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Review

A Review on Electrochemical Parameters of Ion Exchange Composite Membrane and their Permeable Characteristic

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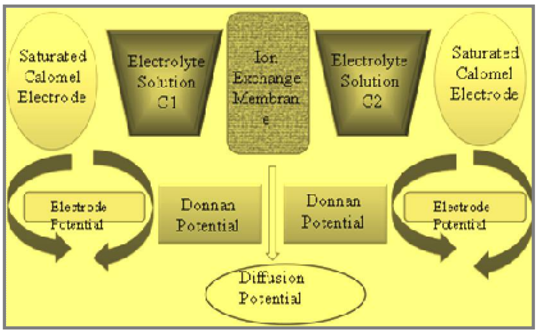
ABSTRACT

The electrochemical properties of composite membranes, particularly ion exchange membranes which are characterized by the presence of some functional groups that differ in both chemical structure as well as properties. So the membrane with modified surface and ion-exchange characteristic consist from cationic or anionic layers of different nature as well as bipolar modification. The major distinction of such membrane is the anisotropy of their structure and physicochemical properties due their charge characteristics. The diffusion flow of salt through them and forming diffusion potential differ from one another depending on the orientation of layers relative to the diffusion flow direction. When the membrane simultaneously is under effect of the both gradients of concentration and electric fields, the value of electric current passing through a membrane also depends on a disposition of membrane layers. These phenomena, which are typical for these membranes, make asymmetric transport properties. Due to the unequal concentration of electrolyte solutions separated by an ion exchange membrane with the fixed charge groups arises potential difference at the constant temperature and pressure. At the interface between membrane and electrolyte solutions, the Donnan potential occurs due to the transfer of ions. Donnan potential appears as a result of Donnan equilibrium, which refers to the distribution of ionic species between two ionic solutions separated by the permeable membrane. There are various methods, but particularly Teorell, Meyer and Sievers (TMS) method has been mostly used to determine the electrochemical parameters like transport number, mobility ratio, surface charge density etc of the membrane.

Graphical Abstract



Electrochemical setup used for ionic potential measurement.

Keywords: Polymeric-Inorganic composite, Electrochemical Parameters, Permeable Characteristic, Donnan potential, Teorell-Meyer and Sievers (TMS) method.

INTRODUCTION

The electrochemical processes involving the electron transfer to or from a molecule or ion changing its oxidation state. This reaction can occur through the application of an external voltage. When the membranes are in contact with some electrolyte salt solutions, the electrochemical characterization allows the determination of different membrane transport parameters and ionic permeabilities, fixed charge concentration, ion transport numbers, ions mobility ratio and membrane conductance [1]. As a consequence of the carrier, a small fixed charge for the activated membranes was obtained from membrane potential measurements; if the characteristics of membranes are negatively charged they have transform the positive ions of salt solutions while the positively charged membranes transported the negatively charged ions. The impedance spectroscopy measurements permit us to determine separately both the membrane and electrolyte electrical resistance; the increase of the membrane electrical resistance when the concentration of carrier in the membrane increases is due to a higher compaction of the carrier filling the pores of the polymeric support [2]. This fact allows the use of this physical parameter to correlate the degree of activation of these membranes (content of carrier) by means of a non-destructive technique and when they are in working conditions (in contact with electrolyte solutions).

Membrane potential is defined as a potential difference arising between the solution of an electrolyte with different concentrations at the constant temperature and pressure separated by a uniform membrane with fixed ionizable groups [3]. At the interface between membrane and electrolyte solutions, the Donnan potential occurs due to the transfer of ions. Donnan potential appears as a result of Donnan equilibrium, which refers to the distribution of ion species between two ionic solutions separated by a semi permeable membrane or boundary. The boundary layer maintains an unequal distribution of ionic solute concentration by acting as a selective barrier to ionic diffusion. Some species of ions may pass through the barrier while the others may not. Electric potential arising between two solutions is called Donnan potential. Inside the membrane, the diffusion potential arises since ions would diffuse from the high concentration side to the low concentration side under a certain concentration gradient. Diffusion potential is the potential difference generated across a membrane because of the concentration difference of an ion. It can be generated only if the membranes are permeable to the ions. The size of the diffusion potential depends on the size of the concentration gradient. The sign of diffusion potential depends on whether the diffusing ion is positively or negatively charged. Diffusion potentials are created by the diffusion of very few ions which do not result in changes in concentration of the diffusing ions. Membrane potential is the summation of the Donnan potential and the diffusion potential, and it can also be named as the exclusion-diffusion potential [4]. Membrane potential can be measured directly or by determining the electrical properties of a membrane or the activities of ions inside the membrane. The earlier theoretical studies on membrane potential were almost based on the Teorell, Meyer and Sievers (TMS) model and also developed by Kobatake et.al. [5, 6], Lakshminarayanaiah *et. al*, [7]. Kobatake et.al, derived an equation of membrane potential for uni-univalent electrolyte solutions and first time proved that the derived equation agreed well with typical corresponding experimental data, Nikonenko *et.al*, [8] investigated the influence of the 1:1 salt concentration, and the ratio of the diffusion boundary layer length and the counter-ions diffusion coefficient on the membrane potential of an ion-exchange membrane. This review work concluded that the membrane potential determined numerically by the TMS model were similar to those obtained experimentally by Dammaket.al, if the salt concentration was less than 100 mL mol. Lefebvre et al. [9], derived the general equations of the membrane potential, and the filtration potential of a charged membrane in an arbitrary electrolyte solution using an analytical approach.

The group limited their studies to the related aspects of the comparison of normalized filtration potential calculated numerically and analytically with no discussion on membrane potential. The above analysis demonstrates that most studies of membrane potential evaluated by the TMS model have been emphasized with the attention being given to the uni-univalent electrolytes. Nevertheless, there is not enough convincing theoretical investigation concerning the other kinds of electrolytes. It is worthwhile clarifying the fact whether the TMS model can be employed to evaluate membrane potential in multivalent electrolyte solutions [**10**]. In contact with external electrolyte solutions of low or moderate concentration the membrane excludes the co-ions (Donnan exclusion) by electrostatic repulsion while the counter ions are admitted to the membrane and experience negligible resistance in passing through from one solution to the other. At higher concentration, the Donnan exclusion becomes less effective and thus perm selectivity gets reduced. The permselectivity [**11**] is reflected not only in the differences in permeability, but also in the electric potential difference which arises between the two solutions.

In the absence of an electric field, the migration of an ionic species across the membrane involves a transfer of electric charge and this charge transfer has been balanced by one or more other fluxes. The compensation of the fluxes is brought about by the electric potential gradient, called the diffusion potential, built up by the process of diffusion. These characteristics of the fluxes, the action of the diffusion in the membrane and the permselectivity for counter ions are the key to the understanding of diffusion phenomena in membrane systems. When a membrane is between two solutions of the same electrolytes of different concentrations, the membrane potential is called concentration potential. In such a concentration cell, the counter ions diffuse more rapidly than the co ions, due to permselectivity, resulting in a net transfer of electric charge. With cation selective membranes, the electric potential in the dilute solution thus is thus more positive than in the concentrated solution. With anion-selective membranes, the opposite is true. The important parameters of membrane like ionic mobility which is defined as the velocity attained by an ion moving through a medium under an electric field. The effective charge fixed density of membranes which refers to the charge distribution over the volume of a particle, such as a molecule, atom or ion. Charge density is the central parameter that controls the membrane phenomenon, calculated by using the observed potential values of different used electrolyte solutions as well as TMS theoretical potential values [**12, 13**]. The other important parameters of membrane which include the transport number, mobility ratio and charge effectiveness and distribution coefficient have been easily calculated by the above discussed TMS equations. The transport number is another very important factor of membrane defined as the mobility of the ion divided by the sum of mobilities of the two ions. It is also called as the transference number which is the fraction of the total current carried in an electrolyte by a given ion. The transport number has been obtained by using the above Nerst-Planck equations [**14**]. So, the electrochemical studies of membrane have been done by observing the membrane potential by using the digital potentiometer. Different univalent and divalent electrolytes like KCl, NaCl, LiCl and CaC12, $MgCl_2$, $BeCl_2$ respectively are used to observe the membrane potential. The measurement of membrane potential is used to obtain the transport property of ions across an incubated charged membrane. Hypothetically the membrane potential for aqueous electrolytes or heavy metal ions solution system can determined by many theories like TMS [**15-17**], Altug and Hair [**18**], Kobatake *et.al*. [**19, 20**] as well as the most new one is Nagasawa and coworkers [**21, 22**]. Among these the TMS theory is used, which can treated by the help of Donnan equilibrium and Nemst Planck equation. The Donnan potential totally depends on the membrane charge density which plays a significant role in the selectivity and applications of charged membrane The diffusion potential depends on the mobility of ions through membrane that affects the transport property of ions, through which the measurement of diffusion as well as Donnan potential will be very easy and give the important parameters like ionic mobility and effective charge fixed density of membranes. The study of membrane potential is commonly used for the electrochemical characterization of composite membranes [**23**]. The most important TMS equation is generally used to obtain the different parameters of membrane described as follows.

Teorell-Meyer-Sievers (TMS) Equations: TMS equations are widely employed to calculate the membrane potential of charged porous membranes in electrolyte solutions. Membrane potential can be evaluated by using TMS Equation which is given as.

$$\Delta\overline{\Psi}_m = 59.2\left(\log\frac{C_2}{C_1}\frac{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}}{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}}+\overline{U}\log\frac{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}\,\overline{U}}{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}\,\overline{U}}\right) \qquad \text{Eq. 1}$$

$$\overline{U}=(\overline{u}-\overline{v})/(\overline{u}+\overline{v}) \qquad \text{Eq. 2}$$

Where C_1 and C_2 represents the concentrations of feed electrolyte solutions, $\overline{D}$ is the charge density in equivalents per unit volume of the membrane and $\overline{v}$ and $\overline{u}$ are the mobilities of anion and cation respectively ($m^2v^{-1}s^{-1}$) respectively in the membrane phase. TMS equation in terms of donnan and diffusion potential is as follows.

$$\Delta\overline{\Psi}_{m;e} = \Delta\Psi_{Don}+\Delta\overline{\Psi}_{diff} \qquad \text{Eq.3}$$

Where

$$\Delta\overline{\Psi}_{Don} = -\frac{RT}{V_kF}\ln\left(\frac{\gamma_{2\pm}C_2\overline{C}_1}{\gamma_{1\pm}C_1\overline{C}_2}\right) \qquad \text{Eq. 4}$$

The R, T and F have their usual meaning; $\gamma_{1\pm}$ and$\gamma_{2\pm}$ are mean activity coefficients, C_{1+} and C_{2+} are the cation concentration in membrane phase first and second respectively.
The cation concentration is given by the equation;

$$\overline{C}_\pm = \sqrt{\left(\frac{V_x\overline{D}}{2V_k}\right)^2+\left(\frac{\gamma_\pm C}{q}\right)^2}-\frac{V_x\overline{D}}{2V_k} \qquad \text{Eq. 5}$$

Where V_k and V_x are the valency of cation and fixed charge group on the membrane matrix, q represents charge effectiveness of the membrane which is given as;

$$q = \sqrt{\frac{\gamma_\pm}{K_\pm}} \qquad \text{Eq. 6}$$

Here, $K_\pm$ is the distribution coefficient expressed by the equation below as;

$$K_\pm = \frac{\overline{C}_\imath}{C_i} \qquad \text{Eq. 7}$$

$$\overline{C}_\imath = C_i - \overline{D}$$

Where $\overline{C}_\imath$ is the I th concentration of ion in the membrane phase and C_i is the concentration of ion in solution phase.

The diffusion potential $\Delta\Psi$ diff , is expressed in the form

$$\Delta\overline{\Psi}\text{diff} = -\frac{RT}{V_kF}\frac{\overline{\omega}-1}{\overline{\omega}+1}\times\ln\left(\frac{(\overline{\omega}+1)C_{2+}+(V_x/V_k)\overline{D}}{(\overline{\omega}+1)C_{1+}+(V_x/V_k)\overline{D}}\right) \qquad \text{Eq. 8}$$

Where $\overline{\omega} = \frac{\overline{u}}{\overline{v}}$ Eq. 9

ϖ is the mobility ratio of cation and anion in the membrane phase. Addition of equations 4 and 8 gives total membrane potential. The total membrane potential $\Delta\Psi_{m,e}$ was thus obtained by simple addition of Eqs.(4) and (8)

$$\Delta\bar{\Psi}_{m,e} = -\frac{RT}{V_k F} ln\left(\frac{\gamma_{2\pm} C_2 \bar{C}_{1+}}{\gamma_{1\pm} C_1 \bar{C}_{2+}}\right) - \frac{RT}{V_k F}\frac{\varpi - 1}{\varpi + 1} \times \ln\left(\frac{(\varpi + 1)C_{2+} + (V_x/V_k)\bar{D}}{(\varpi + 1)C_{1+} + (V_x/V_k)\bar{D}}\right)$$

Membrane transport properties in different feed solutions may be calculated as follows using Eq. (10)

$$\Delta\bar{\Psi}_m = \frac{RT}{F}(t_+ - t_-) \ln\frac{C_2}{C_1} \qquad \text{Eq. 10}$$

The above 1MS theory has several important limitations and postulates which are described as follows:

From either side of membrane the transference of water in unequal electrolyte on concentrations may be ignored which means that it cannot affect the potentiometer response. The movement of ions and concentration of fixed charges are constant throughout the composite membrane. It is indicated that there must be development of equilibriumat all the solution and membrane interfaces which have an accurate similarity with Donnan equilibrium [**24, 25**]. It shows independent behavior with respect to the concentration of solutions while the activity coefficient of salt is similar in both the solution and membrane phases. The activities of salt concentration can only be agreed through donnan potential either by using the Planck's or Henderson equation. Inspection of surface charge density is a prominent factor that decides the performances of membrane and accordingly their nature can be determined by the observed and calculated potential values [**26, 27**]. The electrochemical setup which can be used to measure the potential observation of membranes is represented as follows by Figure 1.

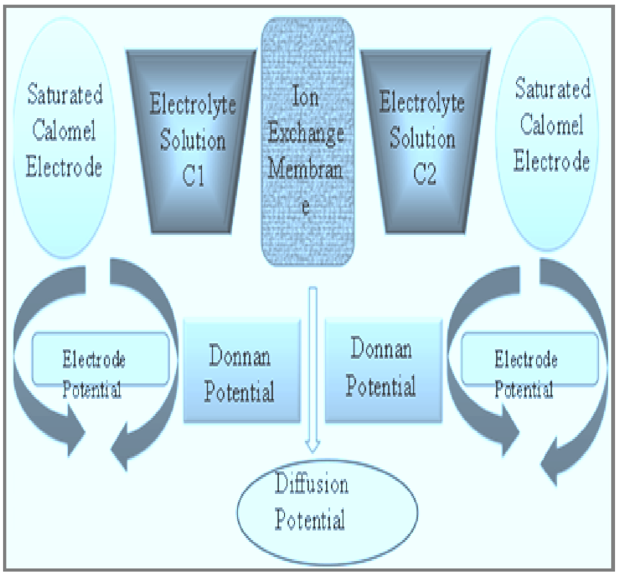


Figure 1. Electrochemical setup used for ionic potential measurement.

Membrane potential: Membrane potential or transmembrane potential or membrane voltage is the difference in electric potential between the interior and exterior environment of a biological membrane or the electric potential difference between the unequal concentrations of any electrolytic solutions separated by any composite artificial membrane. Membrane potential is a potential gradient that forces the ions to passively move in one direction, positive ions are attracted by the negative charged membrane and negative ions by the positive charged membrane. The electrical potential difference across the membrane that exactly balances the concentration gradient for an ion is known as the equilibrium potential. Because the system is in equilibrium, the membrane potential will tend to stay at the equilibrium potential.Membrane potentials are determined primarily by factors like the concentration of ions on the each side of membrane and the permeability of the membrane to those ions i.e. ion conductance [28].

The electrochemical observation of composite membrane potential can easily measured by using digital potentiometer. In this observation the freshly prepared charged membrane was installed at the center of a special measuring cell, which had two glass containers, on either side of the membrane. The various salt solutions such as chlorides of K+, Na+, and Li+ were prepared by using deionized water. The above both collared glass containers has a cavity for introducing the electrolyte solutions as well as saturated calomel electrodes. The half-cell contained nearly 25 ml of the electrolyte solution while the capacity of each of the half cells is more than that the given capacity. When the unequal concentration of electrolyte solutions are filled into both of the collared chamber separately, the have tried to make the equilibrium state through which a regular pattern of membrane potential arises in the potentiometer readings which designated as observed membrane potentiall [29].

Charge density: The charge density is a measure of how much electric charge is accumulated in a composite membrane. Depending on the nature, the formula of charge density can be shown as (λ=ql) where λ is the linear charge density, q is the charge and l is the length over which it is distributed. Therefore, according to electromagnetism charge density is a measure of electric charge per unit volume of the space in one, two or three dimensions. The surface charge describes the electric potential difference between the inner and outer surface of different states of the object. The surface charge density will be there only in conducting surfaces and describes the whole amount of charge per unit amount of the area [30].

In case of composite membrane the fixed-charge density is the most important parameter which governs the transport phenomena in composite membranes. It is estimated by the TMS method; it is dependent on the feed composition due to the prefential adsorption of some ions. In the case of composite membrane it is indicate that the applied pressure is also an important variable to modify the charge density which in turns the performance of membrane. In the electrochemical approach the membrane which is fixed between the two unequal concentrations of electrolyte solutions which indicated that the surface charge density is found to depend on the initial stage of membrane preparation weather it is having positive or negative charged characteristics [31]. Therefore on the basis of charge density further parameters of membrane like transport number mobility ratios etc can also easily be calculated, and it can indicated the variations according to the nature of the used electrolyte solutions.

Distribution coefficient (D): The partition-coefficient or the distribution-coefficient is the ratio of the respective equilibrium concentrations of a chemical in a mixture of two immiscible phases and is also a measure of the difference in solubility of the chemical in the two phases. In other words a partition coefficient is the ratio of the concentration of a substance in one medium or phase (C_1) to the concentration in a second phase (C_2) when the two concentrations are at equilibrium; that is, partition coefficient = (C_1/C_2) equil. The units of C_1 and C_2 may be different. The greater the solubility of a substance the higher its partition coefficient and the higher the partition coefficient the higher the permeability of the membrane for that particular substance [32].

The partition coefficient generally refers to the concentration ratio of un-ionized species of compound, while the distribution coefficient refers to the concentration ratio of both the ionized plus un-ionized compounds. n chemical and pharmaceutical sciences where both phases usually are solvents. Most commonly one of the solvents is water and another one is hydrophobic. Hence the partition coefficient measures the hydrophilicity or hydrophobicity of the chemical substances. By electrochemical analysis the membrane which is fixed between the two electrolyte solutions of unequal concentrations which indicated the partition coefficient due to the electrolyte ions and it is found to depend on the concentration differences of solutions as well as membrane characteristics [33].

Mobility ratio (M): Mobility ratio is defined as the mobility of displacing fluid may be gas divided by the mobility of displaced fluid like crude oil. The mobility ratio is a single term that describes the rate and efficiency of oil displacement by other immiscible fluids. If the values of $M > 1$ are generally considered as favorable values, and if increasing values of $M < 1$ are considered as unfavorable values. In the matter of composite membrane where prepared charged membrane was installed at the center of a special two collared measuring cell. In each of the cell the various salt solutions of different concentrations like chlorides of K+, Na+, and Li+ were filled. When these electrolyte solutions are filled into both of the collared glass chamber, shows a regular pattern of membrane potential. The values of observed membrane potential has been applied with the theoretical membrane potential values which comes from the TMS equation, results to make the values of charge density of membrane. By the help of TMS theoretical equation it can easily be calculated the value of mobility ratio which is having a regular order of increasing or decreasing due to the characteristics of used electrolyte solutions as well as the nature of composite membrane [34, 35].

Transport numbers: Transport numbers is the ratio of the current carried by a given ionic species through a cross section of an electrolytic solution through which the total current passing through the cross section. Differences of transport number arise from differences in electrical mobility. For example in an aqueous solution of NaCl, less than half of the current is carried out by the positively charged Na^+ and more than half is carried by the Cl^- because the chloride ions are able to move faster, i.e., chloride ions have higher mobility than sodium ions. The sum of the transport numbers for all of the ions in solution always equals unity. The transport number describes the fraction of the total current that is carried by the ion. This number depends on the relative mobility of the ions, and ultimate gives the relative contribution to conductivity of each of the ions [36]. A rise in temperature tends to bring the transport number of cation and anion more closely to 0.5. There are two Hittorf and moving boundary experimental methods are used for the determination of transport numbers. The Hittorf method is based on the measurements of ion concentration changes near the electrodes, while the moving boundary method involves measuring the speed of displacement of the boundary between two solutions due to an electric current [37].

Permselectivity: Permselectivity is the term used to define the preferential permeation of certain ionic species (on the basis of size, charge, and physical configuration)through an ion-exchange membrane. It is the most important membrane property to evaluate the quality of membrane separation. The capability of a membrane to separate different components from each other can be expressed by selectivity. Perm-selective membranes are selectively permeable to water vapor but retain larger molecules such as chemical toxins etc. Permselective membrane allows specific species to be transported while restricting the passage of other species. In other words it is a measure of the characteristic difference in the membrane permeability for counter-ions and co-ions. The cation exchange membrane is said to be perfectly permselective if it allows only the transport of counter-ions while blocking the transport of co-ions. The permselectivity depends on the properties of the electrolyte ions used in the study. The nature of the counter-ions influences the membrane water content, which is often linked to ion transport properties and binding affinity between counter ions and fixed charge groups within the membrane. The presence of a selectively permeable membrane allows the cell to exercise control over the quantum, timing and rate of movement of these molecules. Movement across a selectively permeable membrane can occur actively or passively. For example, water molecules can move passively through small pores on the membrane [38, 39].

Water Flux of membrane: Flux or water flux is typically expressed as volume per area per unit of time. Flux is used to express the rate at which water permeates a reverse osmosis membrane. While the Flux of a membrane is defined as the amount of permeate produced per unit area of membrane surface per unit time. Generally flux is expressed as gallons per square foot per day

(GFD) or as cubic meters per square meters per day. The high water flux and elevated rejection of salts and contaminants are two primary goals for membrane distillation processes. It is imperative to study the factors affecting water flux and solute transport in membrane distillation, the fundamental mechanisms, and practical applications to improve system performance. Therefore water flux is very important process which has decided the efficiency and performances of particular membrane [**40**].

APPLICATION

This review article may be helpful to understand the electrochemical parameters of composite membrane, through which it must be easier to analyse the application of membrane used for water filtration.

CONCLUSION

The electrochemical parameters of membranes, particularly those which have some functional groups decided their negative or positive characteristics. Such membranes showing ion-exchange nature as well as modified surface indicated cationic or anionic layers of changed nature and modifications. These anisotropic membranes show different structure and physicochemical properties due the presence of positive or negative charges. These phenomena, which are typical for these membranes, make asymmetric transport properties. In this review it is indicated that the presence of unequal electrolyte concentrations at both side of the membranes makes an interface between them, which leads the Donnan potential occurs at both the junctions due to the transfer of used electrolyte ions. These Donnan potential occurs as a result of Donnan equilibrium, which refers to the distribution of ionic species between two ionic solutions. There are various theories like Teorell, Meyer and Sievers (TMS), Altug and Hair, Kobatake as well as the most new one is Nagasawa and co-workers are used to determine the electrochemical parameters of membranes, but particularly TMS method is mostly used to determine the exact values of parameters like membrane potential, distribution coefficient, transport number, mobility ratio, surface charge density etc.

Conflict of Interest: The authors declare that there is no conflict of interests regarding the publication of this paper.

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