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Synthesis, Characterization and Electrochemical Properties of Composite Membrane by an Aqueous Sol-Gel Method

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Abstract

The composite membranes were prepared by sol-gel process, and the membrane potential has been measured for characterizing the ion-transport phenomena across a charged membrane using electrolytes (KCl, NaCl and LiCl). The membrane potential offered by the electrolytes is in the order of LiCl>NaCl>KCl. The results have been used to estimate fixed-charge density, distribution coefficient, charge effectiveness and transport properties of electrolytes of this membrane. The fixed-charge density is the most important parameter, governing transport phenomena in membranes. It is estimated by the TMS method; it is dependent on the feed composition due to the preferential adsorption of some ions. The results indicate that the applied pressure is also an important variable to modify the charge density and, in turn, the performance of membrane. The experimental results for membrane potential are quite consistent with the theoretical prediction. The morphology of the membrane surface is studied by Scanning Electron Micrographs (SEM).

Keywords: Composite membrane; Membrane potential; Electrolytes; SEM; Sol-gel method

List of Symbols

Nomenclature

AR: analytical reagent

C_1,C_2: concentrations of electrolyte solution on either side of the membrane (mol/l)

$\overline{C}_{2+}$: cation concentration in membrane phase 1 (mol/l)

$\overline{C}_{2+}$: cation concentration in membrane phase 2 (mol/l)

C_i: ith ion concentration of external solution (mol/l)

$\overline{D}$: ith ion concentration in membrane phase (mol/l)

$\overline{D}$: charge density in membrane (eq/l)

F: Faraday constant (C/mol)

$K_{\pm}$: distribution coefficient of ions

80-160: pressure (MPa)

q: charge effectiveness of the membrane

R: gas constant (j/K/mol)

SCE: saturated calomel electrode

SEM: scanning electron microscopy

TMS: Teorell, Meyer and Sievers

t_+: transport number of cation

t_-: transport number of anion

$\overline{\nu}$: mobility of cations in the membrane phase (m^2/v/s)

$\bar{U}$: ($\overline{\nu}$ - $\overline{\nu}$)/($\overline{\nu}$ + $\overline{\nu}$)

$\overline{\nu}$: Mobility of anions in the membrane phase (m2/v/s)

V_k: Valency of cation

V_x: Valency of fixed-charge group

$\gamma'_{\pm}, \gamma''_{\pm}$: mean ionic activity coefficients

$\overline{\omega}$: Mobility ratio

$\Delta\overline{\Psi}_m$: Observed membrane potential (mV)

$\Delta\overline{\Psi}_m$: Theoretical membrane potential (mV)

$\Delta\overline{\Psi}_{diff}$: Donnan potential (mV)

$\Delta\overline{\Psi}_{diff}$: Diffusion potential (mV)

Introduction

Ion-exchange membranes (IEM) carry the fixed positive or negative charges (called anion-exchange membranes, AEM or cation-exchange membranes, CEM, respectively). They are generally used in the treatment of ionic aqueous solutions, e.g., electrodialytic concentration of seawater, desalination of saline water, demineralization process, acid and alkali recovery and others [1-4]. Ion-exchange charged membranes, which are now extensively utilized in industries, have attracted considerable attentions due to their extraordinary properties and practical demands and thus a large number of researchers have concentrated on these investigations for many years [5]. With the rapid development of industry and population explosion throughout the world, the demand for fresh water has become increasingly urgent due to the scarcity of drinking water resource and the contamination of industry to environment. Thus, the treatment of industrial wastewater is becoming imperative; while innovative technologies, which are used to prepare fresh water such as the desalination of brackish water and to treat the industrial refuses, have attracted numerous researchers. Among these novel methods, ion-exchange membrane-based technologies have been regarded as both effective and economical due

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to its lower operation expense and secure process, etc. [6-8]. Composite membranes have high thermal and chemical stability, long life and good defouling properties in their application, and they can have catalytic properties [9]. These properties have made these membranes desirable for industrial applications in the food, pharmaceutical and electronic industries. The sol-gel technique is an extremely flexible method to produce inorganic materials with highly homogeneous and controlled morphology [10-12]. Recently, due to the mild reaction conditions that can be used, the great potential of sol-gel processes, both hydrolytic and non-hydrolytic, has been extensively investigated for the synthesis of organic/inorganic materials [13].

A potential difference can be observed and measured, at least partly ionically perm selective, membrane in contact with two solutions at following cases: (1) same electrolyte of different concentration; and (2) same ionic strength but different counter-ions or co-ions. The former is called concentration potential and the latter bi-co-ionic/bi-counter-ionic potential [14,15]. These potentials are of great interest in connection with the analysis of effective charge density, ionic transport number, and selectivity as well as interaction between charged species and membranes in both single charged membrane and bipolar membranes and thus caused great attention for many years [16-18]. For this purpose, a potential model correlating the intrinsic parameters of the membrane and ionic species with transport properties is actually needed and a body of such models has been obtained for single charged membranes and bipolar membranes [19-22]. It is now recognized that the electrical charge on the pore wall of membranes plays an important role in its separation performance and fouling behavior [23-25]. The choice of a membrane with suitable charge or electrical potential property can lead to optimization of existing processes or allow selective separations. For these reasons there is much interest in characterizing the charge or potential property of membranes. The electrical potential difference which is generated when an electrolyte solution flows across a charged membrane under a concentration gradient is among the most convenient experimental techniques for studying such electrical potential properties of porous membranes [26].

In the present investigation, a composite titanium-vanadium phosphate membrane is developed by sol-gel process using polystyrene as a binder. Fixed-charge density, the most effective parameter, has been evaluated and utilized to calculate membrane potentials for different electrolyte concentrations using TMS method [27-31]. In addition to the fixed-charge density, distribution coefficient, transport numbers, mobility, charge effectiveness and other related parameters were calculated for characterizing the composite membrane.

Materials and Methods

Preparation of membrane

Titanium-Vanadium phosphate precipitate was prepared by mixing a 0.2 mol titanium (III) chloride (Otto Kemi, India with 99.989% purity) and vanadium (III) chloride (Merck, Germany with 99.989% purity) with 0.2 mol tri-sodium phosphate (E. Merck, India with 99.90% purity) solutions. The precipitate was washed properly with deionized water to remove free electrolytes and then dried at 100°C. The precipitate was ground into fine powder and was sieved through 200 mesh (granule size <0.07 mm). Pure crystalline polystyrene (Otto Kemi, India, AR) was also ground and sieved through 200 mesh. The titanium-vanadium phosphate along with appropriate amount of polystyrene powder was mixed thoroughly using mortar and pestle. The mixture was then kept into a cast die having a diameter of 2.45 cm and placed in an oven maintained at 300°C for about an hour to equilibrate the reaction mixture [32]. The die containing the mixture was then transferred to a pressure device (SL-89, UK), and various pressures such as 80, 100, 120, 140 and 160 MPa were applied during the fabrication of the membranes. As a result titanium-vanadium phosphate membrane of approximate thicknesses 0.095, 0.090, 0.085, 0.080 and 0.075 cm were obtained, respectively. The membranes prepared by embedding 25% of polystyrene by weight were suitable, and the greater or lesser than this weight did not show reproducible results and appeared to be unstable. Membranes prepared in this way were stable and further subjected to microscopic and electrochemical examinations for cracks and homogeneity of the surface.

Scanning electron microscopy (SEM)

The prepared samples at various pressures was heated in the tabular furnace for 3 hours and then cooled. A very thin transparent polymer glue tape was applied on the sample and then placed on an aluminum stub of 15 mm diameter. Thereafter, the sample was kept in a chamber at a very low pressure where the entire plastic foil containing the sample was coated with gold (60 µm thickness) for 5 minutes. The scanning electron micrograph of gold coated specimen was recorded, operating at an accelerating voltage of 10 kV using the scanning electron microscope (GEOL JSM-840).

Measurement of membrane potential

The freshly prepared charged membrane was installed at the center of the measuring cell, which had two glass containers, one on either side of the membrane. Both collared glass containers are having a hole for introducing the electrolyte solution and Saturated Calomel Electrodes (SCEs). The half-cell contained 40 ml of the electrolyte solutions. Electrochemical cells of the type C_1 SCE Solution and C_2 Membrane Solution SCE were used for measuring membrane potential using Osaw Vernier Potentiometer. In all measurements, the electrolyte concentration ratio across the membrane was taken as $C_2/C_1=10$. All solutions were prepared by using Analytical Reagent (AR) grade chemicals and ultra-pure distilled water. The electrodes used were saturated calomel electrode and were connected to a galvanometer. The solutions in both containers were stirred by a magnetic stirrer to minimize the effects of boundary layers on the membrane potential. The pressure and temperature were kept constant throughout the experiment and the potentials were measured at 25°C.

Results and Discussion

The composite membranes using polystyrene as a binder were prepared by sol-gel process. The membranes were found to have the following properties:

- They were thermally stable up to 500°C.
- They were resistant to compaction.
- They were inert to harsh chemical ($K_2Cr_2O_7$, H_2O_2, HNO_3, H_2SO_4, etc.) as they did not decompose in their presence.
- They did not show any swelling.
- They were stable after long usage, i.e., they were durable.

The characterization of membrane morphology has been studied by using SEM [33]. The information obtained from SEM images have provided guidance in the preparation of well-ordered precipitates, composite pore structure, micro/macro porosity, homogeneity, thickness, surface texture and crack-free membranes [34]. The SEM surface images of the composite membranes were taken at different applied pressure and are presented in Figure 1. Inorganic composite membranes have the ability to generate potential when two electrolyte solutions of unequal concentration are separated by a membrane and driven by different chemical potential acting across the membrane [35]. The electrical character of the membrane regulates the migration of charged species, and diffusion of electrolytes from higher to lower concentration takes place through the charged membrane. The values of membrane potential $\Delta\overline{\Psi}_m$ measured across membranes in contact with various 1:1 electrolytes (KCl, NaCl and LiCl) were dependent on concentration of electrolytes present on both sides of the membrane at 25 ± 1°C are given in Table 1. The observed potential was low (mV, +ve). It was found to increase on decreasing the concentration of electrolytes (KCl, NaCl and LiCl), which is a usual behavior of inorganic membranes. The selectivity character of ion-exchange membranes were reported on the basis of membrane potential values, performed on uni-uni and multi-uni valents electrolytes as 1:1, 2:1 and 3:1. The reversal in sign from positive to negative values of membrane potential occurred with the 2:1 and 3:1 electrolytes. This is evidently due to the adsorption of multivalent ions, which led to a state where the net positive charge left on the membrane surface made the anion selective with 2:1 or 3:1 electrolytes. The membrane potential was also seen to be largely dependent on the pressure applied during the membrane fabrication. Application of higher pressure at composite membranes led to reduction in their thicknesses, contraction in pore volume and consequently offered a progressively higher fixed-charge density [36].

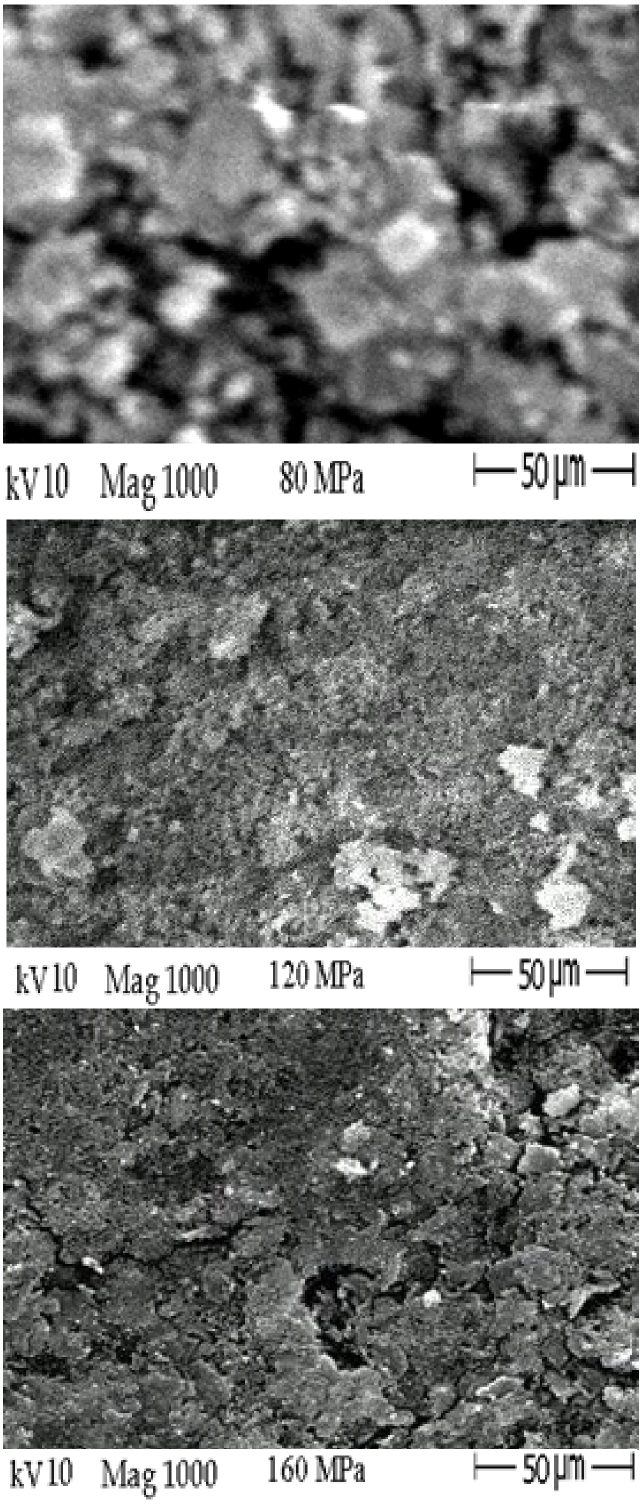

Figure 1: SEM images of composite membranes prepared at different applied pressures (80 MPa, 120 MPa and 160 MPa).

The charge property of the membrane matrix greatly influences the counter-ion than co-ion as well as the transport phenomena in the solutions. The surface charge concept of the TMS model for charged membrane is an appropriate starting point for the investigations of actual mechanisms of ionic or molecular processes which occur in membrane phase [27-31]. The TMS model assumes uniform distribution of surface charge and consists of Donnan potential and diffusion potential. According to the TMS, the membrane potential $\Delta\overline{\Psi}_m$ is applicable to an idealized system and is given by

$$\Delta\overline{\Psi}_m = 59.2\left(\log\frac{C_2}{C_1}\frac{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}}{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}}+\overline{U}\log\frac{\sqrt{4C_2^2+\overline{D}^2}+\overline{D}\overline{U}}{\sqrt{4C_1^2+\overline{D}^2}+\overline{D}\overline{U}}\right),\ \overline{U}=(\overline{u}-\overline{v})/(\overline{u}+\overline{v}) \quad (1)$$

Where $\overline{v}$ and $\overline{v}$ are the ionic mobilities ($m^2/V/s$), of cation and anion, respectively, in the membrane phase. The charge densities of inorganic membranes were estimated from the membrane potential measurement and can also be estimated from the transport number. From the plots in Figure 2, the charge density parameters can be evaluated for a membrane carrying various charge densities, $\overline{D} \leq 1$ for different 1:1 electrolytes systems. The theoretical and observed potentials were plotted as a function of $-\log C_2$ as shown in Figure 2. Thus, the coinciding curve for various electrolytes system gave the value for the charge density $\overline{D}$ within the membrane phase.

Therefore, the increase in the values of $\overline{D}$ with higher applied pressure is due to successive increase of charge per unit volume as well as the modification in the surface microstructure of the membrane. The plot of charge density $\overline{D}$ of the membrane for 1:1 electrolytes (KCl, NaCl and LiCl) versus pressures is shown in Figure 3. The order of charge density of various electrolytes is found to be KCl>NaCl>LiCl throughout the range of applied pressure at which the membranes were prepared. The surface charge model may work as a tool to improve the performance of the membrane filtration process. Since, the charge density is an important parameter governing transport phenomena and the charge property of the membrane dominates the electrostatics interaction between the membrane and particles in the feed solution due to the prefential adsorption of some ions. Therefore, by controlling the solution physico-chemistry, the optimum charge property of the membrane can be obtained as desired.

The TMS equation (1) can also be expressed by the sum of Donnan potential $\Delta\Psi_{Don}$ between membrane surfaces and external solutions and the diffusion potential $\Delta\overline{\Psi}_{diff}$ within the membrane.

Applied pressure (MPa)															
Membrane Potential (O)															
C_2 (mol/l)	80			100			120			140			160		
	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl
0.001	49.5	50.6	51.7	50.6	52.0	53.2	52.2	53.3	54.4	53.3	54.5	55.8	54.3	55.4	56.4
0.001	45.0	45.9	47.1	46.2	47.3	48.5	47.1	48.2	49.3	48.0	49.2	50.3	49.3	50.6	51.8
0.01	22.5	23.4	24.8	24.0	25.2	26.3	25.0	25.9	27.3	25.5	27.2	28.5	27.0	28.4	30.0
0.1	7.53	8.53	9.62	9.02	10.5	12.2	10.0	11.1	12.3	11.0	12.3	13.5	12.1	13.6	15.1
1.0	5.08	6.09	7.50	6.50	7.60	9.00	7.50	8.54	9.60	8.52	9.57	10.6	9.60	10.3	11.9
Applied pressure (MPa)															
Membrane Potential (T)															
C_2 (mol/l)	80			100			120			140			160		
	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl
0.001	58.94	58.94	58.94	59.02	59.01	59.01	59.12	59.13	59.12	59.14	59.15	59.15	59.16	59.16	59.16
0.001	47.25	47.25	47.25	49.57	49.47	49.57	54.48	54.49	54.49	55.90	55.90	55.90	56.78	56.78	56.78
0.01	11.45	11.46	11.48	13.44	13.45	13.47	20.40	20.41	20.43	24.01	24.02	24.04	27.13	27.15	27.16
0.1	1.32	1.35	1.36	1.55	1.58	1.59	2.47	2.50	2.51	3.05	3.07	3.09	3.62	3.65	3.66
1.0	0.24	0.26	0.28	0.26	0.28	0.30	0.36	0.37	0.39	0.41	0.43	0.45	0.47	0.48	0.51
Charge density (eq/l)	1.48	1.27	0.99	1.74	1.43	1.20	4.14	3.41	2.68	6.91	4.76	3.63	10.2	6.74	4.34

Table 1: Observed and theoretical membrane potentials (mV) across the composite membranes in contact with 1:1 electrolyte solution at different concentrations C_2/C_1=10 at 25 ± 1°C.

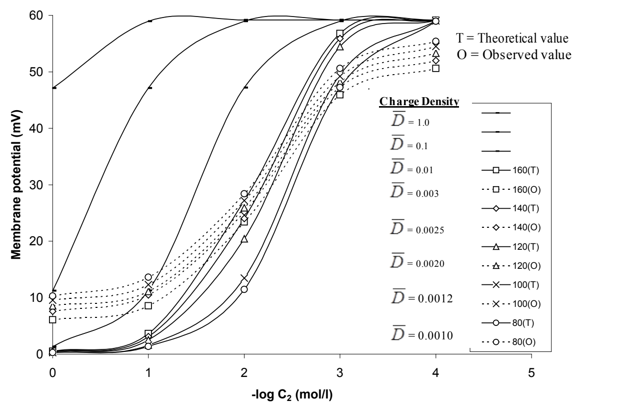

Figure 2: Plots of membrane potentials versus –log C_2 at different concentrations of NaCl electrolyte solution for composite membranes prepared at different pressures 80-160 MPa.

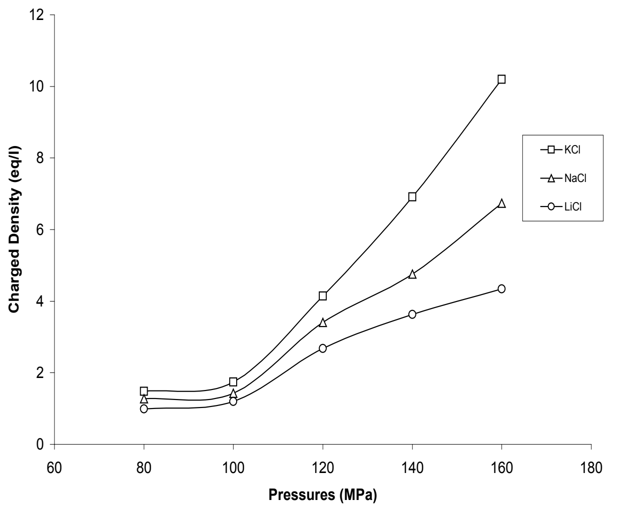

Figure 3: Plots of fixed-charge density $\bar{D}$ versus pressures (80-160 MPa).

$$\Delta\bar{\Psi}_m = \Delta\Psi_{Don} + \Delta\bar{\Psi}_{diff} \quad (2)$$

$$= -\frac{RT}{V_k F}\ln\left(\frac{\gamma''_{\pm} C_2 \bar{C}_{1+}}{\gamma'_{\pm} C_1 \bar{C}_{2+}}\right) - \frac{RT}{V_k F}\frac{\bar{\omega}-1}{\bar{\omega}+1}\times\ln\left(\frac{(\bar{\omega}+1)\bar{C}_{2+} + (V_x/V_k)\bar{D}}{(\bar{\omega}+1)\bar{C}_{1+} + (V_x/V_k)\bar{D}}\right) \quad (3)$$

The R, T and F have their usual significance; $\gamma''_{\pm}$ and $\gamma''_{\pm}$ are the mean ionic activity coefficients; $\bar{\omega} = \frac{\bar{u}}{\bar{v}}$ is the mobility ratio of the cation to the anion in the membrane phase and $\bar{C}_{2+}$ and $\bar{C}_{2+}$ are the cation concentrations in the membrane phase first and second, respectively. The cation concentration is given by the equation

$$\bar{C}_{+} = \sqrt{\left(\frac{V_x\bar{D}}{2V_k}\right)^2 + \left(\frac{\gamma_{\pm}C}{q}\right)^2} - \frac{V_x\bar{D}}{2V_k} \quad (4)$$

Here V_k and V_x refer to the valency of cation and fixed-charge group on the membrane matrix, q is the charge effectiveness of the membrane and is defined by the equation

$$K_{\pm} = \frac{\bar{C}_i}{C_i}, \quad (5)$$

Where $K_{\pm}$ is the distribution coefficient. It is expressed as

$$K_{\pm} = \frac{\bar{C}_i}{C_i}, \quad (6)$$

Where $\bar{C}_i$ the i^th ion concentration in the membrane is phase and C_i is the i^{th} ion concentration of the external solution. The transport properties of the membrane in various electrolyte solutions are important parameters to further investigate the membrane phenomena as shown in Eq. (7)

$$\Delta\bar{\psi}_m = \frac{RT}{F}(t_+ - t_-)\ln\frac{C_2}{C_1}, \quad \frac{t_+}{t_-} = \frac{\bar{u}}{\bar{v}} \quad (7)$$

Equation (7) was first used to calculate the values of transport numbers t_+, mobility ratio $\bar{\omega} = \frac{\bar{u}}{\bar{v}}$ and finally Ū as given in Table 2. The values of mobility $\bar{\omega}$ of the electrolytes in the membrane phase were found to be high at lower concentration of all the electrolytes (KCl, NaCl and LiCl). Further increase in concentration of the electrolytes led to a sharp drop in the values of $\bar{\omega}$ as given in Table 2. The high mobility is attributed to higher transport number of comparatively free cations of electrolytes and also be similar trend as the mobility in least concentrated solution. The values of the parameters K_{+}, q and $\bar{C}_{+}$ derived for the system have also been included in Table 2. Using Eq. (6) it was found that the values of distribution coefficients increased at lower concentration of electrolytes. As the concentration of electrolytes increased, the values of distribution coefficients sharply dropped and, thereafter, a stable trend was observed as shown in Figure 4. The large deviation in the value of $K_{\pm}$ at the lower concentration of electrolytes was attributed to the high mobility of comparatively free charges of the strong electrolyte and thus, reached into the membrane phase easily compared to higher concentrated electrolytes solution. In order to interpret the variation of the charge effectiveness depending on those values, that the ion-pairing effect causes the difference between the effective charge density and the fixed-charge density in membrane phase. In our membrane, counter ion Cl^{-} is same for 1-1 electrolytes therefore, the variation in the q values are follow the similar trend and

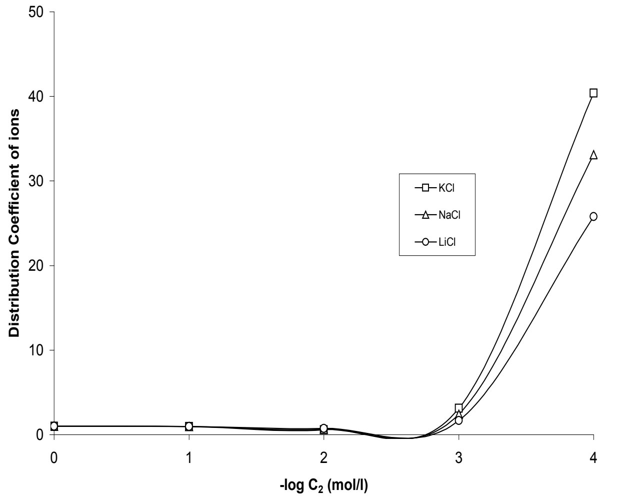

Figure 4: Plots of Distribution coefficient of ions ($K_{\pm}$) versus –log C_2 (mol/l).

the order is LiCl>NaCl>KCl up to the C_2=0.01 mol/l and then drop in the q values were analyzed from Figure 5. When, the external electrolyte concentration is higher or lower, a number of counter ions go into the membrane due to imbalance in the counter ion concentration of external electrolyte and fixed charged group in the membrane phase. Therefore, the ion association with the fixed charged group and counter ions in the membrane is enhanced as a result the charge effectiveness has a lower value whereas in the moderate concentration region the counter ion concentration in the external electrolyte and the fixed-charge density in the membrane are comparable. Therefore, a less number of ion pair formation and consequently higher values of the charged effectiveness, the optimum value of charge effectiveness are obtained at C_2=0.01 mol/l and then decreased steeply. The order of the charge effectiveness of 1-1 electrolytes may depend on increasing ionic charge density of co-ion adsorption on the charged membranes. The membrane potential derived in this way (theoretical) and the experimentally obtained membrane potentials at different concentrations for various electrolytes systems have been compared and provided in Figure 6. It may be noted that the experimental data follow the theoretical curve quite well. However, some deviations may be due to various non ideal effects, such as swelling effect and osmotic effects. These effects are often simultaneously present in the charged membranes.

Conclusion

In the present study, the composite membranes were prepared by sol-gel process, and results indicate that the sol-gel approach is appropriate for composite membrane synthesis. The sol-gel technique is an extremely flexible method to produce inorganic materials with highly homogeneous and controlled morphology. The experimental results were analyzed on the basis of the TMS approach, and it was found that the calculated values agree well with the experimental results. The fixed-charge density is the central parameter governing transport phenomena in membranes. The electrical charge on the pore wall of membranes plays an important role in its separation performance and fouling behavior and it depends upon the feed composition and applied

KCl (Electrolyte)						
C_2(mol/l)	t_+	Ū	$\bar{C}_+$	$K_\pm$	q	$\bar{C}_+$
0.0001	0.93	0.86	13.3	40.40	0.157	0.00002
0.0010	0.89	0.78	8.09	3.140	0.554	0.00023
0.0100	0.71	0.42	2.45	0.586	1.239	0.00334
0.1000	0.58	0.16	1.38	0.958	0.895	0.07993
1.000	0.56	0.12	1.27	0.995	0.780	0.77073
NaCl						
0.0001	0.94	0.88	15.7	33.10	0.173	0.00002
0.0010	0.90	0.80	9.00	2.410	0.633	0.00021
0.0100	0.72	0.44	2.57	0.659	1.170	0.00413
0.1000	0.59	0.18	1.44	0.965	0.897	0.08176
1.000	0.57	0.14	1.33	0.996	0.811	0.80377
LiCl						
0.0001	0.95	0.90	19.0	25.80	0.196	0.00001
0.0010	0.91	0.82	10.1	1.680	0.758	0.00018
0.0100	0.73	0.46	2.70	0.732	1.111	0.00505
0.1000	0.60	0.20	1.50	0.973	0.901	0.08375
1.000	0.58	0.16	1.38	0.997	0.881	0.87453

Table 2: The values of t_+, Ū, $\bar{C}_+$, $K_\pm$, q, $\bar{C}_+$ evaluated from using Equation 7 and Equations 4-6 respectively, from observed membrane potentials for various electrolytes at different concentrations for composite membranes prepared at 120 MPa pressure.

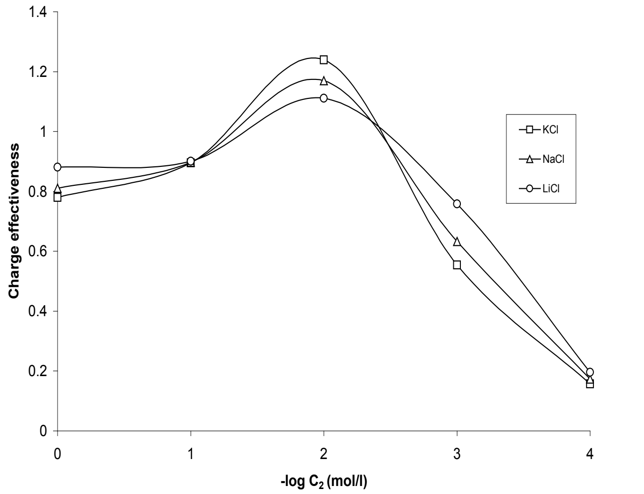

Figure 5: Plots of Charge effectiveness versus –log C_2 (mol/l) for 1:1 electrolyte at different concentrations.

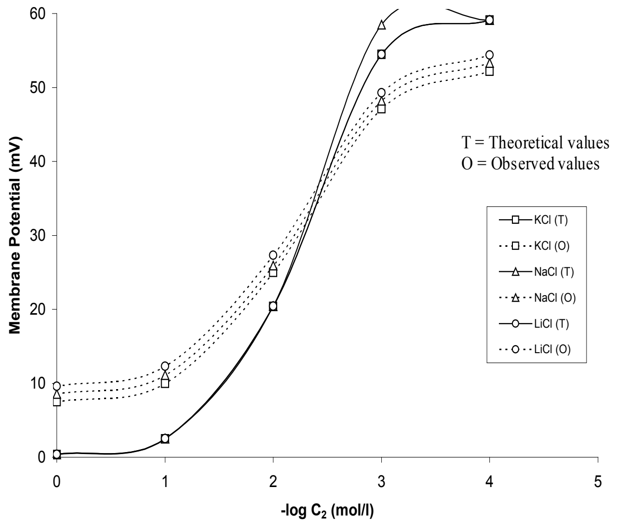

Figure 6: Membrane potentials across composite membranes using various electrolyte (1:1) solutions at different concentrations.

pressure due to the prefential adsorption of some ions. The charge effectiveness of membrane is greatly influenced form applied pressure and increase in adsorption of co-ions on charged membrane, order is KCl<NaCl<LiCl. Thus, this membrane can be suited for commercial application.

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