Membrane Concentration Potentials Across Heavy Metal Soap Membranes

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ABSTRACT

The alumina mixed copper soap pellets of different fatty acids (C_6-C_{16}) have been prepared. The pellets are used as membranes of electropositive character. The concentration potential studies have been carried out with potassium chloride solutions. Transport number of counterions and selective ionic permeability through these membranes have been calculated. The values of both these parameters increase with increase in the number of C- atoms of the hydrocarbon chain of copper soaps. This seems to be due to lowering in solubility and increase in crosslinking in the membrane material.

INTRODUCTION

In our work (1-3) on inorganic precipitated membranes, we have studied in detail their charge densities, permselectivities, transport number of counterions, and diffusion rates of various biologically important electrolytes to elucidate more clearly the electrochemical nature of the diffusion process across natural membranes. According to Teorell, Meyer, and Sievers (TMS) theory (4-9), the walls of the membrane pores carry a number of fixed charges due to either adsorption or ionization. The membrane behavior is largely dependent upon factors like adsorption, structure of the respective gels, and nature of the electrolytes. Multiplicity of charge sites on heavy metal soaps of plycarboxylic acids promises it as a suitable material for membrane. A literature survey reveals that little work has been done on soap membranes. Gregor and Schonhorn (10-12) were the first to report the multilayer membrane electrodes of calcium, barium, and magnesium stearate to measure the activities of physiologically important ions, namely Ca^{2+} and Mg^{2+} existing in the cell membrane or in mixed electrolytes. Lipid-collagen membranes, on treatment with sodium lauryl sulphate, start behaving as a bipolar system (13). It is, therefore, of interest to investigate the soap membranes. This article deals with the preparation and the evaluation of the physicochemical properties of heavy metal soap pellets using them as membranes. Further work is in progress.

METHODS AND MATERIALS

Chemicals

Caproic, caprylic, lauric, myristic, and palmitic acids were reagent-grade products purified by repeated crystallization from distilled ethanol. Potassium chloride, copper sulphate, and alumina (for chromatographic analysis) were of British Drug House (BDH) AnalaR grade. The electrolyte solutions were prepared in deionized water. Araldite adhesive (CIBA, Bombay, India) was used for fixing the membrane.

Preparation of Sodium Soaps

The sodium soaps of caproic, caprylic, lauric, myristic, and palmitic acids were obtained (14) by refluxing equivalent amounts of fatty acids and sodium hydroxide in distilled alcohol for 10-12 hr on a water bath. These soaps then were purified by extraction within a soxhlet. Finally, the soaps were crystallized twice from alcohol.

Preparation of Copper Soap Pellets

The copper soaps were prepared by the following method (15). Hot and dilute solution of copper sulphate was added to an equivalent amount of a hot and dilute solution of sodium soap under vigorous stirring. The flocculent precipitate of copper soap was obtained. The soaps (C_6-C_{16}) then were washed thoroughly, first with hot distilled water and then with distilled ethanol. The soaps were dried at 110-120 C and stored in a desiccator. The copper soaps were amorphous solids, fluffy and unctuous in nature, bluish green in color and soluble in organic solvents. They were analyzed for their metal content.

The copper soap was mixed with three times of its wt of aluminum oxide and crushed in a mortar till a fine powder was obtained. A known quantity (2.5 g) of this powder was transferred to a die and the die then was put into a hydraulic press. (Apex hydraulic press, type M_1, serial no. A/205413, London, England) The die then was heated by the built-in electrical heaters to 80 C, and a pressure of 6000 psi was applied. After 5 min, the pressure was released, and the pellet was taken out from the die. The pellet was hard and stable against swelling in water. The membrane had a thickness of 0.15 cm. The effective membrane area in contact with the solutions was ca. 6.4 cm^2. The pellets were stored in a desiccator.

Potential Measurements

The membrane of copper soap was fixed on one end of a glass cylinder (open at both ends) with Araldite adhesive. The electrical potential arising across the membrane separating the electrolyte solutions was measured as before (1,2) by constructing the cell·

SCE | Solution(C_1) ¦ Anionic soap membrane ¦ Solution(C_2) | SCE

The glass cylinder fitted with the soap membrane containing potassium chloride (KCl) solution of concentration C_1 was suspended into a beaker, having KCl solution of concentration C_2 ($C_1 > C_2$). The two electrolyte solutions were allowed to stand til the potential continued to rise. The solutions on either side of the membrane were replaced (three or four times) with fresh ones until the potential was maximum. All potential measurements were made at 25 ± 0.1 C with the help of Pye-Cambridge Universal potentiometer (catalog no. 7568).

RESULTS AND DISCUSSION

The results described in the following pages may be discussed in terms of physicochemical properties of the membrane and the composition of the surrounding solution. In the solution-membrane-solution system, there exist permanent Donnan equilibria between the external solutions and the membrane surfaces, and the total membrane potential is the sum of (A) two Donnan potentials at the membrane-phase boundaries and (B) a diffusion potential within the membrane. To understand more clearly the diffusion process and the character of soap membranes in this respect, the membrane concentration potential studies have been done. It was found that the copper soap membrane of 0.15 cm thickness does not respond to any potential development. To increase the porosity of soap membranes, the copper soap was mixed with three times its wt of alumina. The alumina mixed soap membrane was almost ideally permselective. The membrane potential values for the alumina mixed copper soap membranes in potassium chloride solutions are presented in Table I.

The sign and magnitude of the membrane concentration potential depend upon absolute concentration, concentration ratio of the two adjacent electrolyte solutions, and also on the nature of the electrolyte and that of the membrane. With membranes of highest porosity, the membrane potentials are, in sign and magnitude, the same, or almost the same, as the liquid junction potential. The direction of deviation of the membrane potential from liquid junction potential depends upon the electrokinetic charge of the membrane. The dilute side of our system (Table I) was negative, thereby showing that the anion was the faster moving ion and that the membrane is of electropositive nature.

The increase in membrane potential (Table I) with increase in dilution points to the increase in permselectivity (1,2) of the membrane. The Donnan potential is known to increase with dilution of the solution and the increasing molality of the fixed ionic groups (16), whereas the diffusion potential changes are otherwise. Thus, in our case, the increase in Donnan potential with dilution seems to outweigh the decrease in diffusion potential. Further, the charge density ($\bar{X}$) of the membranes (calculated by TMS method) also rises with the number of carbon atoms in the hydrocarbon chain of the copper soaps.

To have an insight into the physicochemical behavior of these metallic soap membranes, the transport number of counterions and selective ionic permeability were calculated. The transport numbers of anions in the membrane, $\bar{t}_-$, for univalent electrolytes, were calculated using Kittelberger's equation (17):

$$\bar{t}_- = \frac{1}{2}\,\frac{E_m \cdot F}{RT \ln \dfrac{f_1 c_1}{f_2 c_2}} + \frac{1}{2},$$

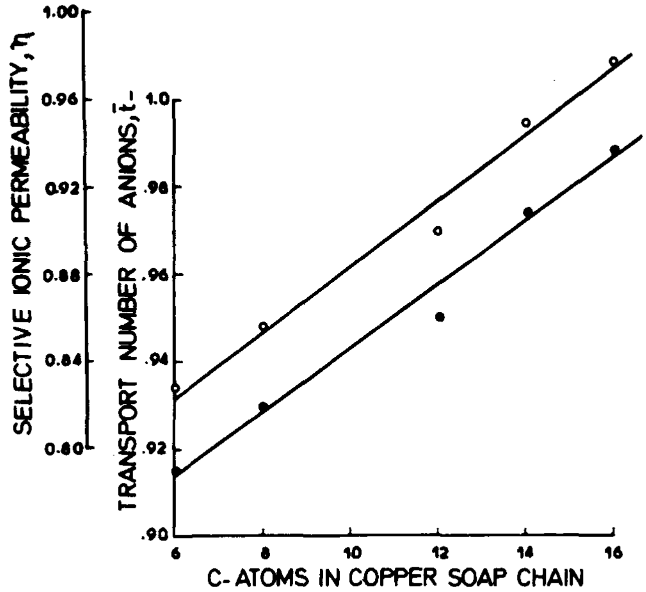

FIG. 1. Plots of transport number of counterions $\bar{t}_-$, ●, and selective ionic permeability, η, ○, as a function of C atoms in copper soap chain.

where Em is the measured membrane potential, C_1 and C_2 the concentrations of electrolytes in g/equivalent/liter, and f_1,f_2 are the corresponding activity coefficients. The selective ionic permeability, η, was calculated using the realtion:

$$\eta = \frac{E_m}{E_{th}},$$

where E_m is the observed potential and E_{th} the theoretical potential value calculated using Nernst equation.

The anionic transport number inside the membrane, $\bar{t}_-$, and selective anionic permeability, η, for potassium chloride solutions are given in Table I. The decrease in $\bar{t}_-$ and η in the higher concentration ranges suggests that, with increase in external electrolyte concentration, more coions enter the pores and, thus, render the membrane less selective.

TABLE I

Dependence of Concentration Potentials on Number of Carbon Atoms in Hydrocarbon Chain and on Concentration of Electrolyte, Selective Ionic Permeability, and Transport Numbers of Anions across Alumina Mixed Copper Soap Pellets in Potassium Chloride Solutions at 25 C

Number of C atoms in Cu soap	Electrolyte concentration C_1/C_2, equivalent/1	Theoretical concentration potential E_{th}(mv)	Observed concentration potential E(mv)	Selective ionic permeability η	Transport number of permeability $\bar{t}_-$	Charge density of the membrane $\bar{X}$
C_6	0.001/0.0001	−58.19	−48.24	0.829	0.915	0.0039N
	0.01/0.001	−57.35	−24.56	0.428	0.714	
	0.05/0.005	−55.80	− 8.37	0.150	0.575	
	0.1/0.0.01	−55.03	− 4.12	0.075	0.537	
C_8	0.001/0.0001	−58.19	−49.78	0.856	0.928	0.0071N
	0.01/0.001	−57.35	−28.15	0.491	0.746	
	0.05/0.005	−55.80	−14.26	0.256	0.628	
	0.01/0.01	−55.03	− 6.30	0.115	0.555	
C_{12}	0.001/0.0001	−58.19	−52.30	0.898	0.949	0.0174N
	0.01/0.001	−57.35	−35.78	0.624	0.812	
	0.05/0.005	−55.80	−33.08	0.593	0.796	
	0.1/0.01	−55.03	−17.40	0.316	0.658	
C_{14}	0.001/0.0001	−58.19	−55.16	0.948	0.974	0.0220N
	0.01/0.001	−57.35	−43.68	0.762	0.881	
	0.05/0.005	−55.80	−41.72	0.748	0.874	
	0.1/0.01	−55.03	−26.14	0.475	0.737	
C_{16}	0.001/0.001	−58.19	−56.85	0.977	0.988	0.0326N
	0.01/0.001	−57.35	−49.70	0.867	0.933	
	0.05/0.005	−55.80	−45.19	0.810	0.822	
	0.1/0.01	−55.03	−30.48	0.554	0.777	

It is interesting to note that anion transport numbers inside the membrane $\bar{t}_-$ and selective ionic permeability η increase with the number of carbon atoms in the hydrocarbon chain of copper soaps and, for the most dilute range, the plots (Fig. 1) of $\bar{t}_-$ and η against the number of carbon atoms yield straight lines. Increase in the number of carbon atoms in the hydrocarbon chain increases the hydrophobicity of the soap, and MacDonald and Toth (18) have remarked that a more insoluble material is a better ion exchanger. Further, with increased chain length, the possibility of crosslinking is increased, and again the selectivity of an ion enchanger is known to increase with increase in crosslinking (19). Thus, increase in membrane potential with the increase in the number of carbon atoms seems to be due mainly to an increase in the charge density of the membrane and an increase in the crosslinking of membrane material. Thus, alumina mixed membranes of copper soaps of fatty acids are positively charged and almost ideally permselective due to the extremely high order of insolubility and inter-, as well as intra-, molecular crosslinking in soap molecules. The selective ionic permeability of these membranes increases linearly (Fig. 1) with the number of carbon atoms in the hydrocarbon chain of the acids.

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