PUBLICATIONS
INTRODUCTION

The response of cation exchange members to any one cation and of anion exchange membranes to any one anion is a rule but response to an ion when it is present with other ions is an exception which has been noted only in a few cases and has proved very useful. 1-4 Hills have made efforts to find ion exchange resins specific to particular ions. Collodion and paraffin membranes containing nickel dimethylglyoxime, cobalt phosphate, and manganese oxalate have been used as electrodes to estimate Ni$^{2+}$, Co$^{2+}$, and Mn$^{2+}$, respectively. 6 Gregor and Schonhorn reported the measurement of activities of Ca$^{2+}$, and Mg$^{2+}$ using multi-layer membrane electrodes of calcium and magnesium stearate. A literature survey reveals that no other work has been done on the use of heavy metal soap membranes. The high insolubility and intermolecular crosslinking in the material are suggestive of its usefulness for the development of ion selective electrodes. This paper, therefore, deals with the preparation of heavy metal soap discs and their use as membrane electrodes. Some of the metal soap membrane electrodes show Nernstian response for the cation of the soap.
**METHODS AND MATERIALS**

**Chemicals:** All the chemicals used were (BDH) Reagent grade. Palmitic acid was purified by repeated crystallization from distilled ethanol before use. The electrolyte solutions were prepared in deionized water. Araldite adhesive (CIBA Bombay, India) was used for fixing the membrane.

**Preparation of Sodium Soaps:** Alcoholic solution of palmitic acid was added to a little less than its equivalent of semi-normal aqueous caustic soda and refluxed for about twelve hours. The clear solution was filtered through a cotton pad, which retained the small globules of uncombined acid.

**Preparation of Heavy Metal Soaps:** Copper palmitate was prepared as described below. The warm and dilute solution of the sodium soap was poured slowly into a warm and well stirred solution of copper sulphate to a stage where copper sulphate was about 1% in excess. The flocculent precipitate of copper palmitate was washed with distilled water until the washings were free from soluble salts and dried in an air oven at 115°-120° for twenty four hours. Nickel, cobalt, zinc, & chromium palmitates were prepared likewise and dried at 80°-85°, 55°-60°, 115°-120°, 45°-50°, respectively.

**Preparation of Soap Pellets:** The heavy metal soap was mixed with three times its wt. of pyrex glass powder (150-200 mesh)
in a mortar till a fine powder was obtained. 2.0 gm of this powder was transferred to a die and the die was then put into a hydraulic press and heated to 40\(^\circ\) by the built in electrical heaters. A pressure of 10,000 psi was applied. After five minutes, the pressure was released and the disc (0.2 cm thick) out from the die. It was hard and stable against swelling in water. The effective area of the disc in contact with the solution was 6.4 cm\(^2\).

**Measurements of the Membrane Potentials:** Following cell was set up and the membrane potentials, \(E\), was determined by the Michaelis method\(^{12,13}\) with the help of Hye-precision vernier potentiometer (No. 7568).

\[
\text{SCE} | \text{Solution(C}_1\text{)} | \text{Disc} | \text{Solution(C}_2\text{)} | \text{SCE}
\]

The same electrolyte was used on both sides of the disc and the concentration ratio \(C_1/C_2\) was always kept equal to 10.0. For each electrolyte, fresh discs were employed. The two electrolyte solutions were allowed to stand till the potential continued to rise. The solutions on either side of the disc were then replaced with fresh ones. Replacement of electrolyte solutions with fresh ones was continued till a steady potential was reached. This value was taken as the true membrane potential.
All the potential measurements were made at 25° ± 0.1°. The stability of the soap discs was checked by determining the concentration potential which remained reproducible for six days. Hence no disc was used for more than five days.

RESULTS AND DISCUSSION

To understand more clearly, the diffusion process and the character of soap discs in this respect, the membrane concentration potential studies were done. It was found that metallic soap discs about 0.2 cm thick were completely impervious. To increase the porosity of the disc, the soap was mixed with three times its wt. of pyrex glass powder (150-200 mesh). The powder mixed soap disc was almost ideally permselective. The potential response was almost instantaneous. The dilute side of our system was positive, thereby showing that the cation was the faster moving ion and that the discs were of electronegative nature. The discs were also prepared at different temperatures and pressures. But potential measurements showed that these parameters had no effect on the magnitude of the membrane concentration potential. If glass powder was not mixed thoroughly with the soap, the discs had asymmetric potential. But discs made out of thoroughly mixed material showed no asymmetric potential. The concentration
potentials in alkali and alkaline earth chloride solutions which were below the theoretical values had the sequences $\text{BaCl}_2 > \text{SrCl}_2 > \text{CaCl}_2 > \text{KCl} > \text{NaCl} > \text{LiCl}$. The charge density (determined by TMS method) of these discs when in contact with alkali halides was very low (of the order of 0.00032n) as compared to those of parchment supported membranes\textsuperscript{14,15} (of the order of 0.045 n) where alkali halides are known to give concentration potentials close to the theoretical values. The low concentration potentials of soap discs in alkali halides are due to poor electrostatic attraction between the alkali metal cations and fixed charge sites on the discs. For divalent cations, this attraction is, however, appreciably greater and is reflected into better concentration potential values. While Gregor\textsuperscript{16,17} emphasized the importance of hydrated ionic size, Sherry and Eisenman\textsuperscript{18-20} regarded the energetics of hydration and ion site interaction as of key importance. According to Eisenman for ion exchangers with weak field strength, the selectivity sequence is governed by hydration energies of counter-ions. In such cases the normal selectivity sequence would be $\text{K} > \text{Na} > \text{Li}$. Sherry working on the lines of Eisenman predicted the sequence $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$ for weak field strength and a completely reversed sequence for high field strength. According to Eisenman-Sherry theory, the membrane potential sequences obtained in our case viz, $\text{BaCl}_2 > \text{SrCl}_2 > \text{CaCl}_2 ; \text{KCl} > \text{NaCl} > \text{LiCl}$ point towards the weak...
field strength of charge groupings of the soap discs. For membranes with weak field strengths selectivity sequences predicted by Gregor are the same as those predicted by Eisenman and Sherry. Thus the potential sequenc, obtained in our case show dependence upon hydrated ionic size on one hand and on the hydration energies of the counter-ions on the other. On the basis of activity coefficients, Boyd et al. suggested that adsorbability sequence for alkaline earth cations which do not exhibit ion association should be in the reverse order of their activity. Kressman and Kitchner verified this view for phenol sulphonate cation exchange resins and reported the adsorption sequences Ba > Sr > Ca. Larger hydrated ionic radii result in a weaker electrostatic interaction between the cations and the fixed charge on the membrane. Thus Ca$^{2+}$ which has the largest hydrated radius of the three alkaline earth cations should also have the smallest adsorbability and therefore the membrane potential is minimum in this case. On the same principle they have also predicted the affinity sequence for transition metal cations as Zn$^{2+}$ > Cu$^{2+}$ > Ni$^{2+}$ > Co$^{2+}$ which is the same as reported here. It seems interesting to point out that the behavior of Zn and Cu palmitate discs in dilute range is Nernstian and can be used for concentration measurement.
ACKNOWLEDGEMENT

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TABLE I

Concentration potentials across glass mixed metal soap discs at different concentrations of the electrolytes at 25°.

<table>
<thead>
<tr>
<th>Soap discs</th>
<th>Electrolyte</th>
<th>Electrolyte concentration C1/C2 equivalent/l</th>
<th>Theoretical concentration potential E_th (mv)</th>
<th>Observed concentration potential E_m (mv)</th>
<th>Hydrated cationic radii in Å</th>
<th>Heat of hydration of cations Kcal/mole</th>
<th>Charge density of the membrane X</th>
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<tr>
<td>Zinc - palmitate</td>
<td>ZnSO4</td>
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<td>28.20</td>
<td>28.1</td>
<td>6.8</td>
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<td></td>
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<td>25.2</td>
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<td></td>
<td></td>
<td>0.05/0.005</td>
<td>25.02</td>
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<td></td>
<td></td>
<td>0.1/0.01</td>
<td>23.94</td>
<td>17.0</td>
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<tr>
<td>Copper - palmitate</td>
<td>CuSO4</td>
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<td>0.1/0.01</td>
<td>23.94</td>
<td>14.5</td>
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<tr>
<td>Cobalt - palmitate</td>
<td>CoSO4</td>
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* The heat of hydration for various cations have been taken from Noye's data (23).
REFERENCES