

# Preparation and Development of the Surface Charge Density of Vanadium Phosphate Membranes in Electrolyte Solutions

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**ABSTRACT:** Polystyrene-based vanadium phosphate membranes prepared by a sol-gel route process from aqueous solutions were studied. The uni-univalent electrolytes (KCl, NaCl, and LiCl) were diffused from the feed solution as a carrier through the prepared membranes with saturated calomel electrodes. The Teorell, Meyer, and Sievers equation was used to estimate the membrane potential, surface charge density, distribution coefficient, transport numbers, and other electrochemical parameters to characterize the prepared membranes. The membrane potentials offered by the uni-univalent electrolytes through prepared membranes were cation selective and found to be in the order  $\text{LiCl} > \text{NaCl} > \text{KCl}$ . The membranes prepared at lower pressures had wider pores and an essen-

tially low surface charge density, whereas membranes prepared at higher pressures carried a high surface charge density and narrow surface openings. The order of charge effectiveness of the electrolytes in the membranes depended on the hydration of the solute-solute interaction and ionic radii of the counterions. The experimental results for membrane potential were consistent with the theoretical prediction. The morphology of the membrane surface was studied by scanning electron microscopy. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3023–3030, 2008

**Key words:** composites; electrochemistry; electron microscopy; inorganic materials; polystyrene

## INTRODUCTION

The application of extraction techniques for the removal and recovery of metals is very significant nowadays. An increasing demand for metal production led to the research of more efficient and economical methods of purification required by the industry. Membrane technology has become an important alternative to the normal processes used for wastewater (electroplating, mining, etc.) treatment, separation, and recovery of target metals. The selective transport of metal ions has been widely studied with supported liquid membranes.<sup>1,2</sup> A membrane is said to be ideally ion selective if only either positively or negatively charged ions pass through it. On the other hand, if the migration of ions through a membrane is not affected at all, the membrane is said to be nonselective. Most often, the membranes are neither ideally ion selective nor entirely nonselective in nature; they exhibit ion selectivity in some measure, depending on the nature of the membrane-forming materials and their dimensional and electro-

chemical characteristics. Membrane potential studies are commonly used for the electrochemical characterization of membranes.<sup>3,4</sup> Their high selectivity, high diffusion rates, and the possibility of concentrating ions make membranes particularly useful. Despite the well-known advantages of supported liquid membranes, they are not often used for practical separation processes because of their low stability and high degradation rate. These membranes suffer a loss of carrier by dissolution into the aqueous phases, and many different studies have been performed to stabilize them.<sup>5–7</sup> Some researchers have impregnated the membranes with low-molecular-weight strong acids (e.g., phosphoric acid, sulfuric acid,  $\text{CFSO}_3\text{H}$ ).<sup>8,9</sup> The conductivity of acid-doped membranes can be as twice high as that of Nafion.<sup>9</sup> Unfortunately, these low-molecular-weight acids are leached out of the membranes over 10s to 100s of hours. Increased mechanical strength and decreased swelling has been achieved by the crosslinking of the polymer chains in the membrane. The addition of resin to the composite membrane increases the ion-exchange capacity, decreases the extent of swelling with water absorption, and increases the mechanical strength.

Inorganic filtration membranes show a number of advantageous properties that make them attractive

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for filtration tasks in the beverage and textile industry, medicine, pharmacy, chemical industry, and wastewater treatment. These properties are attributed to their high thermal resistance, chemical resistance, and mechanical strength. Inorganic membranes are prepared stepwise according to traditional inorganic processing steps<sup>10</sup> and show excellent cleaning conditions, especially by sterilization.

In this article, we describe the preparation of vanadium phosphate membranes by a sol-gel route with polystyrene as a binder by the application of different pressures. The surface charge density ( $\bar{D}$ ) is considered the most effective parameter that controls the membrane phenomena; this quantity was derived and used to calculate the membrane potentials for different electrolyte concentrations with the method of Teorell, Meyer, and Sievers (TMS)<sup>11-14</sup> and to test the applicability of TMS equations for membrane potential for the system under investigation. In addition to the evaluation of the surface charge density  $\bar{D}$ , the distribution coefficient, transport numbers [of the cation ( $t_+$ ) and the anion ( $t_-$ )], mobility, charge effectiveness ( $q$ ), and other related parameters were calculated to characterize the prepared membranes.

## EXPERIMENTAL

### Preparation of the membranes

Vanadium phosphate precipitate was prepared by the mixture of 0.2 mol of vanadium(III) chloride (99.989% purity, Merck, Darmstadt, Germany) with 0.2 mol of trisodium phosphate (99.90% purity, E. Merck, Mumbai, India) solution. The precipitate was washed well with deionized water (Mumbai, India) (water purification system, Integrate; reverse osmosis [RO] conductivity = 0–200  $\mu\text{S}/\text{cm}$ , ultra pure [UP] resistivity = 1–18.3  $\text{M}\Omega\text{ cm}$ ) to remove free electrolyte and dried at 50°C. The precipitate was ground into a fine powder and was sieved through 200 mesh (granule size < 0.07 mm). Pure crystalline polystyrene (analytical-reagent grade, Otto Kemi, Mumbai, India) was also ground and sieved through 200 mesh. The membranes were prepared by the method suggested by Beg and coworkers.<sup>15-17</sup> Different proportions of polystyrene and vanadium phosphate precipitate were mixed thoroughly with a mortar and pestle. The mixture was then kept in a cast die with a diameter of 2.45 cm and placed in an oven (Oven-Universal, Memmert type, Mumbai, India) maintained at 200°C for about half an hour to equilibrate the reaction mixture. The die containing the mixture was then transferred to a pressure device (SL-89, hydraulic press machine, Kent, UK), and various pressures, such as 4, 5, 6, 7, and 8 t, were applied during the formation of the membranes. As a result, vanadium phosphate

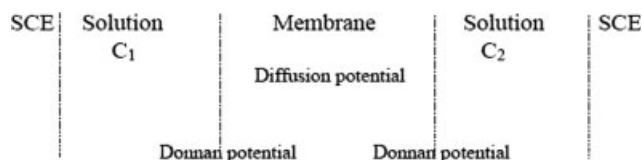
membranes with approximate thicknesses of 0.095, 0.090, 0.085, 0.080, and 0.075 cm, respectively, were obtained. Our effort was to get membranes with adequate chemical, thermal, and mechanical stabilities. The membranes that we prepared by embedding 25% polystyrene were most suitable for our purposes; larger amounts (>25%) and lesser amounts (<5%) of polystyrene did not give reproducible results and appeared to produce unstable membranes. The total amount of the mixture, thus, used for the preparation of the membrane contained 0.125 g of polystyrene and 0.375 g of vanadium phosphate. Membranes were fabricated under optimum conditions of temperature and pressure. Membranes prepared in this way were quite stable and did not show any dispersion in water or in other electrolyte solution. The membranes were subjected to microscopic and electrochemical examinations for cracks and homogeneity of the surface, and only those that had smooth surfaces and generated reproducible potentials were assured by the careful control of the conditions of fabrication.

### Scanning electron microscopy (SEM)

The prepared samples at various pressures were heated in a tabular furnace for 3 h and then cooled. A very thin transparent polymer glue tape was applied on the sample, and then, the sample was placed on an aluminum stub 15 mm in 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 (thickness = 60  $\mu\text{m}$ ) for 5 min. The scanning electromicrograph of the gold-coated specimen was recorded with a scanning electron microscope (GEOL JSM-840, Japan) operating at an accelerating voltage of 10 kV.

### Measurement of the 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 had a hole for the introduction of the electrolyte solution and saturated calomel electrodes. The half-cell contained 25 mL of the electrolyte solution, whereas the capacity of each of the half-cells holding the membrane was about 35 mL. Electrochemical cells of the following type



were used to measure the membrane potential<sup>15-17</sup> with an Osaw Vernier potentiometer (catalog number

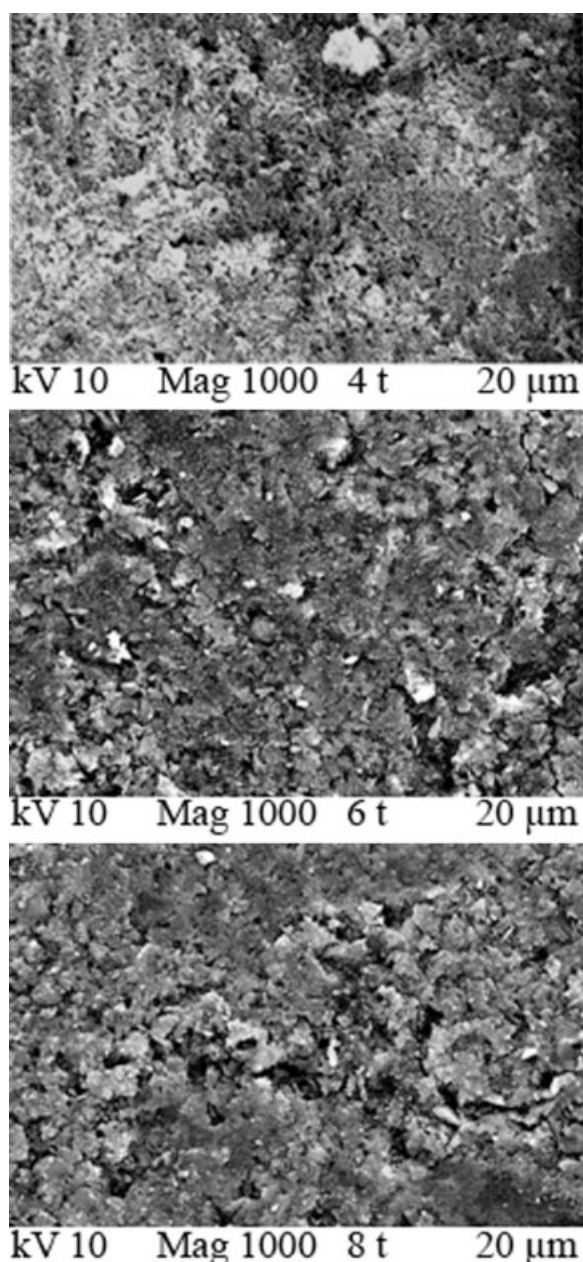
30071, Germany). In all measurements, the electrolyte concentration ratio across the membrane ( $C_2/C_1$ , where  $C_1$  and  $C_2$  are the concentrations of electrolyte solution on either side of the membrane) was taken as 10. All solutions were prepared with analytical-reagent-grade chemicals and ultrapure distilled water. The electrodes used were saturated calomel electrodes and were connected to a galvanometer (Osaw spot reflecting galvanometer S.G. 77.08, catalog number 30241,  $R$  (resistance)  $\cong 100 \Omega$ , Germany). The solutions in both containers were stirred with a magnetic stirrer (catalog number 2 ML, Serial number LHMS 182, 220/230 V,  $50 \approx 1\Phi$  Ac (alternating current), Am (ampere) 0.25, Remi-Equipments, Mumbai, India) 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  $25^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The characterization of membrane morphology has been studied by a number of investigators with SEM.<sup>18,19</sup> The information obtained from SEM images have provided guidance in the preparation of well-ordered precipitates, composite pore structure, microporosity and macroporosity, homogeneity, thickness, surface texture, and crack-free membranes.<sup>20,21</sup> SEM surface images of the vanadium phosphate membranes were taken at different applied pressures, and they are presented in Figure 1. The SEM images were composed of dense and loose aggregations of small particles and formed pores, probably with nonlinear channels that were not fully interconnected. The particles were irregularly condensed and adopted a heterogeneous structure composed of masses of various sizes. The surface openings seemed to decrease with increasing applied pressure.

Inorganic membranes have the ability to generate potential,<sup>22,23</sup> when two solutions of unequal concentrations of electrolytes are separated by a membrane, the solute and solvent are driven by the differences in their chemical potential across the membrane. The electrical character of the membrane regulates the migration of charge species for the membrane and the diffusion of electrolytes from the region of higher to lower concentration, and the flow of water in the opposite direction take place.<sup>24</sup> The values of observed membrane potential ( $\Delta\psi_m$ ) measured across the polystyrene-based vanadium phosphate membranes in contact with various 1 : 1 electrolytes at  $25 \pm 1^\circ\text{C}$  are given in Table I. The values of membrane potential across the membranes with 1 : 1 electrolytes (KCl, NaCl, and LiCl) were dependent on the concentration of electrolytes present on the both sides of the membrane. The potential was low at

higher concentrations, which is usual behavior for inorganic membranes. All of the values of membrane potential across the membranes were found to be positive when the membrane was used to separate various solution of the electrolytes (1 : 1); therefore, the membranes were cation selective. If a value of membrane potential was negative (which was not found in our observations), the membrane would become anion selective. This changing pattern of selectivity of the membrane was not peculiar to this system.<sup>17</sup> The selectivity character of ion-exchange membranes with 1 : 1 and 2 : 1 or 3 : 1 electrolytes



**Figure 1** SEM images of polystyrene-based vanadium phosphate membranes prepared at different applied pressures (4, 6, and 8 t).

TABLE I  
 $\Delta\psi_m \pm 0.5$  mV Across the Vanadium Phosphate Membranes in Contact with 1 : 1  
 Electrolyte Solutions at Different Concentrations

$C_2$ (mol/L; O)	Applied pressure (t)														
	4			5			6			7			8		
	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl
.0001	48.3	49.0	49.9	50.2	51.0	52.2	51.0	51.8	52.9	52.0	53.2	54.7	53.4	54.5	55.6
.0010	43.3	44.0	45.3	45.2	46.0	47.0	46.2	47.3	48.2	47.3	48.5	50.0	48.2	49.3	50.5
.0100	20.8	21.8	23.0	23.0	23.9	24.8	24.2	25.3	26.2	25.2	25.9	27.0	26.0	26.8	27.9
.1000	6.30	7.00	7.96	8.00	8.72	10.0	9.30	10.0	11.1	10.0	10.8	12.6	11.0	12.6	13.3
1.000	4.00	4.63	5.90	5.20	6.08	7.58	7.02	7.59	8.59	7.53	8.50	9.75	8.50	9.50	10.5

$C_2/C_1 = 10$  at  $25 \pm 1^\circ\text{C}$ .  
 O, observed.

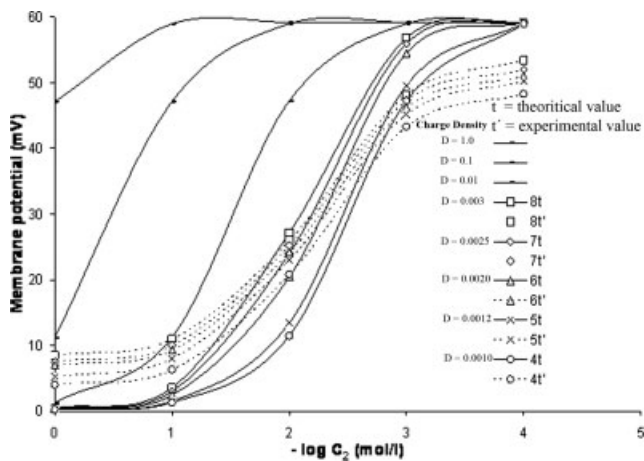
have been reported,<sup>17,25,26</sup> in which the reversal in sign (+ve (positive charge) to -ve (negative charge)) of the membrane potential values occurred was evidently due to the adsorption of multivalent ions, which led to a state where the net positive charge left on the membrane surface made them anion selective with 2 : 1 or 3 : 1 electrolytes. The simplest charged membrane systems interact with four components, such as the solvent water, the counterions, the co-ions, and the fixed charges. Our system carried charges of 0, -1, +1, and +3, respectively. When a charged membrane is in contact with an electrolyte solution, the counterion  $\text{Cl}^-$ , which has the opposite charge as the membrane, will have a higher concentration in the membrane compared to the solution where the co-ions,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ , have the same charge as the membrane and will have a lower concentration in the membrane. The fixed charge concentration in the membrane was because vanadium(III) interacted with hydrated counterions and formed ion pairs by the loss of much of the water content and repelled the co-ions because they were the same charge as that of the fixed charged group. The concentration difference of these charged ions generated an electrical potential difference to maintain electrochemical equilibrium between the membrane and electrolyte solution.<sup>27</sup>

The membrane potential was also seen to be largely dependent on the pressure applied during the membrane formation. The vanadium phosphate membranes prepared at successively higher applied pressures gave progressively higher potentials and reduced thicknesses and pore volumes and increased mechanical transport resistance and surface  $\bar{D}$ 's,<sup>28,29</sup> which in turn, modified other features of the membranes. The membranes were macroscopically uniform in thickness and porous in nature. The pores were modeled as uniform capillaries that extended throughout the membrane. These pores were evenly distributed throughout the surfaces of the membranes (cross section). Entrance and exit effects were ignored because the membrane

thickness was large compared to the pore radius. As the compactness of the membranes increased with increasing applied pressure, the dispersity of the charge distribution on the membrane was modified. However, the thickness was still large compared to the pore radius, and we assumed that the membrane and adjacent solution (interfaces) were in equilibrium. The distributions of  $\bar{D}$  and mobile species within the pores were assumed to be uniform<sup>30</sup> because the surface charge model worked as tool to improve the performance of the membrane filtration process and the charge properties of the membrane matrix more greatly influenced the counterion than co-ion as well as the transport phenomena in the solutions. The surface charge concept of the TMS model<sup>11-13</sup> for charged membranes was an appropriate starting point for our investigation of the actual mechanisms of ionic or molecular processes that occurred in the membrane phase. The TMS model assumes a uniform distribution of surface charge and consists of two Donnan potentials ( $\Delta\Psi_{\text{Don}}$ 's) and diffusion potentials ( $\Delta\Psi_{\text{diff}}$ 's) at the two solution membrane interfaces arising from the unequal concentrations of the mobile ions. The theoretical membrane potential ( $\Delta\bar{\Psi}_m$ ) according to TMS applicable to an idealized system is given by

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

where  $\bar{u}$  and  $\bar{v}$  are the ionic mobilities of the cation and anion, respectively, in the membrane phase ( $\text{m}^2/\text{v}/\text{s}$ ). The  $\bar{D}$ 's of the inorganic membranes were estimated from the membrane potential measurement and could also be estimated from  $t_+$  and  $t_-$ . To evaluate this parameter for the simple case of a 1 : 1 electrolyte and a membrane carrying various  $\bar{D}$



**Figure 2** Plots of the membrane potential versus  $-\log C_2$  at different concentrations of KCl electrolyte solution for vanadium phosphate membranes prepared at different pressures (4–8 t).

values of 1 or lower,  $\Delta\bar{\Psi}_m$  and  $\Delta\psi_m$  were plotted as a function of  $-\log C_2$  as shown by solid and broken lines, respectively, in Figure 2. Thus, the coinciding curve for various electrolyte systems gave a value for  $\bar{D}$  within the membrane phase. The surface  $\bar{D}$  of the vanadium phosphate membranes was found to depend on the applied pressure to which the membrane was subjected to its initial stage of preparation. The successive increases in the applied pressure of the vanadium phosphate membranes decreased the width from 0.095 to 0.075 cm. The microstructure of dense and loose aggregations of small particles that formed the interconnected channel and pores appeared to be more compact and arranged in order with progressive increases in pressure, as also shown in SEM (Fig. 1). Therefore, the increase in the values of  $\bar{D}$  with higher applied pressure was due to the increase of charge per unit volume of the membranes. The applied pressure was related to the thickness and the surface  $\bar{D}$  of the membrane within the studied range. In Figure 3, the applied pressure and their corresponding thicknesses of the membranes were taken at the abscissa and the surface  $\bar{D}$  at an ordinate for 1 : 1 electrolytes (KCl, NaCl, and LiCl). Figure 3 clearly indicates that with increasing pressure, an increase in the compactness (a reduction in width) was observed, which led to a decrease in the pore size of the membrane and, as a result, an increase in the solution flux, and a corresponding increase in the surface  $\bar{D}$  of the membrane appeared for given electrolyte solutions. Membrane performance is significantly modified by permeants of electrolyte solutions; rejection generally increases with increasing pressure (solution flux) and decreasing thickness of membranes. However, when rejection reaches a minimum, the contribution of increasing water flux becomes important; thus,

rejection increases with increasing pressure or decreasing thickness in membranes.<sup>31</sup> Therefore, the orders of rejection of the permeants were according to the surface  $\bar{D}$  of the membranes for the electrolytes: KCl > NaCl > LiCl.

The TMS eq. (1) can also be expressed by the sum of  $\Delta\Psi_{\text{Don}}$  between the membrane surfaces and the external solutions and  $\Delta\bar{\Psi}_{\text{diff}}$  within the membrane:<sup>32,33</sup>

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

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

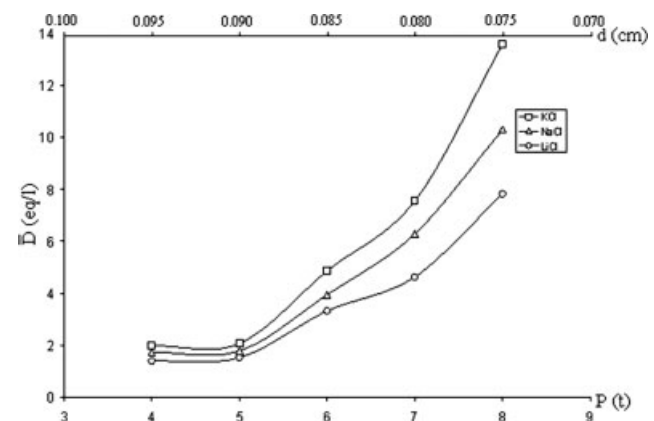
where  $R$  is the gas constant;  $T$  is temperature;  $F$  is the Faraday constant;  $\gamma_{\pm}'$  and  $\gamma_{\pm}''$  are the mean ionic activity coefficients;  $\bar{\omega}$  ( $\bar{u}/\bar{v}$ ) is the mobility ratio of the cation to anion in the membrane phase;  $\bar{C}_{1+}$  and  $\bar{C}_{2+}$  are the cation concentrations in the first and second membrane phases, respectively; and  $V_k$  and  $V_x$  refer the valencies of the cation and fixed charge group, respectively, on the membrane matrix.  $\bar{C}_{1+}$  and  $\bar{C}_{2+}$  are given by the following equation:

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

where  $q$  is the charge effectiveness of the membrane and is defined by the equation

$$q = \sqrt{\frac{\gamma_{\pm}}{K_{\pm}}} \quad (5)$$

where  $\gamma_{\pm}$  is the mean ionic activity coefficient and  $K_{\pm}$  is the distribution coefficient of the ions. The



**Figure 3** Plots of the fixed  $\bar{D}$  versus pressure (4–8 t) and thickness ( $d$ ).  $P$ (t), pressure in ton.

TABLE II  
Values of  $t_+$ ,  $\bar{U}$ , and  $\bar{w}$  and  $K_{\pm}$ ,  $q$ , and  $\bar{C}_{2+}$  as Evaluated with Eqs. (9) and (4)–(6), Respectively, from the  $\Delta\Psi_m$ 's of Various Electrolytes at Different Concentrations for Vanadium Phosphate Membranes Prepared at 6 t of Pressure

$C_2$ (mol/L)	$t_+$	$\bar{U}$	$\bar{w}$	$K_{\pm}$	$q$	$\bar{C}_{2+}$
KCl (electrolyte)						
.0001	0.92	0.84	11.5	47.60	0.144	0.00003
.0010	0.88	0.76	7.33	3.860	0.500	0.00024
.0100	0.70	0.40	2.33	0.514	1.323	0.00267
.1000	0.57	0.14	1.33	0.951	0.899	0.07855
1.000	0.55	0.10	1.22	0.995	0.780	0.76966
NaCl						
.0001	0.93	0.86	13.3	38.50	0.161	0.00005
.0010	0.89	0.78	8.09	2.950	0.572	0.00025
.0100	0.71	0.42	2.45	0.605	1.221	0.00357
.1000	0.58	0.16	1.38	0.960	0.900	0.08074
1.000	0.56	0.12	1.27	0.996	0.811	0.80299
LiCl						
.0001	0.94	0.88	15.7	32.20	0.176	0.00002
.0010	0.90	0.80	9.00	2.320	0.645	0.00021
.0100	0.72	0.44	2.57	0.668	1.163	0.00425
.1000	0.59	0.18	1.44	0.966	0.904	0.08255
1.000	0.57	0.14	1.33	0.996	0.881	0.87358

condition of electroneutrality in the external electrolyte solutions and in the membrane phase requires<sup>30</sup>

$$\sum Z_i C_i + Z_X D_X = 0 \text{ or } \sum |Z_i C_i| = \sum |Z_X D_X| \quad (6a)$$

where  $C_i$  is the  $i$ th ion concentration with the charge  $Z_i$  of the external solution and  $D_X$  is the  $X$ th ion concentration with the charge  $Z_X$  in the membrane phase.  $K_{\pm}$  is expressed as follows:

$$K_{\pm} = \sum \frac{\bar{C}_i}{|Z_i C_i|} \quad (6b)$$

where  $\bar{C}_i$  is the  $i$ th concentration in the membrane phase:

$$\sum \bar{C}_i = \sum |Z_i C_i - Z_X D_X| \quad (6c)$$

$$\bar{D} = \sum Z_X D_X \quad (6d)$$

The transport of electrolyte solutions in a pressure-driven membrane has shown that the transport properties of the membrane are also controlled by ion distribution coefficients. When eqs. (6a)–(6d) were used for the evaluation of the distribution coefficients, they were high at lower concentrations and sharply dropped with the increasing concentration of electrolytes; thereafter, a stable trend was found, which is presented in Table II. The large deviation in  $K_{\pm}$  at lower concentrations was attributed to the high mobility of the comparatively free charges of the strong electrolyte, which, thus, reached into the membrane phase more easily than that of the more highly concentrated electrolyte solution.

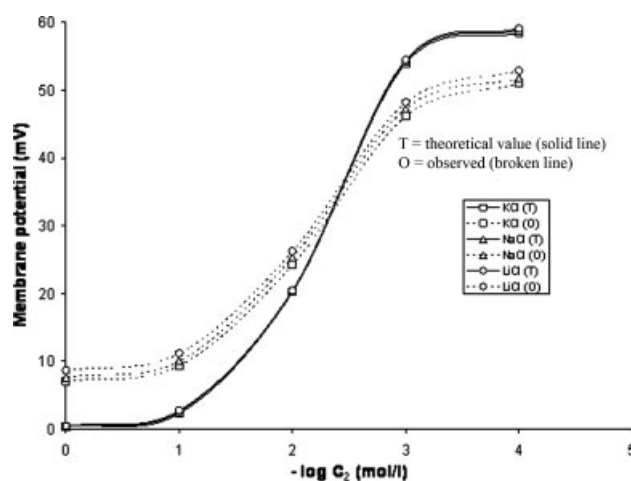
To test the applicability of these theoretical equations for the system under investigation,  $\Delta\Psi_{\text{Don}}$  and  $\Delta\bar{\Psi}_{\text{diff}}$  were calculated separately from the membrane parameters obtained from the membrane potential measurements with a typical membrane prepared at a pressure of 6 t:

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

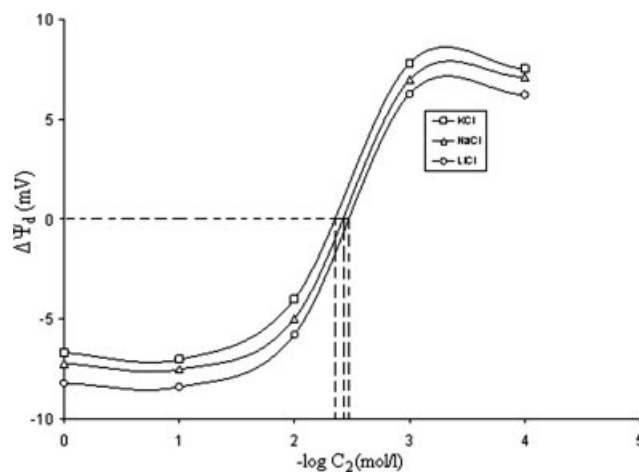
Equation (7) was first used to obtain the values of  $t_+$  and  $t_-$  from the experimental membrane potential data, and consequently,  $\bar{w}$  and  $\bar{U}$  were calculated and are given in Table II.  $\bar{w}$  of the electrolytes in the membrane phase were found to be high at lower concentrations with all of the electrolytes (KCl, NaCl and LiCl); this was followed by a sharp drop in the values with further increasing concentration, as shown in Table II. The high mobility was attributed to higher  $t_+$  values of the comparatively free cations of electrolytes; a similar trend was also found with the mobility in the least concentrated solution.  $\Delta\Psi_{\text{Don}}$  and  $\Delta\bar{\Psi}_{\text{diff}}$  at various electrolyte concentrations could be calculated from the parameters  $\gamma'_{\pm}$ ,  $\gamma''_{\pm}$ ,  $\bar{C}_{1+}$ ,  $\bar{C}_{2+}$ ,  $\bar{w}$ ,  $V_x$ ,  $V_k$ , and the experimentally derived values of  $\bar{D}$  with eq. (3). The values of the parameters  $K_{\pm}$ ,  $q$ , and  $\bar{C}_{2+}$  derived for the system are also given in Table II. The theoretical prediction suggested that the distribution of the effective charge was not uniform in the membrane, even when the membrane had a homogeneous fixed-charge distribution. The effective  $\bar{D}$ , estimated by the ionic transport procedure, depended on the ionic radii and valence of the counterions; several authors have found that the effective  $\bar{D}$  increased with

increasing adsorption of co-ion for electrolyte solutions of charged membranes.<sup>34,35</sup> To interpret the variation of  $q$  depending on those values, the ion-pairing effect caused the difference between the effective  $\bar{D}$  and the fixed  $\bar{D}$  in the membrane phase. In our membrane, the counterion  $\text{Cl}^-$  was same for 1–1 electrolytes; therefore, the variation in the  $q$  values followed a similar trend, and the order was  $\text{LiCl} > \text{NaCl} > \text{KCl}$  up to  $C_2 = 0.01$  mol/L. Then, a drop in the  $q$  values was analyzed. When the external electrolyte concentration was higher or lower, a number of counterions went into the membrane because of the imbalance in the counterion concentration of the external electrolyte and fixed charged groups in the membrane phase. Therefore, the ion association with the fixed charged groups and counterions in the membrane was enhanced; as a result,  $q$  had a lower value, whereas in the moderate concentration region, the counterion concentration in the external electrolyte and the fixed  $\bar{D}$  in the membrane were comparable.<sup>36</sup> Therefore, for a lower number of ion-pair formations and, consequently, a higher values of  $q$ , the optimum value of  $q$  were obtained at  $C_2 = 0.01$  mol/L, and then,  $q$  decreased steeply. The order of  $q$  of 1–1 electrolytes may have depended on the increasing ionic  $\bar{D}$  of co-ion adsorption on the charged membranes.

$q$  depends on the hydration of the solute–solute interaction and the ionic radii of the counterions. According to the structural hydration interaction<sup>37</sup> model, which uses that effect to account for the many thermodynamic properties of small solutes in water, it seems to be that the effect of hydration on the solute–solute interaction with the fixed charge group is overcome by the electrostatic interaction between the fixed charge groups and the counterion. Therefore,  $q$  values increase with the hydration radii of the electrolytes ( $\text{KCl} < \text{NaCl} < \text{LiCl}$ ).



**Figure 4** Membrane potential across vanadium phosphate membranes with various electrolyte solutions (1 : 1) at different concentrations.



**Figure 5** Plots of  $\Delta\Psi_d$  versus  $-\log C_2$ .

The membrane potential derived in this way (theoretical) and the experimentally obtained membrane potentials at different concentrations for various electrolytes systems were compared, as shown in Figure 4. The experimental data followed the theoretical curve quite well. However, some deviations may have been due to various nonideal effects, such as swelling and osmotic effects. As shown in Figure 5, the plot describes the deviation of the potential from the theoretical values ( $\Delta\Psi_d$ ; ideal) versus  $-\log C_2$ . These deviations were due to various nonideal effects, such as swelling and osmotic effects, which were prominent and simultaneously present in the membrane.<sup>33</sup> The ratio of the swelling effects to the osmotic effects could also be explained by  $\Delta\Psi_d$  of the membrane. The swelling effects dominated the osmotic effects in the higher concentration region and resulted in a negative deviation from ideality, whereas at lower concentrations, the osmotic effects overcame the swelling effects because of the excess of solvent molecules and resulted in a positive deviation from the ideal values.<sup>27</sup> Between the two extreme concentrations, the ratio of the swelling effects to the osmotic effects approached 1 but reversed in sign and reached the optimum concentration ( $C_{op}$ ), at which  $\Delta\Psi_d$  approached zero or the theoretical potential coincided with the observed potential, for various 1 : 1 electrolytes. The  $C_{op}$  values for various 1 : 1 electrolytes were found in the range 0.01–0.001 mol/L.

## CONCLUSIONS

Polystyrene-based vanadium phosphate membranes were prepared by a sol–gel route, and we found that the prepared membranes were quite stable and did not show any dispersion in water or other electrolyte solutions. The membranes prepared at lower pressures had a low fixed  $\bar{D}$ , whereas membranes prepared at higher pressures carried a higher  $\bar{D}$  and

essentially wider and narrow surface openings. Membranes with a higher fixed  $\bar{D}$  offered high membrane potentials for a given electrolyte solution, and the membrane potential and the distribution coefficient values were observed to diminish with increasing electrolyte concentration; their order was  $\text{KCl} > \text{NaCl} > \text{LiCl}$ . The experimental values were found to be quite close to the theoretical values. Therefore, we concluded that the TMS equation could be used to obtain the membrane potential and derived parameters for the membranes under investigation and would be applicable to other composite membranes.

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### NOMENCLATURE

$C_1$ and $C_2$	Concentrations of electrolyte solution on either side of the membrane (mol/L)
$\bar{C}_{1+}$	Cation concentration in membrane phase 1 (mol/L)
$\bar{C}_{2+}$	Cation concentration in membrane phase 2 (mol/L)
$C_i$	$i$ th ion concentration of the external solution (mol/L)
$\bar{C}_i$	$i$ th ion concentration in the membrane phase (mol/L)
$C_{op}$	Optimum concentration
$\bar{D}$	Charge density in the membrane (equiv/L)
$D_X$	$X$ th ion concentration
$F$	Faraday constant (C/mol)
$K_{\pm}$	Distribution coefficient of the ions
$q$	Charge effectiveness of the membrane
$R$	Gas constant (J/K/mol)
SEM	Scanning electron microscopy
$t_+$	Transport number of the cation
$t_-$	Transport number of the anion
TMS	Teorell, Meyer, and Sievers
$\bar{u}$	Mobility of cations in the membrane phase ( $\text{m}^2/\text{v/s}$ )
$\bar{U}$	$(\bar{u} - \bar{v})/(\bar{u} + \bar{v})$
$\bar{v}$	Mobility of anions in the membrane phase ( $\text{m}^2/\text{v/s}$ )
$V_k$	Valency of the cation
$V_x$	Valency of the fixed charge groups
$Z_i$	Charge in the external solution
$Z_X$	Charge in the membrane phase

### Greek symbols

$\gamma'_{\pm}$ and $\gamma''_{\pm}$	Mean ionic activity coefficients
$\bar{w}$	Mobility ratio
$\Delta\psi_d$	Deviation of the potential from the theoretical value
$\Delta\psi_m$	Observed membrane potential (mV)
$\Delta\Psi_m$	Theoretical membrane potential (mV)

$\Delta\bar{\Psi}_{diff}$	Diffusion potential (mV)
$\Delta\Psi_{Don}$	Donnan potential (mV)

### References

- de Gyves, J.; Rodríguez, E. *Ind Eng Chem Res* 1999, 38, 2182.
- Oleinikova, M.; González, C.; Muñoz, M.; Valiente, M. *Polyhedron* 1999, 18, 3353.
- Singh, K.; Tiwari, A. K. *J Membr Sci* 1987, 34, 155.
- Singh, K.; Shahi, V. K. *J Membr Sci* 1990, 49, 223.
- Kemperman, A. J. B.; Rolevink, H. H. M.; Bargeman, D.; Boomgaard den, T. V.; Strathmann, H. *J Membr Sci* 1998, 138, 43.
- Yang, X. J.; Fane, A. G.; Bi, J.; Griesser, H. J. *J Membr Sci* 2000, 168, 29.
- Wijers, M. C.; Jin, M.; Wessling, M.; Strathmann, H. *J Membr Sci* 1998, 147, 117.
- Samms, S. R.; Wasmus, S.; Savinell, R. F. *J Electrochem Soc* 1996, 143, 1225.
- Peled, E.; Duvdevani, T.; Melman, A. *Electrochem Solid State Lett* 1998, 1, 210.
- Moritz, T.; Benfer, S.; Arki, P.; Tomandl, G. *J Sep Purif Tech* 2001, 25, 501.
- Teorell, T. *Proc Soc Exp Biol* 1935, 33, 282.
- Teorell, T. *Proc Natl Acad Cad. Sci (USA)* 1935, 21, 152.
- Meyer, K. H.; Sievers, J. F. *Helv Chim Acta* 1936, 19, 649, 665, and 987.
- Chou, T. J.; Tanioka, A. *J Phys Chem B* 1998, 102, 7198.
- Beg, M. N.; Siddiqi, F. A.; Singh, S. P.; Prakash, P.; Gupta, V. *Electrochem Acta* 1979, 24, 85.
- Beg, M. N.; Siddiqi, F. A.; Shyam, R.; Altaf, I. *J Electronal Chem* 1978, 89, 141.
- Beg, M. N.; Siddiqi, F. A.; Shyam, R. *Can J Chem* 1977, 55, 1680.
- Santos, L. R. B.; Pulcinelli, S. H.; Santilli, C. V. *J Sol Gel Sci Technol* 1997, 8, 477.
- Wakeman, R. J.; Henshall, J. L.; Ng, S. G. *Trans IChemE A* 1996, 74, 329.
- Huang, L.; Wang, Z.; Sun, J.; Zhili, L. M. Q.; Yan, Y.; Zhao, D. *U. J Am Chem Soc* 2000, 122, 3530.
- Izutsu, H.; Mizukami, F.; Nair, P. K.; Kiyozumi, Y.; dab Mae, K. *J Mater Chem* 1997, 7, 767.
- Eisenman, G. In *Membrane Transport and Metabolism*; Kleinsler, A.; Koty, A., Eds.; Academic: New York, 1961; p 163.
- Barragan, V. M.; Rueda, C.; Ruiz-Baura, C. *J Colloid Interface Sci* 1995, 172, 361.
- Lakshminarayanaiah, N. *Transport Phenomena in Membranes*; Academic: New York, 1969.
- Siddiqi, F. A.; Khan, I. R.; Saksena, S. K.; Ahshan, M. A. *J Membr Sci* 1977, 2, 245.
- Singh, K.; Tiwari, A. K. *Proc Indian Natl Sci Acad A* 2004, 70, 477.
- Hills, G. J.; Jacobs, P. W. M.; Lakshminarayanaiah, N. *Proc R Soc London Ser A* 1961, 262(1309), 246.
- Helfferrich, F. *Ion-Exchange*; McGraw-Hill: New York, 1962.
- Winter, R.; Czeslik, C. *Z Kristallogr* 2000, 215, 454.
- Garcia-Aleman, J.; Dickson, J. M. *J Membr Sci* 2004, 235, 1.
- Garcia-Aleman, J.; Dickson, J. M. *J Membr Sci* 2004, 239, 163.
- Matsumoto, H.; Tanioka, A.; Murata, T. J.; Higa, M.; Horiuchi, K. *J Phys Chem B* 1998, 102, 5011.
- Chou, T. J.; Tanioka, A. *J Colloid Interface Sci* 1999, 212, 293.
- Bowen, W.; Mohammad, A.; Hilal, N. *J Membr Sci* 1997, 126, 91.
- Wang, X.; Tsuru, T.; Togoh, M.; Nakao, S.; Kimura, S. *J Chem Eng Jpn* 1995, 28, 186.
- Tanioka, A.; Matsumoto, H.; Yamamoto, R. *Sci Tech Adv Mater* 2004, 5, 461.
- Desnoyers, J. E.; Arel, M.; Perron, G.; Jolicoeur, C. *J Phys Chem* 1969, 73, 3346.