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Thermodynamic evaluation and electrochemical parameters of PVC-based ion-exchange nickel tungstate composite membrane and their potential applications

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ABSTRACT

PVC-based nickel tungstate is a newly synthesized composite material that has been used to make mechanically and thermally well-stable membrane. The composite material was qualitatively synthesized by the sol–gel method of material preparation. The composite material and prepared membrane have been selected and characterized on the basis of their chemical composition, ion-exchange capacity, and FTIR, TGA, and SEM analysis. It has verified the material nature, functional groups, thermal stability plus the phase transition, surface structure, porosity, ion transportation, etc. For the measurement of ionic potential, KCl, NaCl, and LiCl strong electrolytes are used, which helps to obtain the charge density of the membrane that decided the nature of membrane performance accordingly. Teorell–Meyer–Sievers theoretical approach is used to obtain the important parameters of examined membrane that included the transport number, mobility ratio, charge effectiveness, etc.

Keywords: PVC-based NT composite membrane; Teorell–Meyer–Sievers method; Ion-exchange property; TGA analysis; Fixed charge density

1. Introduction

New type of organic–inorganic composite membrane has flexible and very stable nature due to the versatile properties of both the used materials. Organic polymer gives the appropriate flexibility and binding property, whereas inorganic material provides the good mechanical stability plus ion-exchange property. The polymer has the property to withstand in the harsh chemical conditions due to chains rigidity, chain interactions, stereo regularity, and the polarity of functional groups. PVC has the ability to bind with the inorganic materials and also the easily obtainable and reasonable-priced values to comply with the low-cost criteria of membrane formation [1–3]. The major function of inorganic material is to control the exchange property of ionic species between the two adjacent fluid phases. So, on the basis of the above properties of composite material, the prepared membrane shows a lot of applications in different fields like foods, drugs, dairy, and beverages, as well as pollution control, waste water treatment, fuel cells, power generation, energy saving, etc. Consecutively, it also uses, in many another processes like electro dialysis, membrane electrolysis and electro-deionization [4,5].

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The ion-exchange membranes are broadly accepted for the treatment of that water which contains heavy toxic metal ions [6]. PVC-based NT-mixed matrix membrane has unique electrochemical, chemical, optical, magnetic, thermal, and mechanical stabilities that can be used for the selective separation of heavy toxic metal ions such as Pb^{2+}, Cd^{2+}, and Hg^{2+}, as well as strong electrolyte cations like K^+, Na^+, and Li^+ also [7,8]. The mechanical and electrochemical parameters are the main important factors which help to show the good results of an ideal ion-selective membrane [9].

The most valuable parameter of membrane phenomenon is the surface charge density that controls the selectivity of ions. The measurement of charge density is an important task which elaborated the membrane model to understand the industrial application approaches. It has been derived by theoretical and observed potential values of above electrolyte solutions using the Teorell–Meyer–Sievers (TMS) theoretical equation. Along the charge density of membrane, the other important parameters that included the transport number, mobility ratio, charge effectiveness, and perm selectivity have also been calculated very easily [10,11].

2. TMS theory

TMS theory says that there must be an equilibrium development at each of the solution and membrane interfaces which have an appropriate resemblance with the Donnan equilibrium. There are some related assumptions which are as follows:

(1) Mobility of ions and concentration of fixed charged groups are constant throughout the membrane phase and it is independent on salt concentration.
(2) The water transference may be neglected.

The implications of these assumptions have been discussed earlier. Apart from these, further assumptions have also been made and they are as follows: The activity coefficient of salt is similar in solution phase, in membranes phase, and in both solution and membrane phases, and the interface must be produced between them. The activities for ion concentration can only be corrected by Donnan potential either using the integration of Planck's or Henderson equation [12,13].

3. Experimental

3.1. Chemicals and materials

KCl, NaCl, and LiCl electrolytic solutions of different concentrations are required to make the stock solutions, 200 mesh size of PVC powder is used as a binder, 0.2 M $NiCl_2$ and Na_2WO_4 solutions of 99.90% purity are required to make the NT-precipitated material. All these reagents must be of analytical grade, and double-distilled water is used to prepare the above solutions.

3.2. Synthesis of NT material

By sol–gel method of material preparation, the clear solution of Na_2WO_4 has been added into the greenish solution of nickel chloride which turns into the fine precipitation. Then a constant stirring of the precipitated solution for 1–2 h has been done which has to change into NT-inorganic material, and pH of solution must be maintained before filtering the material. The resulting precipitate should be washed well at least 4–5 times with DMW to remove the free electrolytes and ions, and then it has to be transferred into an advance oven for 3–5 h by maintaining the temperature at 100˚C. Lastly, the dried NT material is powdered by pestle and mortar until its size becomes 200 meshes [14].

3.3. Membrane frame of PVC-based NT

To prepare the PVC-based NT composite membrane, the important criterion is that the members of the composite material should be mixed in a particular ratio of percentages. To make a stable composite membrane, the binder and inorganic material should be mixed in 1:3 ratios which mean that 25:75%, respectively. The mixing of materials must be very cautiously and homogeneously done until it gets totally mixed with each other. Now the composite mixture is transferred into a cast die of (2.45 cm) diameter which is placed into the oven for 2–3 h by maintaining a temperature of 200˚C to equilibrate the reaction mixture [15]. Then the dried material is transferred into a pressure device of "SL-89-UK" to apply 100 MPa pressure to make a good fabricated membrane. However, it is well known that the increase in the pressure leads to reduction in the thickness of membrane. If the granules of PVC and NT exceeded or decreases from the above-mentioned ratio, it does not show better mechanical and morphological stability and functions. It is analyzed by subjecting it for microscopic and electrochemical examinations to see the cracks, porosity, and homogeneity of the membrane. Now the membrane is ready to observe the potential of electrolytes solution which leads to obtaining further parameters of the membrane.

3.4. Potential observation

The potential of ions through the membrane was obtained by the digital potentiometer "Electronics India-118." It has obtained the potential of membrane which is placed at the centre of the two-chambered glass cell. The collar-shaped glass cell has the cavity to introduce the electrolyte solutions and saturated calomel electrodes. The different cations of electrolyte solutions such as chlorides of K^+, Na^+, and Li^+ are activated to show the potentiometer responses, whereas the anions did not influence the same. The used electrochemical setup of potential measurement is represented by Fig. 1.

3.5. Chemical stability

By the method which has already been discussed, Rafiuddin et al. analyze the morphological changes of membrane in which the changes in color, surface, brightness, decomposition, splits, holes, etc. have been observed.

3.6. Ionic-exchange capacity

Titration method is used to obtain the ion-exchange capacity of composite material in which, firstly, the HNO_3 treatment for 24 h took place and then the material was washed more than two times with DMW. By titration with the 0.01 M NaOH solution, the H^+ ions release Na^+ ions due to an ion-exchange reaction. Regarding this titration, phenolphthalein was used as an indicator. The equation which is used to determine the ion-exchange capacity of composite material is as follows:

$$\text{IEC} = \text{Volume of consumed NaOH} \times \text{molarity of NaOH} / \text{Weight of a dried membrane}$$

4. Characterization

4.1. Morphological and structural characterization of membrane

The surface structure of the membrane is determined by the SEM characterization. It has been done by "Leo 4352" through an accelerating voltage of 20 kV. Copper stub is used to mount the sample and is gold sputter-coated to minimize the charging of it [16].

4.2 FTIR characterization

FTIR study analyzes the chemical structure, the present group, and the existence of hydrogen or covalent bonding between the phases. This was done by "Interspec-2020, FTIR spectrometer" spectrolab-UK [17].

4.3. Thermal characterization

It has associated with TGA characterization that describes the weight loss in material either as a function of increasing temperature or time. It has also determined the behavior of material which stated the endothermic or exothermic nature. The TGA analysis has been done by "Shimadzu DTG-60H."

5. Results and discussion

SEM images are represented in Fig. 2 that demonstrated the morphological structure of membrane

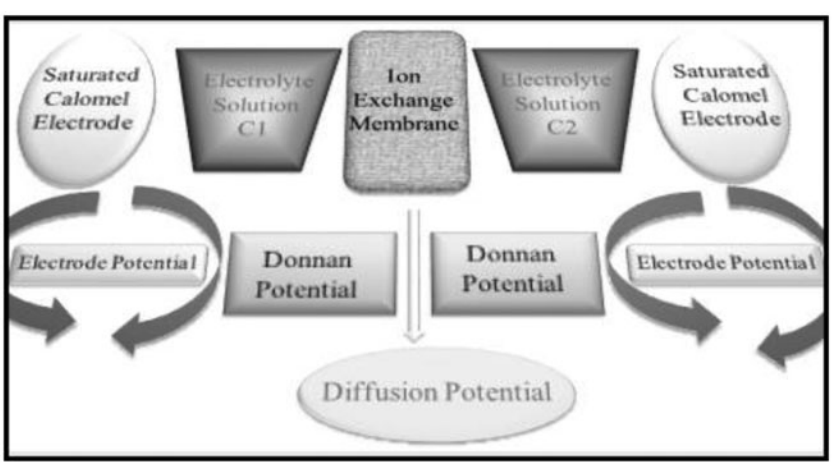

Fig. 1. Electrochemical setup for potential observation.

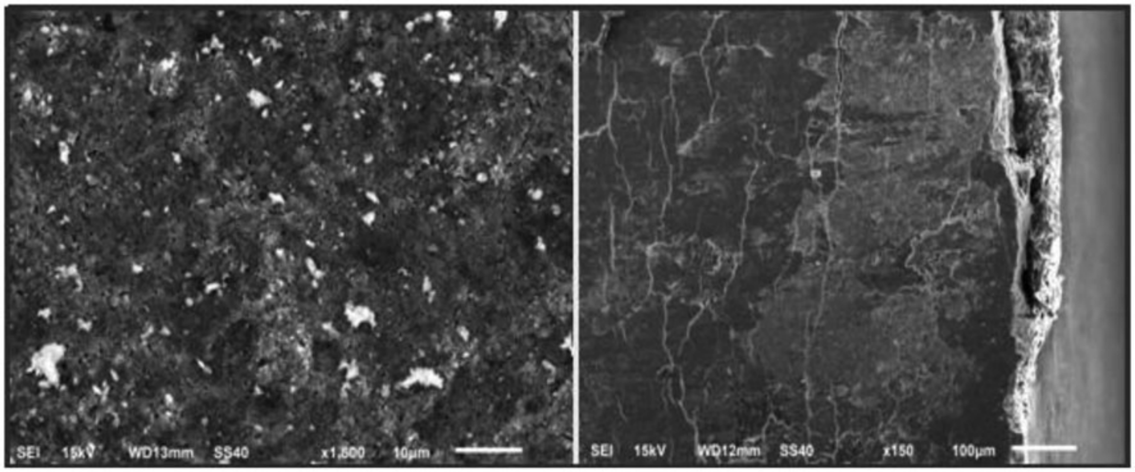

Fig. 2. SEM images of PVC-based NT composite membrane by two different magnifications.

which is illustrating that the mixing of materials is very well and the membrane shows very porous surface. It is clear that the distribution of both the materials is homogeneous and uniform throughout the medium and there are no any breakages or cracks that are found in the porous surface of membrane [18]. FTIR spectra of PVC, NT and PVC-based NT composite materials are shows in Fig. 3. The top most spectra reveal that there is a very intensive and sharp peak found in the range of 1,093.68 cm^{-1} which indicated the C–H bond of PVC, whereas the small peaks which appear in the range from 818.64 to 565.92 cm^{-1}show the C–Cl bond of polymer. The water peaks are also found in the range of 3,433.47–2,926.01 cm^{-1} but it appears to be very less intensive and broad. In the central figure, the spectra of only NT material are present which declared that the intense peaks found in the range of 861.66–465.86 cm^{-1} indicated the presence of phosphate group in the material. The sharp peak of water in the range of 3,415.14 cm^{-1} is clearly found which stated that the NT material easily absorbs the water from the surrounding atmosphere. The bottom figure shows the spectra of PVC-based NT composite material which clearly indicated the presence of C–Cl, C–H, and NT peaks at different ranges. The stretching mode of water and the metallic peaks is found in the range of 3,411.04 and 864.79–469.79 $cm^{-}1$, respectively. Therefore, the FTIR analysis shows that the composite material has the property of both constituents of membrane matrix [19].

Thermo gravimetric analysis curves of PVC, NT, and PVC-based NT composite material is present from top to bottom in Fig. 4. From the figure, it is clear that the PVC shows very minute weight loss of 0.052 mg (1.929%) at the temperature of 216.28℃. The inorganic material NT shows two times weight loss of 0.575 mg (7.930%) and 0.195 mg (2.689%) at temperatures of 142.53 and 403.41℃, respectively. On the other hand, PVC-based composite material also shows two times weight loss of 0.620 mg (8.321%) and 0.138 mg (1.852%) at temperatures of 140.18 and 423.39℃, respectively. Therefore, the TGA curves stated that the composite material of membrane shows very high stability due to the low percentage of weight loss [20].

After a certain period, the membrane that was incubated in acidic, basic, as well as alkaline medium lost its mechanical stability, which stated that the membrane is exhaustive in the above-discussed solutions. Such type of morphological changes was seen after passing 12, 24, or 36 h by putting membrane into the solutions. So, it is also a very exclusive feature of membrane that indicated the high thermal and chemical stabilities [21].

The PVC-based NT composite membrane created potentials due to the presence of interphase between the unequal electrolytes concentration. The observed potential data show the selectivity of ions due to the charge present on membrane surface. The activity of ions is more flourished in the concentration range through which the membrane performed as cation or anion selectivity. In the above-mentioned membrane, the anions did not broadly influence the potentiometer respond through which it shows the positive mV potential order and ideally follows the Nernst equation [22]. Therefore, it is clear that the potential readings are increased by decreasing the electrolyte's concentration which indicated that the membrane is perfectly cation-selective i.e. negatively charged. The observed potential data of used electrolyte ions are represented in Fig. 5.

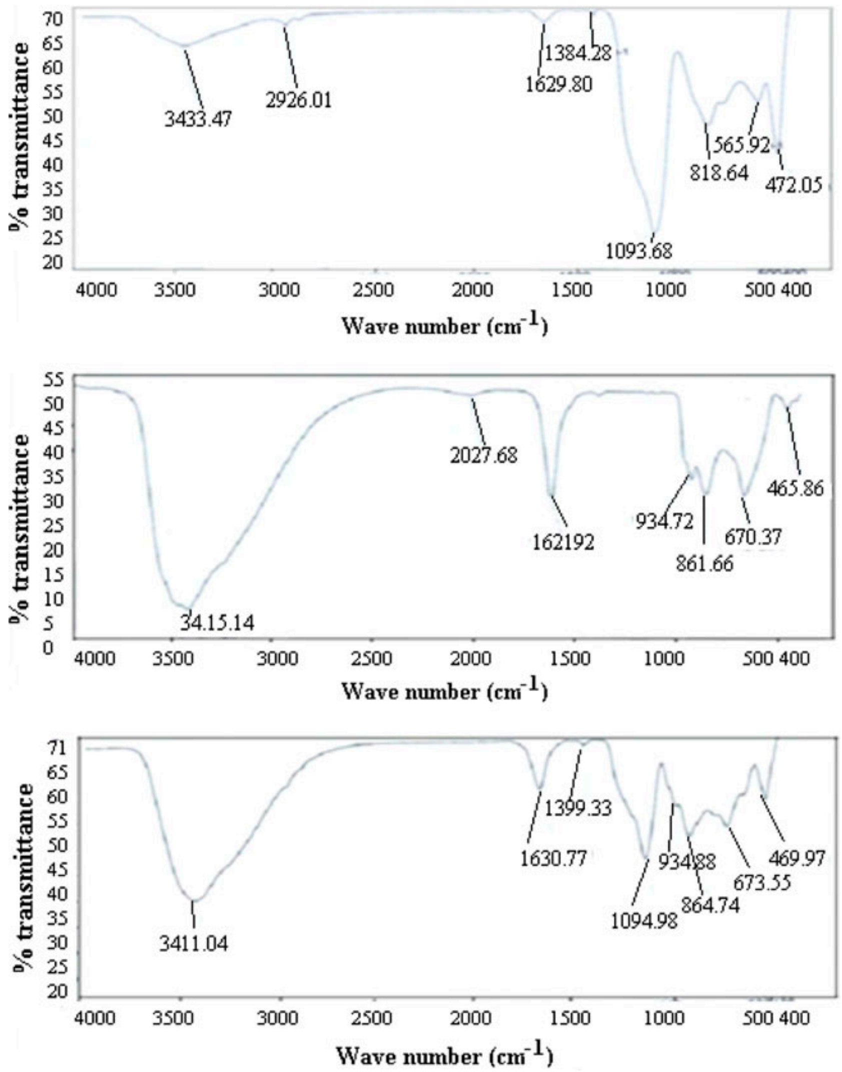

Fig. 3. FTIR Spectra of only PVC, NT, and PVC-based NT composite materials.

In synthetic or ordinary membrane, the most important electrochemical property is the differences in permeability of co-ions, counter ions, as well as neutral molecules. The charge on membrane produces adsorption and transportation of ions which shows less activity in dilute region. Charges on membrane are required to generate the potential that is totally dependent on the porosity of membrane. If pores are broad, a lot of charges are required to generate the good potential, whereas in a narrow one, a little quantity can give rise to the appropriate potential values [23]. The transport property of ions has been completed through evaluating the thermodynamically effective fixed charge density of membrane [24]. The theoretical and observed potentials are designated by dark and broken lines, respectively, and these readings are plotted as a function of –log C_2 which is represented in Fig. 6. The coinciding position into the graph gives the value of charge density $\bar{D}$ within the membrane phase. The charge density of membrane always shows $\bar{D} \leq 1$ and it follows KCl > NaCl > LiCl order, and this order is due to the size factor of used electrolytes. The charge density is found to depend on the initial stage of composite material preparation. [25].

The electrochemical setup shows that there are two Donnan potentials produced at the two solutions–membrane interfaces and the incubated membrane produces diffusion potential due to the unequal electrolytes concentration. So an equilibrium process must be found at both the solution and membrane interfaces which have the proper similarity with Donnan

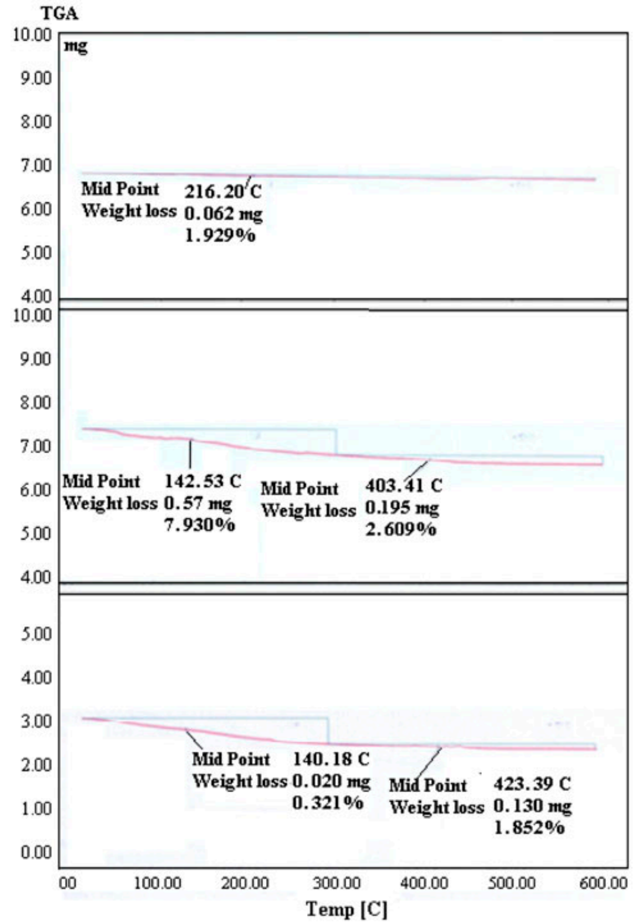

Fig. 4. TGA spectra of only PVC, NT, and PVC-based NT composite materials.

equilibrium. It is resulting that there should be an internal salt diffusion potential which was represented by Henderson equation and leads to Planck expression. It is also clear that the TMS method will be more valid in higher concentration range because the deviation between the observed and calculated potential is quite high in low concentration. According to TMS method, the membrane potential is shown by the following equation at 25˚C.

$$\Delta\bar{\psi}_m = 59.2\left(\log\frac{C_2}{C_1}\frac{\sqrt{4C_1^2+\bar{D}^2}+\bar{D}}{\sqrt{4C_2^2+\bar{D}^2}+\bar{D}} + \bar{U}\log\frac{\sqrt{4C_2^2+\bar{D}^2}+\bar{D}\bar{U}}{\sqrt{4C_1^2+\bar{D}^2}+\bar{D}\bar{U}}\right) \quad (1)$$

where

$$\bar{U} = (\bar{u}-\bar{v}) \,/\, (\bar{u}+\bar{v})$$

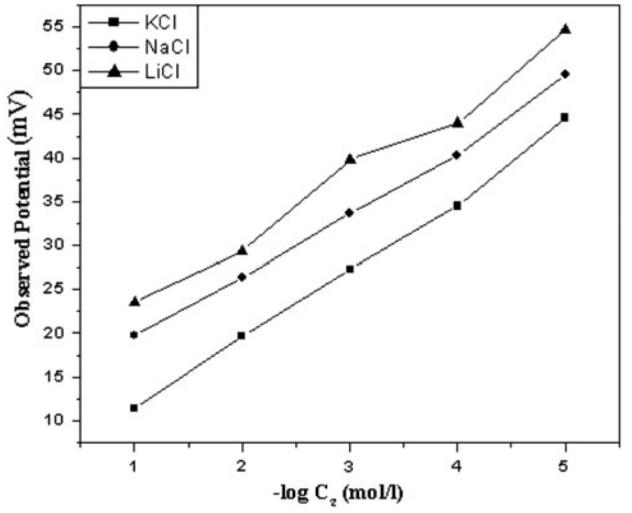

Fig. 5. Plots of observed membrane potentials against logarithm of concentration for PVC-based NT composite membrane.

where $\bar{u}$ and $\bar{v}$ are the ionic mobility of cations and anions, C_1 and C_2 are concentration of phase 1 and 2, and $\bar{D}$ is charge density of membrane. The TMS graphical method determines the fixed charge and cation-to-anion mobility ratio [26,27].

The above TMS equation can also be expressed by the sum of Donnan ($\Delta\psi_{Don}$) and diffusion potentials ($\Delta\bar{\psi}_{diff}$).

$$\Delta\bar{\psi}_{m,e} = \Delta\psi_{Don} + \Delta\bar{\psi}_{diff} \quad (2)$$

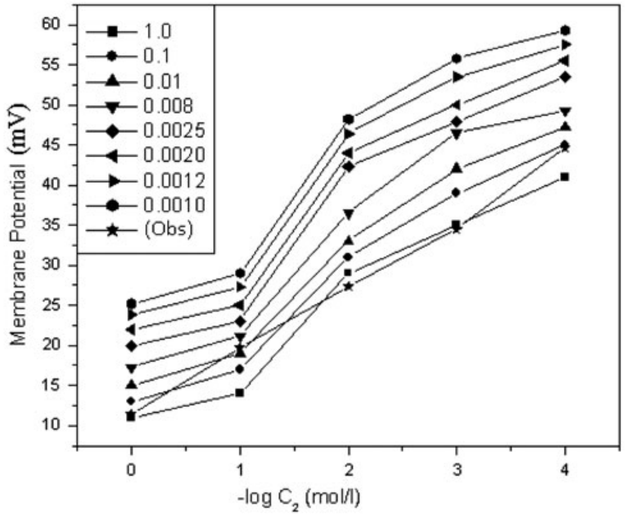

Fig. 6. Plots of theoretical and observed membrane potentials at different concentration of KCl, NaCl, and LiCl electrolyte solutions for PVC-based NT composite membrane.

$$\Delta\psi_{\mathrm{Don}} = -\frac{RT}{V_{\mathrm{k}}F}\ln\left(\frac{\gamma_{2\pm}C_2\bar{C}_{1+}}{\gamma_{1\pm}C_1\bar{C}_{2+}}\right) \quad (3)$$

R, T, and F have their standard meanings, $\gamma_{1\pm}$ and $\gamma_{2\pm}$ are mean ionic activity coefficients, and C_{1+} and C_{2+} are the cation concentration on two sides of membrane.

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

where V_{k} and V_{x} are the valencies of cation and fixed-charge groups on membrane, respectively, and q is the charge effectiveness of membrane, which is as follows:

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

where $K_{\pm}$ is the distribution coefficient expressed as:

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

$\bar{C}_i$ is ith ion concentration in membrane phase and C_i is ith ion concentration of external solution.

The diffusion potential is as follows:

$$\Delta\bar{\psi}_{\mathrm{diff}} = -\frac{RT\bar{\omega}-1}{V_{\mathrm{k}}F\bar{\omega}+1} \times \ln\left(\frac{(\bar{\omega}+1)\bar{C}_2 + (V_{\mathrm{x}}/V_{\mathrm{k}})\bar{D}}{(\bar{\omega}+1)\bar{C}_1 + (V_{\mathrm{x}}/V_{\mathrm{k}})\bar{D}}\right) \quad (7)$$

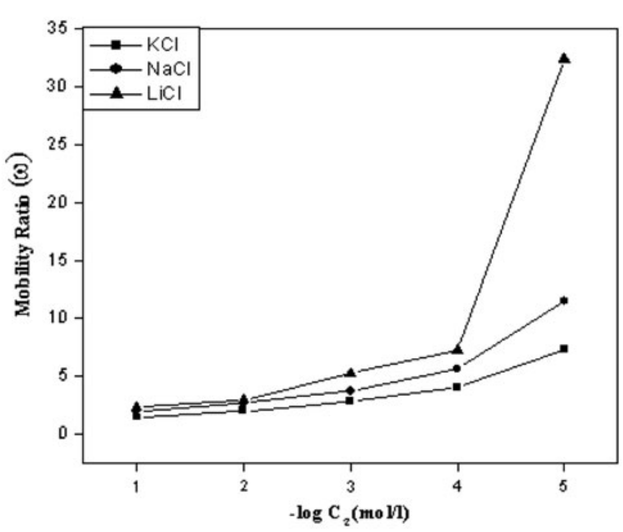

Fig. 7. The plot for mobility ratio of PVC-based NT composite membrane for different used electrolytes.

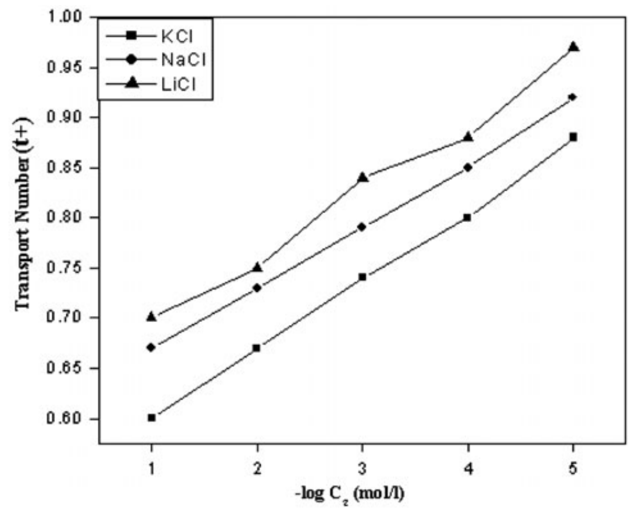

Fig. 8. Plot showing the transport number of PVC-based NT composite membrane for different used electrolytes.

Here, $\bar{\omega} = u/v$ is the mobility ratio of cation to anion in membrane phase. Therefore, the total membrane potential can be obtained by the simple addition of $\Delta\psi_{\mathrm{Don}}$ and $\Delta\psi_{\mathrm{diff}}$

$$\Delta\bar{\psi}_{\mathrm{m,e}} = -\frac{RT}{V_{\mathrm{k}}F}\ln\left(\frac{\gamma_{2\pm}C_2\bar{C}_{1+}}{\gamma_{1\pm}C_1\bar{C}_{2+}}\right) - \frac{RT\bar{\omega}-1}{V_{\mathrm{k}}F\bar{\omega}+1} \times \ln\left(\frac{(\bar{\omega}+1)\bar{C}_2 + (V_{\mathrm{x}}/V_{\mathrm{k}})\bar{D}}{(\bar{\omega}+1)\bar{C}_1 + (V_{\mathrm{x}}/V_{\mathrm{k}})\bar{D}}\right) \quad (8)$$

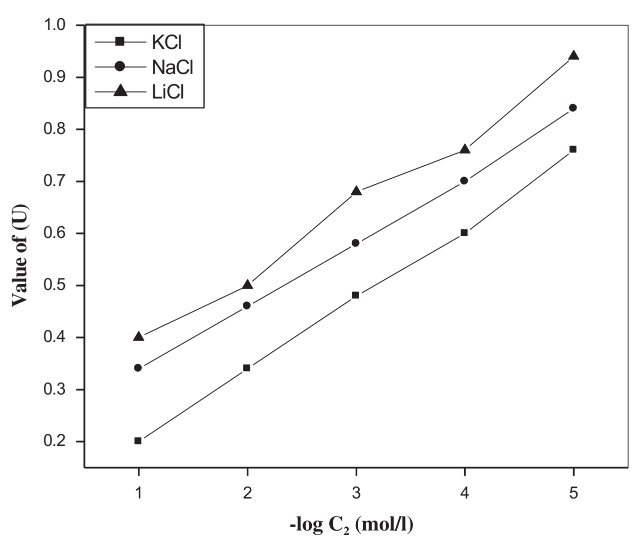

Fig. 9. The values of $\bar{U}$ against the logarithm of various concentrations for PVC-based NT composite membrane.

Table 1
Observed membrane potential and surface charge density of PVC-based NT composite membrane of different concentrated electrolyte solutions

Membrane potential Conc	KCl	NaCl	LiCl
1	11.4	19.7	23.6
0.1	19.7	26.4	29.4
0.01	27.3	33.7	39.8
0.001	34.5	40.3	44.0
0.0001	44.6	49.5	54.6
Charge densities	KCl	NaCl	LiCl
	0.007	0.086	0.097

$$\Delta\bar{\psi}_m = -\frac{RT}{F}(t_+ - t_-)\ln\frac{C_2}{C_1} \tag{9}$$

Where

$$\frac{t_+}{t_-} = \frac{\bar{u}}{\bar{v}} \tag{10}$$

The values of transport number (t_+) and mobility ratios ($\bar{\omega}$) can easily be obtained with the help of Eqs. (9) and (10). To explain the applicability of TMS theoretical equation, the diffusion and Donnan potentials have been easily calculated using the observed potential values. The equation's parameter such as $\gamma_{1\pm}, \gamma_{2\pm}, \bar{C}_{1+}, \bar{C}_{2+}, \bar{\omega}, V_x, V_k$, and $\gamma_{1\pm}$ have the usual charted values. The mobility of ions in the above composite membrane follows the order: LiCl > NaCl > KCl. It is also clear that the higher transport number follows the high mobility ratio which is clearly shown in Fig. 7. The transport number of cation increases by decreasing the concentration of electrolyte solutions which are represented in Fig. 8 [28,29]. The values of $\bar{U}$ that is ($t_+ - t_-$) are also represented in Fig. 9. The charge density calculated by the above Eqs. (3) and (7) is present in Table 1. It is also one of the most important properties of composite membrane that the distribution coefficients of electrolyte solutions decrease by increasing the concentration of solutions [30].

6. Conclusion

The study of PVC-based NT composite porous membrane explained that the membrane performed very high stability due to their good interaction with the polymer. Sol–gel method is used to synthesize the composite material which is an appropriate method for such types of material synthesis. The TMS approach has been well agreed by the observed experimental results. The charge density is the central parameter that governs the transport phenomena of a stable membrane which totally depends on feed composition and applied pressure of the membrane. By ion-exchange capacity, it was clear that the examined membrane has a cation-exchangeable nature. The observed potential and surface charge density of membrane show KCl < NaCl < LiCl and KCl > NaCl > LiCl order, respectively.

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