as indicator 2.45 ml of the same EDTA solution was necessary under the same condition.



Figs. II a, b, c, d.

- IIa : Estimation of Ca^{2+}
2.41 ml EDTA solution required for 2 ml Ca^{2+} solution
IIb : Estimation of Mg^{2+}
0.825 ml EDTA solution required for 1 ml Mg^{2+} solution
IIc : Estimation of $\text{Ca}^{2+} + \text{Mg}^{2+}$
4.25 ml EDTA solution required for 4 ml mixture
IIId : Estimation of Ca^{2+} in mixture at $\text{pH} > 12.5$
2.41 ml EDTA solution required for 4 ml mixture

The e.m.f. decreased with the gradual addition of EDTA in case of estimation of Mg^{++} and afterwards

an increase in e.m.f. with addition of EDTA was observed, thus producing a break in the curve (Fig. IIb), which was considered as the endpoint. Fig. IIb showed the end-point at 0.825 ml of 0.001M EDTA for 1 ml of Mg^{++} solution but from volumetric estimation using eriochrome black T as indicator the value was found to be 0.90 ml.

The difference in the nature of the curves is due to the difference of the exchange (selectivity) of the ions on the particular membrane interface. In case of Ba^{++} , K^+ and Ag^+ , K^+ systems the initial descending and ascending branches of the Figs. are due to the difference in the mobilities of the ion pairs.

An attempt was made to estimate the individual concentration of Ca^{++} and Mg^{++} when present in mixture. Firstly, a potentiometric curve (Fig. IIc) of e.m.f. vs volume of titrant (EDTA) added was obtained for a mixture of 2 ml of $CaCl_2$ and 2 ml of $MgCl_2$ diluted to 100 ml. A second curve (Fig. IId) was obtained for the mixture of Ca^{++} and Mg^{++} in the same proportion but changing the pH of this solution to 12.5. The pH was adjusted by adding NaOH solution. In the first case, the e.m.f. was found (Fig. IIc) to remain constant initially but afterwards with the addition of EDTA, a gradual increase in e.m.f. was noticed. This change over of the nature of the curve indicates the end-point corresponding to the total amount of Ca^{++} and Mg^{++} . In the second case, the rate of increase of e.m.f. with addition of EDTA was constant (Fig. IId) at the beginning but later on the rate changed showing a break in the curve. This break point was the end-point for Ca^{++} only as at $pH > 12$, only Ca^{++} formed complex with EDTA. For a mixture of 2 ml of Ca^{++} and 2 ml of Mg^{++} the end-points corresponded to 4.25 ml for the first case (Fig. IIc) and 2.41 ml for the second case (Fig. IId) using 0.001M EDTA as titrant; with the same mixture of Ca^{++} and Mg^{++} , when estimated volumetrically using eriochrome Black T and Calcon C as indicators for the first and second cases respectively, the end-points were at 4.25 ml for the first case and 2.45 ml for the second case with the same EDTA as titrant. Thus, the amount of EDTA required for complexation with Mg^{++} only was 1.84 ml (4.25-2.41) according to the potentiometric values (Figs IIc and IId) and 1.80 ml (4.25-2.45) from volumetric estimation using indicator.

The nature of the Fig. IIc is due to the superimposition of Figs IIa and IIb. At $pH > 12$, EDTA forms complex with Ca^{++} only; hence, the identical nature of Figs IIa and IId was noticed.

The results obtained can be summarised as in Table 2,

The results obtained were fairly reproducible. The maximum deviation observed from expected molarity was found to be 4.3×10^{-4} (in case of Ba^{++}) and the minimum deviation was 0.1×10^{-4} (in case of Ca^{++} and Mg^{++} in a mixture). Calcium oxalate-calcium fluoride membrane pair (used for Ca^{++} and Mg^{++} estimation) was found to be more sensitive to small concentration changes in solutions, as revealed from the above Table.

The advantage of this method is that during titration the reference electrodes are least disturbed and the chance of gaining asymmetry potentials by the adhered precipitates on the electrode surface is totally removed. Moreover, the method is applicable to coloured solutions also, where indicators can not be used.

Conclusion

An assembly of a cationic and anionic membrane can be used as indicator electrodes in the potentiometric titration of metal ions in solution.

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