Electrochemical studies on polystyrene based membrane of zirconium(IV) antimonoarsenate

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Electrochemical studies have been carried out on heterogeneous ion-exchange membranes of zirconium(IV) antimonoarsenate using polystyrene as a binder. Electrical characteristics like transport number, permselectivity and fixed charge density of the exchanger membrane and halide salts of some alkali and alkaline earth metals as electrolytes have been determined. The membrane potential data conforms to the Kobatake theoretical treatment of irreversible processes. The effect of electrolyte concentration on transport numbers and permselectivity has also been studied. Results indicate that the membrane is permselective for counterions and possesses weak electrical character.

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Inorganic ion exchangers, besides their other advantages, are important due to their high stability at high temperature and radiation fields. These are stable towards chemical degradation and possess sharp selectivity for metal ions over their organic analogs. The most important electrochemical properties of membranes based on inorganic ion exchangers are the pronounced difference in permeability for counterions, co-ions and neutral molecules and their high electrical conductivity. Due to the development of new ion-exchange membranes with better selectivities, lower electrical resistance and improved electrochemical and chemical properties, the charged membranes find applications in food, drug, chemical processes and biotechnology industries. Gmovrin investigated the dependence of a wide number of transport characteristics of inorganic ion-exchange membranes on the concentration. The type and the concentration of the fixed ionic charges determine the permselectivity and the electrical resistance of the membrane.

Herein, a novel inorganic ion exchanger, zirconium(IV) antimonoarsenate has been used for electrochemical studies on the heterogeneous membrane using polystyrene as a binder. Results of the study show the membrane to be permselective.

Experimental
Zirconyl oxychloride (LOBA Chemie, India), potassium pyroantimonate (BDH, England) and sodium arsenate (S.D. Fine Chem., India) were used for the synthesis. All other chemicals used were of AR grade. Standard solutions were prepared either by direct weighing of AR grade reagents or by indirect standardization. Demineralized water was prepared by passing distilled water through a cation exchanger in H + -form (Amberlite IR-120) packed in a column.

Preparation of zirconium(IV) antimonoarsenate
The exchanger was prepared by adding zirconyl oxychloride (0.1 M) solution to a continuously stirred solution of potassium pyroantimonate (0.1 M) and sodium arsenate (0.1 M) at 60°C, in the volume ratio 2:1:1. Gelatinous white precipitates were obtained. The pH of the gel was adjusted to 1.0 by adding either HCl or NaOH solution. Precipitates were filtered, washed with DMW until free from halides. The gel was air dried at 40°C. The dried product was broken down into small granules when immersed in water. The material was converted into the H + -form by treating it with HCl (0.1 M) for 24 hours with occasional shaking and intermittently changing the acid. The precipitates were washed with DMW in order to remove excess acid and were finally dried at 40°C.

Determination of ion-exchange capacity
Ion-exchange capacity was determined by column operation. Exchanger in the H + -form was placed in a column containing a glass wool support. Sodium nitrate solution (1.0 M) was used as an eluent and about 400 mL of it was passed through the ion exchanger column containing 1 g of the exchanger at a rate of 5-10 drops per minute. Hydrogen ions eluted from the column were determined titrimetrically against standard solution of sodium hydroxide.
Preparation of membrane and electrode assembly

Appropriate amount of the finely ground exchanger in H⁺-form was thoroughly mixed with powdered polystyrene to give 1:1 mixture. It was then heated at 99°C for 6 hours under 2 kg/cm² pressure in the polymer film making equipment. After cooling to room temperature, the membrane was removed from the machine. The membranes thus obtained were cut in the shapes of discs of about 2.5 cm diameter using a sharp blade and those of good surface qualities were selected for further investigations.

The selected membrane was pasted on one end of the electrode assembly using epoxy resin as an adhesive. The membrane was fixed on the other side to the other part of electrode assembly in the same way. The electrode chambers on either side of the membrane were filled with electrolyte solution (1.0 M), such as lithium chloride, sodium chloride, potassium chloride, magnesium chloride and barium chloride kept for 16 hours to convert the membrane into the appropriate cationic form. After equilibration, the electrode assembly was washed with demineralized water (DMW). The membrane was then kept immersed in DMW for 2 hours to remove the excess electrolyte solution. When not in use, the electrode chambers were filled with demineralized water.

The electrode assembly was kept immersed in a water thermostat, maintained at 27 ± 0.1°C, throughout the study. Membrane potential measurements were made using saturated calomel electrodes as reference electrodes. The electrode assembly as follows:

Hg-HgCl₂(s), KCl (Sat.) || soln. C₁ || membrane || soln. C₂ || KCl (Sat.), Hg₂Cl₂-Hg

Potential measurements were made for different concentrations of the same electrolyte on the two sides of the membrane in such a way that the concentration ratio, δ (C₂/C₁) = 10. The potential difference developed across the membrane was measured against reference electrodes on either side of the membrane using a digital potentiometer. The electrode chambers were rinsed with the electrolyte solution of next higher concentrations and then filled with the same solution. The membrane was allowed to equilibrate for 2 hours and the new potential difference was then noted.

Membrane potentials across the zirconium antimonooarsenate membrane were determined using 1:1 electrolytes such as lithium chloride, sodium chloride and potassium chloride and some 2:1 electrolytes such as magnesium chloride, calcium chloride, strontium chloride and barium chloride in the overall concentration range of 0.001 M to 0.5 M. Experiments were repeated three times to check reproducibility of the results. A standard deviation of ± 0.5 mV was observed.

Results and discussion

ZrSbAs is a reproducible material having an ion-exchange capacity of 0.40 meq/g for Na⁺ ions. It can be regenerated and used over and over again. Even after five regenerations, the ion exchanger loses 35% of its original capacity. Results of the chemical analysis of the exchanger suggest the mole ratio of Zr:Sb:As as 16:11:1. Based on this, following empirical formula can be suggested for the compound: [(ZrO₂)₁₆ (H₃SbO₄)₁₁ (H₃AsO₄)]·nH₂O. The number of water molecules 'n' can be estimated from the percentage loss of the weight of the exchanger up to 200°C assuming that all the external water molecules are lost at this temperature. ZrSbAs experiences a weight loss of 12.5% up to a temperature of 200°C. Loss of weight beyond this temperature was not considered because that could be due to an irreversible condensation of the acidic groups. The number of external water molecules was determined by using the Alberti formula, 18n = X (M+ 18n)/100, where, X is percentage weight loss of the exchanger at 200°C, M is molecular weight of the exchanger without water molecules and n is number of external water molecules, and found to be 33.25. So, a tentative molecular formula for the exchanger can be written as: [(ZrO₂)₁₆ (H₃SbO₄)₁₁ (H₃AsO₄)]·33H₂O.

A membrane separating the electrolyte solutions of unequal concentrations exhibits a difference in electrical potential due to unequal ionic mobilities and is equal to liquid junction potential in a non-selective membrane. In the case of membrane embedded with ion exchanger, the membrane potential depends on the nature and the concentrations of the electrolytic solutions as well as fixed ionic groups of the exchanger, its magnitude being determined by several factors, viz., the ratio of the counterion mobility, the concentration of salt solution and the exchange characteristics of the membrane materials for various cations.

From Table 1, it is evident that higher membrane potentials are observed at lower concentrations of 1:1
and 2:1 electrolytes and the membrane potentials decrease with increase in concentration of the electrolyte. For 1:1 electrolytes, membrane potentials are in the order: Li⁺ > K⁺ > Na⁺. This order of the membrane potentials prevails over the entire concentration range.

Transport numbers and permselectivity values for 1:1 and 2:1 electrolytes are given in Tables 2 and 3, respectively. It is observed that the transport numbers decrease with increase in concentration for all the electrolytes.

This is in accordance with the fact that with increase in concentration of the electrolyte, Donnan exclusion of the co-ions becomes less efficient resulting in a decrease in transport number of the counterion. This phenomenon supports the hypothesis that the ion-exchange membranes behave in a selective manner and thus, the permselectivity (Pₛ) values decrease with increase in mean electrolyte concentration (Table 3). Permselectivity (Pₛ) has been calculated using the equation,
Table 4—Values of parameters α, β and \( \bar{X} \) for zirconium (IV) antimonoarsenate membrane at \( \delta = 10 \)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \bar{X} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>0.75</td>
<td>1.49</td>
<td>0.0332</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.62</td>
<td>1.75</td>
<td>0.0568</td>
</tr>
<tr>
<td>KCl</td>
<td>0.64</td>
<td>1.66</td>
<td>0.0847</td>
</tr>
</tbody>
</table>

where \( \bar{t}_e \) refers to the value of the transport number in the membrane and \( t_e \) is the value in free electrolyte solution.

Electrical character of a membrane is expressed in terms of its fixed charge density. Fixed charge density of the zirconium (IV) antimonoarsenate membrane for 1:1 electrolytes has been evaluated by using Kobatake's equation

\[
E_m = \frac{RT}{F} \left( \ln \left( \frac{C_2}{C_1} \right) + \frac{\alpha \beta \bar{X}}{C_1 + \alpha \beta \bar{X}} \right)
\]

where, \( \alpha = \frac{u}{u + v} \) and \( \beta = 1 + \frac{KF\bar{X}}{u} \)

For determining the fixed charge density \( \bar{X} \) in dilute concentration range, the value of the slope determined from \( E_m^\circ \) versus \( C_2 \) plots was equated with the slope of Eq. 1. \( \alpha \) and \( \beta \) being known earlier, \( \bar{X} \) can be calculated.

Substitution for \( E_m^\circ \) in Eq. 1 and expanding resultant expression for \( 1/\bar{t}_{app} \) in powers of \( 1/C_2 \) gives

\[
\frac{1}{\bar{t}_{app}} = \frac{1}{1+ \left( \frac{1+\beta-2\alpha}{2(1-\alpha)} \right) \frac{1}{\bar{X}}}
\]

From Eq. 1b, it is clear that a plot of \( 1/\bar{t}_{app} \) versus \( 1/C_2 \) at fixed \( \delta \) value should be a straight line with an intercept equal to \( 1/(1-\alpha) \), from where \( \alpha \) can be evaluated.

It was observed that \( \bar{t}_{app} \) decreases with increase in mean concentration of the electrolyte. Dependence of \( \bar{t}_{app} \) on concentration of the electrolyte is similar to that of membrane potential dependence on concentration. These membrane-permeant interactions are an index of crystalline morphology, being more in amorphous and less in crystalline membranes. The low values indicate lower degree of crystallinity of the exchanger material.

The observed values (Table 4) of the fixed charge density \( \bar{X} \) are much lower than those expected from the fixed charge concentration of the exchanger. This indicates that a larger part of the internal fixed charges remains inactive. This may be due to the reason that the active fixed charges in these membranes are essentially those of the external surface of the grains. Due to the small grain size of the well ground exchanger powder (<250 mesh), the free intergranular spaces are also very small so that Donnan salt exclusion could take place.
References