

Electrical Conductance of Heterogeneous Cation-Exchange Membranes in Electrolyte Solutions

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Heterogeneous cation-exchange membranes differing in their binder poly(vinyl chloride) and ion-exchange resin ratios as well as the mesh size of the resin particles have been prepared by solution casting technique. The conductivities of such membranes in varying concentration of different electrolyte solutions such as HCl, NaCl, KCl, and CuCl₂ have been measured. The membrane conductance values in conjunction with solution conductivities have been used for the estimation of isoconductance points. Considering the membrane as a combination of joint-gel phase and intergel phase, the volume fractions of the respective phases have been evaluated. With the help of isoconductance points, the electroconductivities of the joint-gel phase and counterion diffusion coefficient through that phase of the membrane in equilibrium with different electrolyte solutions have been found. The sequence of ionic mobilities and counterion diffusion coefficient through the joint-gel phase is $H^+ > K^+ > Na^+ > Cu^{2+}$, while ion-exchange capacity of the joint-gel phase decreases as $Cu^{2+} > K^+ \approx Na^+ > H^+$.

Introduction

Ion-exchange membranes find extensive applications in many areas of science and chemical technology. Processes such as electrodialysis, electro-electrodialysis, electrodeionization, etc. are electrically driven membrane processes involving ion-exchange membranes. Electrodialysis process (ED), used mainly for water desalination and concentration of brine from seawater, is now applied for separation of chemicals.^{1–4} Ion-exchange membranes now find applications in the recovery of useful ingredients from wastewater by diffusion dialysis and also in membrane electrolysis, fuel cells, storage batteries, electrochemical synthesis, Donan dialysis,^{5,6} or pervaporation.^{7,8} Ion-exchange membranes act as highly conducting material due to the presence of ionogenic groups in them. Special membranes are needed for some new applications, where membranes should possess any one of some special characteristics such as a very low membrane permeability to divalent ions with respect to monovalent ions, a very low permeability to hydroxyl ions or protons, a high resistivity to poisoning by hydrophobic ions, etc. For a given application, it is necessary to predict the behavior of ion-exchange membranes in relation to their structural properties as well as to know the main transport characteristics of the membranes.

A theory has been developed by Gnusin et al.⁹ to evaluate the specific electrical conductivity and the coefficient of penetrability of ion-exchange resin in dispersed systems in the presence of different forces. Zabolotsky and Nikonenko¹⁰ have developed a three phase model (TPM), which has been chosen by Elatter et al.,¹¹ on a commercial ion-exchange membrane. According to this microheterogeneous model, the inhomogeneities of the microphase of the membrane appeared to be the main factor for relating the membrane transport properties such as electroconductivity, diffusion permeability, and transport number to the ionic concentration of the external aqueous

solution. In their studies on the threshold ionic conductivity in a series of sulfonated polyphenylene oxide matrix, Tongwen et al.¹² applied both TPM and percolation theory.

In an earlier paper,¹³ the effect of variation of a particle's size and the loading of the ion-exchange resin on mechanical properties such as bursting strengths, physicochemical, and electrochemical properties, namely, dimensional stability, ion-exchange capacity, moisture content, electrical resistance and transport numbers, and morphological properties of the heterogeneous cation-exchange membranes, have been discussed. In this investigation, membrane conductance value in conjunction with solution conductivity is used for the estimation of isoconductance points. Special emphasis has been given to elaborate the study of the effect of variation of size and loading of cation-exchange resin particles on the counterion diffusion coefficient of cation-exchange membranes in equilibration with HCl, NaCl, KCl, and CuCl₂ of varied concentrations. The results have been analyzed on the basis of the microheterogeneous model as per the following theory.

Theory

Zabolotsky and Nikonenko¹⁰ have given the theory of the microheterogeneous model. According to them, ion-exchange membranes with a microheterogeneous structure contain at least two microphases; one is a "gel phase" with a relatively uniform distribution of ionogenic groups, i.e., the hydrophilic parts of the matrix polymer chains, and the other is an equilibrium electroneutral solution filling the interstices between the elements of the gel phase known as the "intergel phase".

Using the microheterogeneous model, the specific electroconductivity of the membrane has been deduced as

$$\kappa_m = (f_1 \bar{\kappa}^\alpha + f_2 \kappa^\alpha)^{1/\alpha} \quad (1)$$

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or

$$(\kappa_m)^\alpha = f_1 \bar{\kappa}^\alpha + f_2 \kappa^\alpha \quad (2)$$

where, α is the structural parameter reflecting the reciprocal arrangement of the phase elements in the membrane. $\bar{\kappa}$ and κ are the specific electroconductivities of the joint-gel phase and the solution, respectively. f_1 and f_2 are the volume fractions of the joint-gel phase (the active region) and the intergel phase (the interstitial region) such that

$$f_1 + f_2 = 1 \quad (3)$$

when $|\alpha| \ll 1$, $(\kappa_m)^\alpha = 1 + \alpha \ln \kappa_m$, $\bar{\kappa}^\alpha = 1 + \alpha \ln \bar{\kappa}$, and $\kappa^\alpha = 1 + \alpha \ln \kappa$.

So, eq 2 becomes

$$1 + \alpha \ln \kappa_m = f_1 (1 + \alpha \ln \bar{\kappa}) + f_2 (1 + \alpha \ln \kappa) \therefore 1 + \alpha \ln \kappa_m = (f_1 + f_2) + \alpha (f_1 \ln \bar{\kappa} + f_2 \ln \kappa) \quad (4)$$

$\therefore f_1 + f_2 = 1$ and dividing eq 4 with α , we get

$$\ln \kappa_m = f_1 \ln \bar{\kappa} + f_2 \ln \kappa \quad (5)$$

i.e.,

$$\kappa_m = \bar{\kappa}^{f_1} \kappa^{f_2} \quad (6)$$

Equation 5 shows that $\ln \kappa_m$ varies linearly with $\ln \kappa$.

Experimental Section

Membranes. The cation-exchange membranes were prepared in the laboratory from poly(vinyl chloride) (PVC) and cation-exchange resin of varying mesh size and loading of resin.¹¹ The membranes after preparation were conditioned to Na^+ form by equilibrating in HCl and subsequently in NaCl solution.

Measurement of Moisture Content and Exchange Capacities. The cation-exchange membranes in Na^+ form were dipped in about 1 N HCl for 1 h to convert them into the H^+ form and washed with deionized water. This process was repeated for three cycles. Finally, membranes were converted to the H^+ form by dipping the membranes in 1 N HCl overnight and then washing with deionized water thoroughly to make them free from chloride and acid. The membranes in the H^+ form were then air-dried by mopping them with blotting paper. The air-dried membranes were cut into two pieces. One piece was kept in a weighing bottle, which along with its lid was already weighed. The weighing bottle (with lid) and the piece of air-dried membrane were again weighed and kept in an electrical oven at 105 °C for 3 h. The whole was then kept in a desiccator for 30 min and weighed again. From the loss of weight, the percentage of moisture content of the membrane was found out.

Another piece of membrane was directly weighed and equilibrated with 50 mL of 1 N KCl solution in a stoppered glass bottle for 24 h. The amount of H^+ ion displaced was then determined analytically by titrating suitable aliquots from the equilibrium solution with standard 0.1 N NaOH.

Calculations. Let

W_1 = wt of empty bottle with lid

W_2 = wt of bottle with lid + air-dried membrane

W_3 = wt of bottle with lid + dry membrane

W_C = weight of air-dried membrane

V = volume of aliquot taken for titration

V_1 = Titer volume of 0.1 N NaOH

S = strength of NaOH

V_e = volume of 1 N KCl taken for equilibrium = 50 mL

$$\text{moisture content} = \frac{(W_2 - W_3)}{(W_2 - W_1)} \times 100\% = M\%$$

$$\text{capacity} = \frac{V_1 S V_e}{W_C (100 - M) V} \times 100 \text{ mequiv/g dry membrane}$$

The exchange capacity (Q_0) of the membrane was calculated as

$$Q_0 = E_c \times \rho \text{ (equiv/m}^3\text{)} \quad (7)$$

where ρ is the specific density of the membrane in kg/m^3 . The specific density (ρ) of the membrane was obtained by measuring the dimensions and weight after drying at 60 °C for 24 h.

Measurements of Electroconductivity of Membranes. The membranes were converted into suitable ionic form as per standard procedure and washed with deionized water. The electrical resistance of the membrane in electrolyte solution containing same counterion as in the membrane was then measured. Two half cells of Perspex with a cross-sectional area of 1 cm^2 connected in series for solution flow were used with a resistance bridge to measure the areal resistance of the membrane samples in respective ionic form using the electrolyte solution under test. The electrical resistances of the solution in the cell with and without membranes were measured. The difference of the electrical resistance gave the membrane resistance. The process was repeated until reproducible values within ± 0.01 ohm were obtained. The electrical conductivity of the membrane was then determined by using the formula

$$\kappa_m = (\delta/AR) \quad (8)$$

where δ is the thickness of the membrane, A is its area, and R is its electrical resistance.

Electrolyte solutions of HCl, NaCl, KCl, and CuCl_2 of varied concentrations in the range of 1–100 equiv/ m^3 were taken for different experiments. The experiments were carried out at 30 ± 2 °C.

Results and Discussions

Characteristics of the Membrane. The main characteristics of the ion-exchange membranes are presented in Table 1. The average particle sizes of resin with different mesh sizes of –100 + 200 BSS, –200 + 300 BSS, and –300 + 400 BSS as reported earlier^{13,14} are 33, 18, and 12 μm , respectively. The increase in mesh size results in a higher area. ASAP-2010 (Micromeritics, Norcross, VA) at liquid nitrogen temperature

TABLE 1: Main Characteristics of the Membranes^a

mesh size (BET surface area) of resin	resin loading (%)	membrane	water content (%)	E_c (equiv/kg)	ρ (kg/m ³)	Q_0 (equiv/m ³)
-100 + 200 BSS (0.3325 m ² /g)	70	M(100)C70	43.8	2.42	395	0958.0
	60	M(100)C60	37.9	2.05	442	0906.0
	50	M(100)C50	32.7	1.58	515	0814.0
-200 + 300 BSS (1.4936 m ² /g)	70	M(200)C70	46.2	2.57	590	1520.0
	60	M(200)C60	38.9	2.11	684	1443.0
	50	M(200)C50	33.5	1.75	700	1230.0
-300 + 400 BSS (2.7802 m ² /g)	70	M(300)C70	46.9	2.70	810	2187.0
	60	M(300)C60	43.1	2.25	865	1950.0
	50	M(300)C50	35.8	1.88	900	1690.0

^a Thickness of membrane = 0.02 cm. Temp = 30 ± 2 °C.

measured the BET surface areas of different mesh sizes of resin particles, and the values are presented in Table 1. As discussed in an earlier paper,¹⁴ for a particular particle size of resin, the values of E_c and Q_0 increase but ρ of the dry membrane decreases with resin loading. When the resin loading is more, more exchangeable ions are present in a specific amount of the membrane, which ultimately leads to the enhancement of both E_c and Q_0 . At a definite resin loading, the values of all of the three parameters E_c , Q_0 , and ρ increase with an increase in mesh size (i.e., decrease in particle size). The density of the dry membrane depends on the densities of PVC and resin. The density of PVC (1.4 g/cm³) is more than that of resin in the Na⁺ form (0.85–0.89 g/cm³). So, the density of the membrane decreases with the increase of resin loading. Table 1 also gives an idea about the effect of mesh size of resin particles on the values of E_c , Q_0 , and ρ . For a particular resin loading, all three values increase with an increase in mesh size (or increase in surface area) of the resin particles. The number of functional groups available for the exchange of counterions in solution increases with the increase in surface area leading to higher values of E_c , Q_0 , and ρ . Water content in the membranes decreases with resin loading for the same mesh size but increases with increase in mesh size of resin having the same loading in the membrane.

Electroconductivity. The thickness of the membranes was selected as 0.02 cm for the experiments. The specific conductances of membranes of thickness as selected 0.02 cm are represented in Figure 1a–d. The figure shows that membrane conductivity initially increases with electrolyte concentration and then reaches a limiting point at higher concentration. At very low external concentration, it is possible for the specific conductance of the pore solution to exceed that of the external solution. As the concentration of external solution is increased, conductance increases slowly at first and then more rapidly, until at higher concentration, the two solutions, external and internal, become identical.¹⁵

As expected, membrane conductance increases with increase in loading and mesh size of the resin in the membrane. The ion-exchange resin contains exchangeable ions in it. Hence, it behaves as an electrical conductor while the binder PVC acts as a nonconductor of electricity. With the increase in resin loading in the membrane, the charge group increases and so the electrical conductance of the membrane increases.

The morphological behavior of different membranes, as reported earlier,¹³ also reveals that phase distribution becomes more and more uniform and homogeneous with an increase in loading as well as mesh size of the resin, which ultimately leads to the increase in membrane conductivity.

Isoconductance Point. The ion-exchange membrane may be considered as a combination of gel phase and intergel phase.¹⁰ Near the isoconductance point, κ_m or $\kappa'_{iso} = \bar{\kappa} = \kappa$. The

intercept of curves drawn in $\kappa_m - C$ (solid line) and $\kappa - C$ (dotted line) in Figure 1a–d gave the values of isoconcentration (C_{iso}) and membrane conductivity at the isoconductance point (κ'_{iso}). Comparison of the isoconductivity values (κ'_{iso}) as presented in Table 2 shows the following sequence of ion mobilities through joint-gel phase of the membranes: $H^+ > K^+ > Na^+ > Cu^{2+}$. Because ionic conductances are proportional to ionic mobilities, the experimental conductivity (κ) values of electrolyte solutions as presented in Table 3 indicate also the same sequence of ionic mobilities in water.

For any particular counterion, like the membrane conductance, the specific conductance of the joint-gel phase, $\bar{\kappa}$ (or the isoconductance, κ'_{iso}) of the membranes also increases with the increase in loading and mesh size of the resin in the membrane. The same explanation as discussed in the case of membrane conductance may be given here.

Volume Fractions f_1 , f_2 , and Exchange Capacity \bar{Q} . Equation 5 indicates the linear relationship between $\ln \kappa_m$ and $\ln \kappa$. According to Zabolotsky and Nikonenko,¹⁰ near the isoconductance point C_{iso} , where $\kappa'_{iso} = \bar{\kappa} = \kappa$, κ_m depends slightly on α , and in the range $0.1C_{iso} < C < 10C_{iso}$, the dependence $\ln \kappa_m - \ln \kappa$ may be approximated by a linear relationship up to $|\alpha| = 0.2$. The volume fraction f_2 of the intergel phase can be found out from the slopes of $\ln \kappa_m - \ln \kappa$ curves as shown in representative Figure 2a,b for NaCl and CuCl₂ electrolytes. This figure shows that the interrelation of $\ln \kappa_m - \ln \kappa$ is approximated by a linear relationship, which agrees with the theoretical approach.¹⁰ The volume fraction f_1 and ion-exchange capacity \bar{Q} of the joint-gel phase can be calculated using formulas

$$f_1 = 1 - f_2$$

and

$$\bar{Q} = (Q_0/f_1) \quad (9)$$

respectively. Their values along with f_2 are given in Table 2. As shown in Table 2, for all membranes, the sequence of f_1 is $H^+ > K^+ \approx Na^+ > Cu^{2+}$.

The joint-gel phase is quasi-homogeneous, which is a combination of pure gel phase and inert gel phase. Hence, f_1 depends on three different factors such as size of the counterion in the pure gel phase, relative exchange affinity of the active site toward the counterion, and swelling behavior of pure gel phase. It can also be seen from Table 2 that the \bar{Q} value decreases in accordance with the exchange affinity¹⁴ as $Cu^{2+} > Na^+ \approx K^+ > H^+$. Except in a few cases, both volume fraction f_1 and exchange capacity \bar{Q} in the joint-gel phase increase with increase in loading and mesh size of the resin particles in the membrane (Table 2). Increase in morphological homogeneity

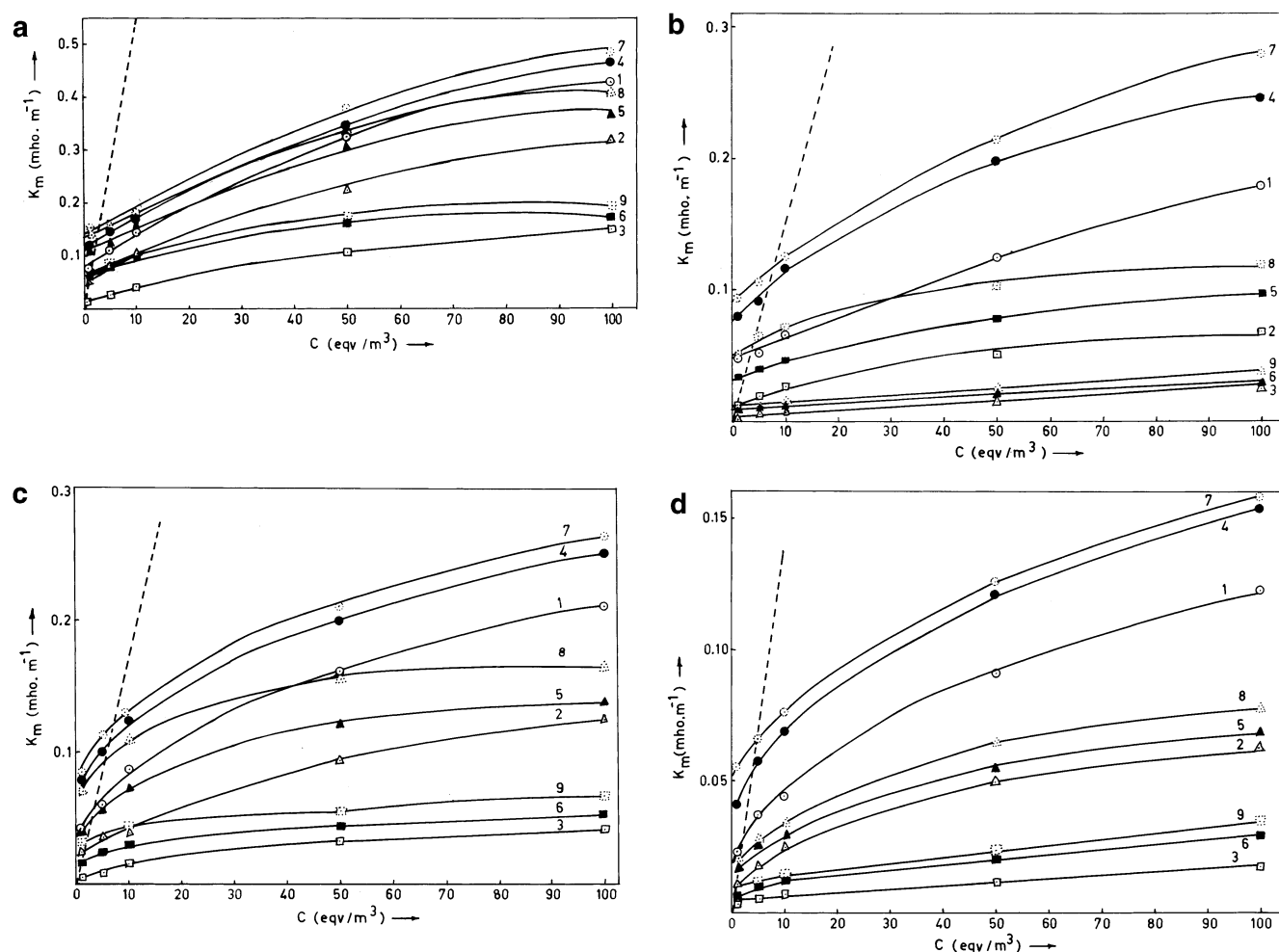


Figure 1. Electroconductivity of membranes in contact with electrolyte solution. (a) HCl, (b) NaCl, (c) KCl, (d) CuCl₂, (1) M(100)C70, (2) M(100)C60, (3) M(100)C50, (4) M(200)C70, (5) M(200)C60, (6) M(200)C50, (7) M(300)C70, (8) M(300)C60, and (9) M(300)C50.

with increase in mesh size and loading of resin particles in the membrane explains this.

Counterion Diffusion Coefficient, \bar{D} . The diffusion coefficient (\bar{D}) of the counterions in the joint-gel phase is calculated by using the following formula

$$\bar{D} = \frac{RT}{F^2} \cdot \frac{\bar{\kappa}}{\bar{Q}} \quad (10)$$

or

$$\bar{D} = \frac{RT}{F^2} \cdot \frac{\bar{\kappa}}{Q_0} \cdot f_1 \quad (11)$$

and their values are presented in Table 2 along with the values of f_1 , f_2 , \bar{Q} , etc. In accordance with the ionic mobilities of the ions selected, the counterion diffusion coefficient values also follow the sequence $H^+ > K^+ \approx Na^+ > Cu^{2+}$. The diffusion coefficient \bar{D} decreases with a decrease in resin loading in the membrane, as shown in Table 2. With some exceptional cases, the \bar{D} values increase with an increase in mesh size of the resin particles in the membranes. These values also show that the diffusion coefficient in the joint-gel phase depends on the heterogeneity of the membrane.

Heterogeneity Factor β , Specific Conductivity of Pure Gel Phase $\bar{\kappa}'$, and Total Conductive Fraction f_c . In the presence of an inert phase, a two phase model of an ion-exchange

membrane can be used by combining the gel phase and the inert phase into a coherent region, which is considered as quasi-homogeneous and called a joint-gel phase. In such a case

$$f_1 = f'_1 + f_{in} \quad (12)$$

where f'_1 and f_{in} are the volume fractions of pure gel phase free of inert inclusions and inert phase, respectively. By knowing the composition of the membranes and the densities of resin and inert binder, the f_{in} can be calculated. Zabolotsky et al.¹⁰ again introduced another parameter β characterizing the arrangement of the "pure" gel and inert binder in the joint-gel phase. β may be derived from the equation

$$\bar{\kappa} = \left(\frac{f'_1}{f_1} \right)^{1/\beta} \cdot \bar{\kappa}' \quad (13)$$

or

$$\ln \bar{\kappa} = \frac{1}{\beta} \ln \left(\frac{f'_1}{f_1} \right) + \ln \bar{\kappa}' \quad (14)$$

where $\bar{\kappa}'$ is the specific conductance of the pure gel phase.

Equation 14 shows that the plot of $\ln \bar{\kappa}$ vs $\ln(f'_1/f_1)$ is a straight line. The data presented in the representative Figure 3 for HCl prove the validity of eq 14. From the slope of the curves and from the intercepts, the values of β and the values of $\bar{\kappa}'$

TABLE 2: Diffusion Coefficient of Cations through Joint-Gel Phase of Cation-Exchange Membranes

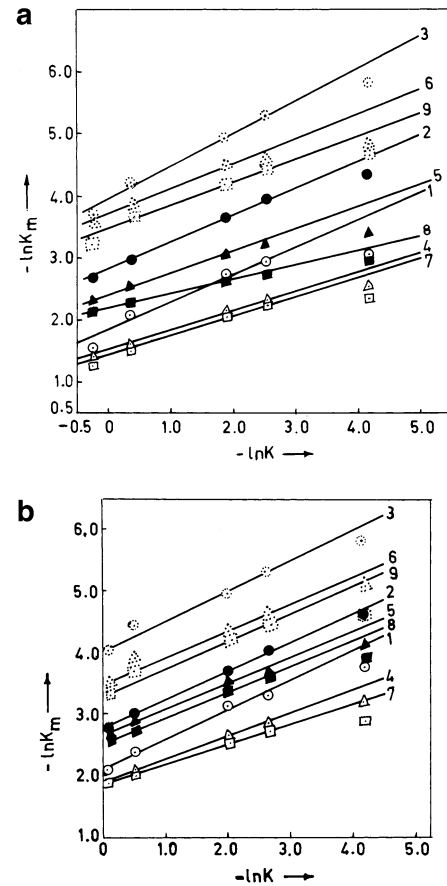
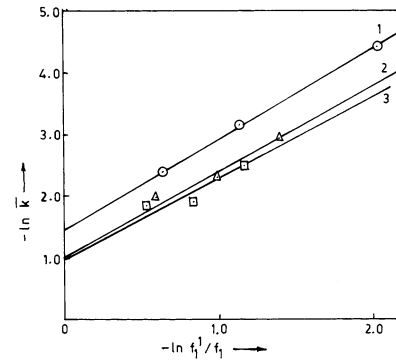
membrane	cation	C_{iso} (equiv/m ³)	$\bar{\kappa} = \kappa_{\text{iso}}^m$ (mho m ⁻¹)	f_2	f_1	\bar{Q} (equiv/m ³)	$\bar{D} \times 10^{11}$ (m ² /s)
M(100)C70	H ⁺	2.0	0.092	0.35	0.65	1474	1.66
	Na ⁺	3.5	0.054	0.44	0.56	1710	0.91
	K ⁺	3.5	0.058	0.44	0.56	1710	0.91
	Cu ²⁺	2.0	0.027	0.48	0.52	1842	0.39
M(200)C70	H ⁺	2.5	0.135	0.31	0.69	2203	1.63
	Na ⁺	7.0	0.104	0.40	0.60	2533	1.10
	K ⁺	6.0	0.106	0.39	0.61	2492	1.14
	Cu ²⁺	3.5	0.053	0.41	0.59	2690	0.55
M(300)C70	H ⁺	3.0	0.157	0.25	0.75	2916	1.44
	Na ⁺	7.5	0.118	0.31	0.69	3169	0.99
	K ⁺	7.0	0.120	0.31	0.69	3169	1.00
	Cu ²⁺	4.5	0.066	0.33	0.67	3264	0.54
M(100)C60	H ⁺	1.0	0.043	0.38	0.62	1461	0.68
	Na ⁺	1.0	0.013	0.45	0.55	1647	0.21
	K ⁺	1.5	0.026	0.46	0.54	1678	0.42
	Cu ²⁺	0.5	0.010	0.46	0.54	1678	0.16
M(200)C60	H ⁺	2.5	0.130	0.33	0.67	2154	1.61
	Na ⁺	2.0	0.036	0.36	0.64	2255	0.43
	K ⁺	3.0	0.048	0.36	0.64	2255	0.57
	Cu ²⁺	1.0	0.016	0.42	0.58	2488	0.17
M(300)C60	H ⁺	3.0	0.150	0.26	0.74	2635	1.52
	Na ⁺	4.0	0.060	0.36	0.64	3047	0.52
	K ⁺	5.5	0.094	0.36	0.64	3047	0.82
	Cu ²⁺	1.5	0.020	0.39	0.61	3197	0.16
M(100)C50	H ⁺	0.20	0.012	0.40	0.60	1357	0.24
	Na ⁺	0.20	0.003	0.47	0.53	1536	0.05
	K ⁺	0.25	0.004	0.48	0.52	1565	0.08
	Cu ²⁺	0.20	0.003	0.50	0.50	1628	0.05
M(200)C50	H ⁺	1.20	0.062	0.32	0.68	1809	0.92
	Na ⁺	0.60	0.009	0.41	0.59	2085	0.11
	K ⁺	0.90	0.016	0.41	0.59	2085	0.21
	Cu ²⁺	0.40	0.006	0.44	0.56	2196	0.07
M(300)C50	H ⁺	1.65	0.082	0.25	0.75	2253	0.98
	Na ⁺	1.65	0.010	0.37	0.63	2682	0.10
	K ⁺	1.90	0.034	0.37	0.63	2682	0.34
	Cu ²⁺	0.65	0.009	0.39	0.61	2770	0.08

TABLE 3: Specific Conductivity of Electrolyte Solutions

C (equiv/m ³)	κ (mho m ⁻¹) of			
	HCl	NaCl	KCl	CuCl ₂
1.0	0.0515	0.0155	0.0181	0.0153
5.0	0.2553	0.0784	0.0868	0.0709
10.0	0.5149	0.1509	0.1720	0.1370
50.0	2.3780	0.6970	0.7990	0.6020
100.0	4.1300	1.2730	1.4880	1.0890

have been presented in Table 4. It can be seen that the parameter β is almost constant at 0.75 ± 0.05 for all of the heterogeneous membranes in different ionic forms studied in this investigation. This shows that the value of β depends on the nature of the inert and pure gel phase in the joint-gel phase. The value of $\bar{\kappa}'$, i.e., the specific conductivity of pure gel phase, is in the order H⁺ form > K⁺ form > Na⁺ form > Cu²⁺ because of the relative ionic mobilities. For any particular ion (Table 4), it has been observed that the specific conductance of the pure gel phase increases with an increase in mesh size (or decrease in particle size) of the resin content in the membrane. The pure gel phase is the ion-exchange resin. An increase in mesh size means the increase in surface area (Table 1); hence, more functional groups will be exposed to external solution leading to an increase in conductance.

On the basis of TPM and percolation theory, Tongwen et al.¹² introduced a factor f_c to obtain the critical threshold at which a membrane transits from an insulator to a conductor. In the present system, the f_c value varies between 0.48 and 0.69 resulting in an ion-exchange capacity of 1.58–2.70 equiv/kg and membrane conductivity between 0.003 and 0.485 mho m⁻¹

**Figure 2.** $\ln \kappa_m$ vs $\ln \kappa$. Determination of volume fraction f_2 . (a) NaCl, (b) CuCl₂, (1) M(100)C70, (2) M(100)C60, (3) M(100)C50, (4) M(200)C70, (5) M(200)C60, (6) M(200)C50, (7) M(300)C70, (8) M(300)C60, and (9) M(300)C50.**Figure 3.** $\ln \bar{\kappa}$ vs $\ln (f_1/f_2)$. Determination of β and $\bar{\kappa}'$.**TABLE 4: Data for β and $\bar{\kappa}'$**

mesh size	β				$\bar{\kappa}'$			
	H ⁺	Na ⁺	K ⁺	Cu ²⁺	H ⁺	Na ⁺	K ⁺	Cu ²⁺
−100 + 200 BSS	0.70	0.80	0.71	0.80	0.234	0.182	0.182	0.122
−200 + 300 BSS	0.73	0.74	0.70	0.80	0.367	0.202	0.301	0.122
−300 + 400 BSS	0.75	0.70	0.72	0.80	0.386	0.301	0.367	0.122

in different electrolytic solutions. These values indicate that the membranes chosen in the present work have the f_c value well above the critical threshold value (i.e., $f_c = 0.18$) predicted by Tongwen et al.¹² Hence, both the percolation theory and TPM are well-suited to derive the different electrotransport parameters of membranes varying in their conducting (resin part) to nonconducting (PVC part) site ratio in different electrolytic solutions having concentration ranges from 1 to 100 equiv/m³.

Conclusions

Specific conductance of the membrane increases with an increase in loading and mesh size of the resin in the membrane. Ion mobility through the joint-gel phase of the membranes decreases as $H^+ > K^+ > Na^+ > Cu^{2+}$, while the counterion diffusion coefficient \bar{D} shows the following sequence: $H^+ > K^+ \approx Na^+ > Cu^{2+}$. \bar{D} increases with an increase in loading and mesh size of resin particles in the membranes. For all membranes, the sequence of f_1 is observed as $H^+ > K^+ \approx Na^+ > Cu^{2+}$, while that of \bar{Q} is $Cu^{2+} > Na^+ \approx K^+ > H^+$. f_1 and \bar{Q} increase with an increase in loading and mesh size of the resin particles in the membrane. The nature of $\ln \kappa_m$ vs $\ln \kappa$ graphs within the concentration range of 1–100 equiv/m³ indicates that $|\alpha| \leq 0.2$ in accordance with the microheterogeneous model.¹⁰ The heterogeneity factor β lies in the range of 0.75 ± 0.05 for the membranes containing different particle sizes of resin as well as counterions used in the present system. The specific conductivity of the pure gel phase decreases in the order H^+ form $>$ K^+ form $>$ Na^+ form $>$ Cu^{2+} . For any particular counterion, the specific conductivity of the pure gel phase increases with an increase in mesh size of the resin content. The higher f_c and conductance value of membranes in different electrolyte solutions of concentrations ranging from 1 to 100 equiv/m³ show that the total conducting sites are much above the critical threshold at $f_c = 0.18$. Hence, both the percolation and microheterogeneous models are applicable to predict the electrotransport properties of such membranes. The application

of both percolation and microheterogeneous models may considerably reduce the number of experimental investigations necessary to predict transport characteristics of ion-exchange membranes.

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