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Synthesis, characterization and influence of electrolyte solutions on electrical properties of organic–inorganic composite membrane

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HIGHLIGHTS

- Membranes potential measured with uni-univalent electrolytes (KCl, NaCl and LiCl).
- Order of surface charge density for electrolytes are found to be KCl > NaCl > LiCl.
- $8E_m$ depend on the size of permeating ions.
- The magnitude of membrane capacitance found to be dependent on capacitance of the double layer.
- The change in membrane capacitance and resistance values with the change in electrolyte concentration and applied frequency.

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ABSTRACT

In this work various electrical properties of titanium molybdate composite membrane had been discussed. The membrane was characterized by X-ray diffraction, scanning electron microscopy, particle size analysis and Infra-red spectroscopy. The effective fixed charge density of the membrane was determined by TMS method and it showed the dependence of membrane potential on, the charge on the membrane matrix, porosity and size of permeating ions. The change in membrane capacitance and resistance values with the change in electrolyte concentration and applied frequency had been interpreted in terms of the charges produced in the electrical double layer at the membrane solution interface. The magnitude of membrane capacitance had been found to be dependent on the capacitance of the double layer. In higher frequency range the impedance data evaluated on the basis of simple equivalent electrical circuit model and had been found to follow theoretical prediction. Other parameters such as transport number, distribution coefficient and charge effectiveness were also calculated.

1. Introduction

During the last decade, there had been a renewed resurgence in developing potentiometric membrane electrodes as devices for rapid, accurate, low cost and non destructive analysis of different samples with small volume samples. An ion-selective membrane based potentiometry had become a well-established electroanalytical technique for the determination and identification of metal ions even in traces. Increased interest in the development of novel sensors for the detection of heavy metals. To monitor different type of metals in a large number of environmental samples, potentiometric detectors based on ion-selective membrane is suited because they offer advantages such as high selectivity, sensitivity, fast response, good precision, simplicity and low cost [1,2]. The use of ion selective membrane (ISMs) for the detection and determination of lead compound has received much interest and many ligands have been investigated as sensing agents in electrodes [3].

Sol–gel derived composite materials had found numerous applications in the areas of chemistry, biochemistry, engineering and material science [4]. The 'organic–inorganic' hybrid materials prepared via the Sol–gel technique had significant attention in the literature [5]. The binding of organic polymer also introduces the better mechanical properties in the end product, i.e. composite ion exchange materials like, polypyrrole–Th(IV) phosphate [6], polyaniline–Sn(IV) arsenophosphate [7] and polystyrene–Zr(IV) tungstophosphate [8] used for the selective separation of Pb^{2+}, Cd^{2+}, Hg^{2+} respectively. Teorell–Meyer–Sievers (TMS) developed a theory of membranes with charges fixed within the lattice. The various attempts made to calculate the membrane potentials and charge density by using the idealized theory of Teorell–Meyer–Sievers (TMS) [9–11]. And Impedance data had also been evaluated on the basis of an equivalent electrical circuit model with membrane under various condition of bathing electrolyte concentration and applied frequency in order to

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Nomenclature

C_1, C_2	concentration of electrolyte solution either side of the membrane (mol/l)
$\overline{C}_{1+}$	cation concentration in membrane phase 1 (mol/l)
C_{2+}	cation concentration in membrane phase 2 (mol/l)
$\overline{C_i}$	*i*th ion concentration of external solution (mol/l)
C_i	*i*th ion concentration in membrane phase (mol/l)
D	charge density in membrane (eq/l)
F	Faraday constant (C/mol)
K	distribution coefficient of ions
K_{2+}	distribution coefficient of ions (electrolyte solution C_2)
q_1	charge effectiveness of membrane phase 1
q_2	charge effectiveness of membrane phase 2
R	gas constant (J/K/mol)
SCE	saturated calomel electrode
SEM	scanning electron microscopy
TMS	Teorell, Meyer and Sievers
XRD	powder X-ray diffraction
FTIR	Fourier Transform Infrared Studies
t_+	transport number of cation
t_-	transport number of anion
u	mobility of cations in the membrane phase (m^2/V/s)
v	mobility of anions in the membrane phase
V_k	valency of cation
V_x	valency of fixed charge group
C_d	capacitance of electrical double layer
C_g	geometric capacitance
C_m	capacitance of membrane
C_x	capacitance
R_x	electrical resistance
R_m	electrical resistance of membrane

Greek symbols

$\gamma'_{\pm}, \gamma''_{\pm}$	mean ionic activity coefficient for electrolytes solution C_1 and C_2
ϖ	mobility ratio (TMS extension theory)
ΔE_m	membrane potential (mV)
$\Delta E_{m,e}$	membrane potential (mV) (TMS extension theory)
ΔE_{don}	Donnan potential (mV)
ΔE_{diff}	diffusion potential (mV)

understand the mechanism of ionic transport and widely used in the studies of gastric mucusa, a variety of epithelia and in polystyrene sulfonic acid membranes [12,13].

2. Experimental

2.1. Preparation of membrane

The titanium molybdate was prepared by Sol–gel method [14]. Obtained precipitate was grounded into a fine powder with pestle and mortar and then sieved through 200 mesh (granule size $\leqslant$0.075 mm), pure amorphous polystyrene (Otto Kemi, India, AR) was used as a binder, also grounded and sieved through 200 mesh and then the mixture was kept into cast die (diameter 2.45 cm) and placed in an oven at 200 °C for about half an hour to equilibrate the reaction mixture, then die was transferred to a pressure device (SL-89,UK) where 60 MPa pressure was applied. This membrane was cemented in a Pyrex glass tube cell for measuring membrane potential ΔE_m.

2.2. Measurement of membrane potential, capacitance and resistance

The cell potential was taken as a measure of membrane potential. The measurements were carried out at 25 °C (±0.1 °C). The Electrochemical cell of the type was used

$$\begin{array}{ccccccccc} \text{SCE} & \vdots & \text{solution} & \vdots & \text{Membrane} & \vdots & \text{solution} & \vdots & \text{SCE} \\ & \vdots & C_2 & \vdots & \text{Diffusion potential} & \vdots & C_1 & \vdots & \\ & & \text{Donnan potential} & & & & \text{Donnan potential} & & \end{array}$$

to measured electrical potentials across the membrane. The various salt solutions (chloride of Li^+, Na^+ and K^+) were prepared from (analytical-grade reagents (BDH)) in deionized water.

For resistance (R_x) and capacitance (C_x) measurements, an electrolyte solution first equilibrated the membrane which was then replaced by purified mercury without removing the adhering surface liquid [15]. Platinum electrode dipping in mercury was used to establish contact. The values obtained with an LCR meter (model 4300).

2.3. Characterization of membrane

2.3.1. Water content (%total wet weight)

First, the membrane was soaked into water to elute diffusible salt, blotted quickly with Whatsman filter paper to remove surface moisture and immediately weighed. The water content (total wet weight) was calculated as,

$$\%\ \text{Total wet weight} = \frac{W^w - W^d}{W^w} \times 100$$

where W^w is the weight of wet membrane and W^d is the weight of dry membrane.

2.3.2. Scanning electron microscopy (SEM)

The pore structure, homogeneity, thickness and surface morphology of composite membrane had been well studied by scanning electron microscope (SEM) micrographs [16,17] Fig. 1. In the SEM, different interactions give images based on topography and elemental composition of sample.

2.3.3. FTIR studies

The FT-IR spectrum used for the study of titanium molybdate (*A*), pure polystyrene (*B*) and composite material (*C*), dried at 40 °C, and were taken by KBr disc method at room temperature Fig. 2.

2.3.4. XRD analysis

The powder X-ray diffraction pattern was obtained in an aluminum sample holder for composite of titanium molybdate and polystyrene using a PW (powder), 1148/89-based diffractometer with Cu Kα radiations shown in Fig. 3.

2.3.5. Particle size analysis

The size of the particle was analyzed by using laser diffraction, for which sample had been mixed with water by Ultrasonic. The suspended particle had been measured as shown in Fig. 4.