

# Studies on the Electrical Diffusivities of Mono-Carboxylates Through Heterogeneous Anion Exchange Membranes

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Received 26 December 2006; accepted 9 April 2007

DOI 10.1002/app.26803

Published online 30 July 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Heterogeneous anion exchange membranes have been prepared by solution casting technique with poly (vinyl chloride) (PVC) as inert binder and anion exchange resin ( $-300 + 400$  mesh) by varying their blend ratio from 60 : 40 to 30 : 70. The membranes were characterized with respect to their physical, mechanical, and electrochemical behavior. The transport behavior of such membranes was studied in the solutions of different homologous monocarboxylate salts starting from formate to butyrate. Membrane conductance values, in conjunction with the solution conductance, were used to determine the isoconductance points following the microheterogeneous model developed by Zabolotsky and Nikonenko, *J Membr Sci* 1993, 79, 181. From the electro conductivity ( $\bar{\kappa}$ ) and exchange capacity ( $\bar{Q}$ )

of the joint gel phase, the diffusion coefficients of different carboxylate anions have been determined. The specific conductivities of the joint gel phase decreases in the order  $\bar{\kappa}$  formate >  $\bar{\kappa}$  acetate >  $\bar{\kappa}$  propionate >  $\bar{\kappa}$  butyrate. For any specific carboxylate counter ion, the  $\bar{\kappa}_{70} > \bar{\kappa}_{60} > \bar{\kappa}_{50} > \bar{\kappa}_{40}$ . For any particular resin loading the diffusion coefficient in membrane for formate > acetate > propionate > butyrate. The membranes studied here (varying in their blend ratios) may be synchronized by nearly same heterogeneity factor  $\beta$  of value  $0.38 \pm 0.04$ . © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2615–2624, 2007

**Key words:** membrane; diffusion; mono-carboxylate anion; isoconductance point; microstructure

## INTRODUCTION

Ion exchange membranes may be defined as the heart of different electro-membrane processes. Being extensively used in fuel cells, storage batteries, etc; these membranes have become an inevitable part of applied electrochemistry. At the same time, the use of such membranes in the areas of separation science and technology generates a demand for the same. Separation processes like electrodialysis, electro-electrodialysis, and electro-deionization are based on ion exchange membranes. Although desalination of brackish and sea water<sup>1–7</sup> was the main driving force behind the development of electrodialysis process but these days the application of this technology covers a broad arena- starting from chemical industries, bio-industries (food, pharmaceuticals, and biotechnology)<sup>8–11</sup> even to the control of environmental pollution. Such diversified applications demand membranes of special characteristics like selective permeability to specific ions, antifouling properties, high conductance to protons etc. As ion exchange

membranes are charged membranes, hence generation of specific characteristics in such membranes depend not only on the relative distribution of the conducting and nonconducting phases of the membranes but also on the nature of ionogenic groups and their distribution in the bulk as well as in the surface matrix of such membranes. Hence to prepare ion exchange membranes well suited for a given application, it is necessary to predict the behavior of the membranes in relation to their structural properties as well as to know the main transport characteristics of them.

The electrolytic conductivity is the main operating criteria of ion exchange membranes, which depends upon the concentration and distribution of the ion exchange groups. In most of the cases, the distribution of ion exchangers is nonuniform in bulk and in the surface of the membranes. This nonuniformity results to the variation on many physical and chemical characteristics of the membranes and also in their operational behavior. Several models have been proposed to correlate the membrane in-homogeneity with the ion-transport through the membranes. Gnusin et al. proposed a theory to evaluate the specific electrical conductivity and the coefficient of penetrability of ion exchange resin in dispersed systems in the presence of different forces.<sup>12–15</sup> Zabolotsky and Nikonenko proposed a three phase (micro-

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Contract grant sponsor: The Ministry of Environment and Forests, India.

heterogeneous) model (TPM) describing the membrane as a combination of gel phase, intergel phase and inert gel phase.<sup>16</sup> They established that the inhomogeneities of the microphase is the main factor for relating the membrane transport properties such as electro-conductivity, diffusion permeability, and transport properties to the ionic concentration of the external aqueous solution. Elattar et al.<sup>17</sup> have chosen the three phase model to establish the transport of anions through commercial anion exchange membranes. Tongwen et al. applied the TPM theory in their studies on the threshold ionic conductivity in a series of sulphonated polyphenylene oxide matrix.<sup>18</sup>

In the present investigation, heterogeneous anion exchange membranes have been prepared varying in their binder:resin ratio. The membranes have been characterized with respect to their mechanical and electrochemical properties. The transport properties of these anion exchange membranes in contact with solutions having different homologous mono-carboxylate anions that have been evaluated. Membrane conductance values in conjunction with solution conductivities are used for the estimation of isoconductance points. Special emphasis has been given to elaborate study of the effect of variation of resin loading to the counter ion diffusion coefficient of the anion exchange membranes in equilibrium with the counter-ions like  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{CH}_3\text{CH}_2\text{COO}^-$ , and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$  of varied concentrations. The results have been analyzed on the basis of microheterogeneous model.

## EXPERIMENTAL

### Materials

Poly(vinyl chloride) (PVC), 67 GEF092, K value 67, flexible lamination film grade, supplied by IPCL (Vadodara), (Mumbai, India). Tetrahydrofuran (THF), as solvent with a refractive index of 1.407–1.409 and a density of 0.886–0.888 g/cm<sup>3</sup> at 25°C. Anion exchange resin (Indion FFIP), a chloromethylated and aminated polystyrene (with 8% crosslink density) with an exchange capacity of 3.4 mequiv/g dry resin, supplied by Ion Exchange India, India. Formic acid (specific gravity 1.18), Acetic acid (specific gravity 1.049), Propionic acid (specific gravity 0.992), Butyric acid (specific gravity 0.957), Sodium formate (98% purity), Sodium acetate (99% purity), Oxalic acid (Ranboxy Laboratory) (Delhi, India), Phenolphthaline indicator, and Sodium hydroxide solution.

### Preparation of membrane

Anion exchange resin particles were dried in an oven at 60°C, for 24 h, and then grinded to very fine particle size (average particle size of 39 μm).<sup>19</sup> The powdered ion exchange resin was then dispersed in

solution of PVC in THF (10% W/V). The membranes were casted on a glass plate by spray coating technique. The membranes were dried at an ambient temperature (30°C) for 30 min and the almost dried membranes were immersed in water. Different loading of resin (70, 60, 50, and 40%) was used to prepare membranes for their comparative studies. The membranes were conditioned by equilibrating in 1N Sodium hydroxide (NaOH) solution and subsequently in 1N hydrochloric acid (HCl) solution.

### Characterization of membranes

#### Ion exchange capacity and moisture content

The ion exchange membranes were converted to its  $\text{OH}^-$  forms by dipping in 1N NaOH solution for 1 h and washed with deionized water. It was then dipped in 1N HCl solution for 1 h to convert the membrane in  $\text{Cl}^-$  form and subsequently washed with deionized water. The process was repeated thrice and the membranes were kept overnight in 1N HCl solution. The membranes were washed thoroughly with de-ionized water to make them acid free. The membranes in  $\text{Cl}^-$  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 solution of 1N potassium nitrate ( $\text{KNO}_3$ ) solution in stoppered glass bottle for 24 h. The amount of  $\text{Cl}^-$  ion displaced was then determined analytically by titrating suitable aliquots from the equilibrium solution with standard 0.1N silver nitrate ( $\text{AgNO}_3$ ) solution.

Calculations: Let  $W_1$ , wt of empty bottle with lid;  $W_2$ , wt of empty bottle with lid + air dried membrane;  $W_3$ , wt of empty bottle with lid + dry membrane;  $W_C$ , wt of air dried membrane;  $V$ , volume of aliquot taken for titration;  $V_1$ , titer volume of 0.1N  $\text{AgNO}_3$ ;  $S$ , strength of  $\text{AgNO}_3$   $V_e$ , volume of 1N  $\text{KNO}_3$  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

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

where  $\rho$  is the specific density of the membrane in  $\text{kg/m}^3$ . The specific density of the membrane was obtained by measuring the dimensions and weight after drying at  $60^\circ\text{C}$  for 24 h.

#### Resistance

The ion exchange membranes were converted to suitable ionic ( $\text{Cl}^-$ ) form and washed with deionized water. The electrical resistance of the membranes in electrolyte solution containing same counter-ion as in the membrane was then measured. Two half cells of Perspex with a cross-sectional area of  $1\text{ cm}^2$  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 resistance of the solution in the cell with and without membranes was measured. The difference of the electrical resistance gave the membrane resistance. Membrane resistance multiplied by the cross-sectional area of the cell gave the areal resistance. The process was repeated until a reproducible value within  $\pm 0.01$  ohm was obtained.

#### Transport number

Anion exchange membranes in  $\text{Cl}^-$  form were kept in  $0.1N$  potassium chloride (KCl) solution for 2 h at  $25^\circ\text{C}$ . Membrane samples were then clamped between two Perspex half-cells fitted with calomel electrodes and stirring arrangements. The two halves of the cell were filled with  $0.2$  and  $0.1M$  solution of KCl on either side of membrane. The potential developed due to the concentration difference was measured with microvolt meter. The transport number was calculated from the observed potential and the theoretical concentration potential as

$$\text{Transport number} = \frac{E_{\text{observed}}}{E_{\text{theoretical}}}$$

#### Bursting strength

Bursting strength tester with a rubber diaphragm, hydraulic compressing arrangement, and a pressure gauge, supplied by Ubique Enterprises, Pune, India, was used for determining the bursting strength in  $\text{kg/cm}^2$ .

#### Conductance of membranes in different mono-carboxylate salt solutions

Preparation of different mono-carboxylate salt solutions

Stock solutions of  $0.2N$  sodium formate and sodium acetate solutions were prepared by dissolving appropriate quantity of the salts in distilled water. Stock solutions of sodium propionate and sodium butyrate were prepared by dissolving appropriate quantity of propionic/butyric acid with definite quantity of NaOH and distilled water. The used NaOH was standardized with standard oxalic acid using phenolphthalein indicator. From the stock solutions different concentrations of sodium formate/acetate/propionate/butyrate solutions (namely  $0.001$ ,  $0.005$ ,  $0.01$ ,  $0.05$ , and  $0.1N$ ) were prepared by appropriate dilution.

#### Conductance in mono-carboxylate salt solution

In all the cases, the membranes were regenerated, by following the normal procedure. The membranes were then converted to its formate/acetate/propionate/butyrate forms by immersing the membranes for 24 h in respective salt solutions ( $1N$ ). The membranes were then washed with distilled water and their resistance was measured in circular resistance cell using the appropriate solution of different concentrations. In all the cases, the membrane thickness was measured using screw gauge. The experiments were carried out at  $(30 \pm 2)^\circ\text{C}$  and the process was repeated till reproducible values within  $\pm 0.01$  ohm were obtained.

The electrical conductivities of the membrane were then determined using the formula

$$K_m = \delta/AR_m \quad (1)$$

where  $\delta$  is the thickness of the membrane,  $A$  is the area, and  $R_m$  is the electrical resistance.

## RESULTS AND DISCUSSION

#### Evaluation of membrane properties

The ion exchange membranes thus prepared contain ion exchange resin particles dispersed in the base poly(vinyl chloride) matrix. The properties of ion exchange membranes are given in Table I.

Table I reveals that increase in resin loading results in a fall in the bursting strength. This indicates that enhancement in resin loading results in a comparatively brittle membrane. With the used resin having an average particle size of  $39\ \mu\text{m}$  it is possible to achieve flexible membrane up to resin loading of  $60\%$ . Increase in resin loading results in enhance-

TABLE I  
General Properties of Anion exchange Membranes: Mesh Size of the Resin Particles –300 + 400 BSS (39  $\mu\text{m}$ )

Resin loading (%)	Moisture content (%)	Capacity $E_c$ (equiv/kg)	Density $\rho$ ( $\text{kg}/\text{m}^3$ )	Capacity $Q_0$ (equiv/ $\text{m}^3$ )	Areal resistance ( $\Omega \cdot \text{cm}^2$ )	Bursting strength ( $\text{kg}/\text{cm}^2$ )	Transport no.
70	48.6	2.8	528.3	1489.8	5.0	1.7	0.92
60	44.7	2.2	629.8	1385.5	10.0	2.3	0.93
50	38.2	1.8	729.6	1327.9	22.0	2.7	0.91
40	31.5	1.5	829.1	1243.6	82.0	2.9	0.92

ment of polystyrene content in the membrane and as a result the crosslinked polystyrene particles tend to form a continuous phase.<sup>19</sup> Polystyrene having a very less impact strength fails to dissipate the absorbed energy and hence crack propagation becomes faster. The density of the dry membrane depends on the densities of PVC and polystyrene and their relative proportion in the membrane. As the density of PVC ( $1.4 \text{ g}/\text{cm}^3$ ) is greater than that of polystyrene, hence increase in resin content in the blend results in the fall in density of the membranes (Table I). The performance of an ion exchange membrane depends upon its exchange capacity with the ions in the solution, which in turn depends on the active functional groups in the membranes. As the polystyrene is the functional group bearing component in the membrane, hence increase in resin content results in a higher capacity and moisture content of the membrane and at the same time the electrolytic conductivity of the membrane increases that is membrane resistance decreases. However, the transport number of the membranes remains unaffected with resin loading.

Hence, it is very clear that the properties of heterogeneous anion exchange membranes depend upon the relative proportion of the binder and the ion exchange resin. Membranes having higher binder content possess a good mechanical strength but they lack in electrochemical properties, whereas membranes having higher resin content possess good electrochemical properties but their mechanical properties are comparatively poor.

### Solution conductance

The studies on the solution conductance of different mono-carboxylate salt solutions are shown in Figure 1. It is observed that at any solution concentration the solution conductance of formate ( $\text{HCOO}^-$ ) > acetate ( $\text{CH}_3\text{COO}^-$ ) > propionate ( $\text{CH}_3\text{CH}_2\text{COO}^-$ ) > butyrate ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$ ). The bulkiness of the butyrate ion in compare to the formate ion results to its low mobility as well as low conductance. There is almost a hundredfold increase in conductivity in the case of all the four different salts as the concentration increases from 1 to 100  $\text{equiv}/\text{m}^3$ . This is

because of the direct dependence of conductivity on concentration.<sup>20</sup>

### Membrane conductance

The resistance of different heterogeneous anion exchange membranes varying in their blend ratios was measured in different mono-carboxylate salt solutions at concentrations varying from 1 to 100 mM. By measuring the thickness of the membranes with the help of a screw gauge, the specific conductance of different membranes was calculated using the Formula (1). The trend of behavior may be visualized from Figures 2–5.

It is observed that like the solution conductivity membrane conductivities also increase with increase in external solution concentrations. It is possible that at very low external solution concentration the conductance of the pore solution may exceed that of the external solution.<sup>20</sup> As the concentration of the external solution is increased the membrane conductance increases slowly at first and then more rapidly. The membranes having higher resin content are characterized by higher conductivities than those with lower resin content that is at any particular solution concentration the membrane conductance increases with increase in resin loading.

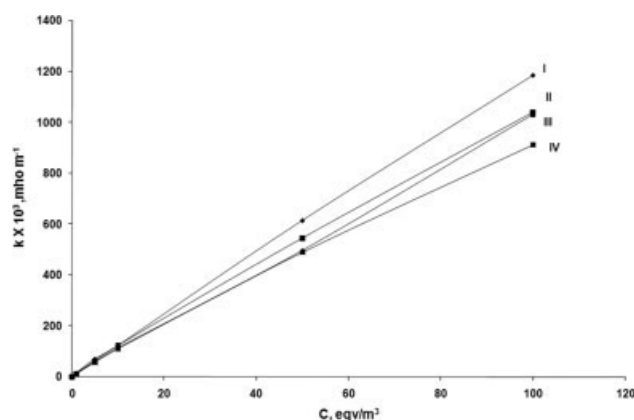
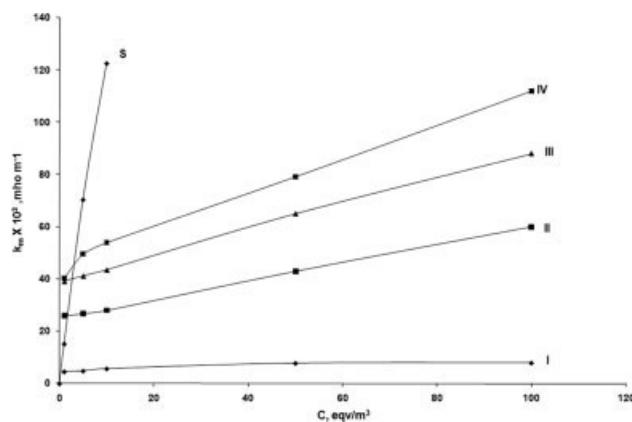


Figure 1 Variation of solution conductivity with concentration. I, Sodium formate; II, sodium acetate; III, sodium propionate; IV, sodium butyrate.

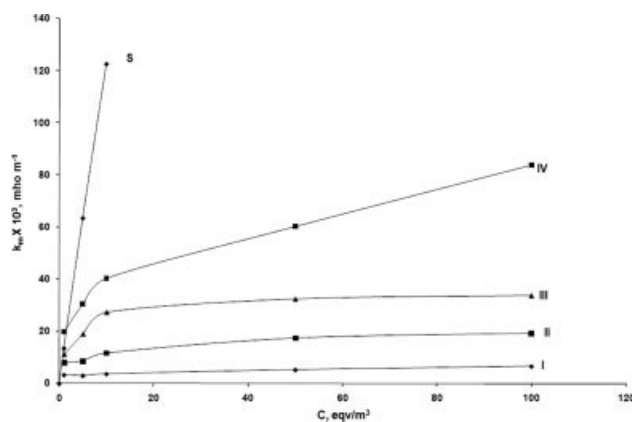


**Figure 2** Electro-conductivity of membranes in sodium formate solution. % Resin loading I, 40%; II, 50%; III, 60%; IV, 70%.

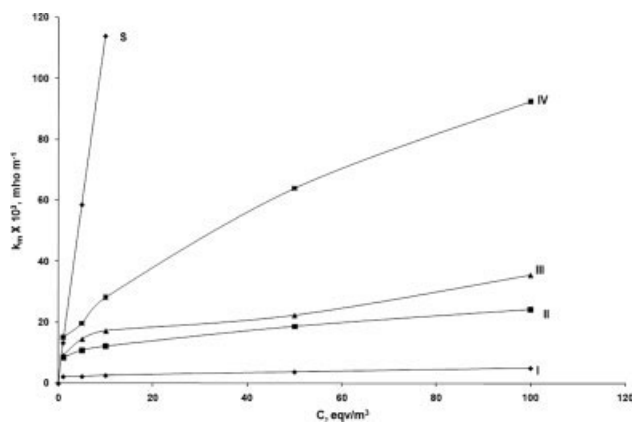
As the resin part having the functional groups acts as the conducting sites of the membrane and PVC is an inert binder, hence enhancement in the resin content results in higher conductivity of the membrane. It is seen in our previous work<sup>19</sup> that enhancement in the resin content results to a more homogeneous phase morphology, which leads to an enhancement in membrane conductance. From a comparison among the Figures 2–5 it is seen that at any particular resin loading the membrane conductance in  $\text{HCOONa} > \text{CH}_3\text{COONa} > \text{CH}_3\text{CH}_2\text{COONa} > \text{CH}_3\text{CH}_2\text{CH}_2\text{COONa}$ , which may be attributed to the higher mobility of formate ion than butyrate ion both in the solution as well as in the membrane. The reporting value of  $\lambda_0$  of formate ion is  $54.6 \times 10^{-4} \text{ m}^2 \text{ s/mol}$  whereas that for acetate, propionate, and butyrate is  $40.9 \times 10^{-4}$ ,  $35.8 \times 10^{-4}$ , and  $32.6 \times 10^{-4} \text{ m}^2 \text{ s/mol}$ , respectively.<sup>21</sup>

### Electroconductivity and heterogeneity of the membranes

The electrolytic conductance of the membranes is a reflection of the transport behavior of the ions



**Figure 3** Electro-conductivity of membrane in sodium acetate solution. % Resin loading I: 40%, II: 50%, III: 60%, IV: 70%.

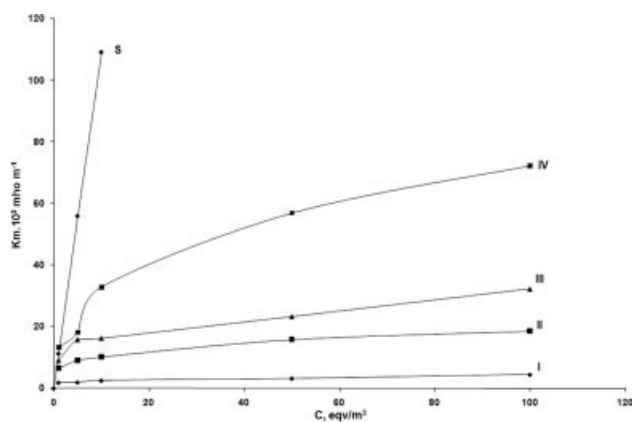


**Figure 4** Electro-conductivity of membranes in sodium propionate solution. % Resin loading I, 40%; II, 50%; III, 60%; IV, 70%.

through an ion exchange membrane, which in turn depends upon the microheterogeneity of the membranes. With the help of their microheterogeneous model, which includes both the surface and bulk inhomogeneity of the membranes, Zabolotsky and Nikonenko<sup>16</sup> showed that the concentration dependence of the different transport properties of ion exchange membranes is due to the in-homogeneity of the membrane in the microphase scale. For our present work, we have selected this particular model. According to this model, an ion exchange membrane in an electrolyte solution may be considered as a combination of two different phases: (1) the joint gel phase and (2) the intergel phase filled with the electrolyte solution with which the joint gel phase is in equilibrium. If the volume fraction of joint gel phase is  $f_1$  and the volume fraction of the intergel phase  $f_2$  then

$$f_2 = 1 - f_1 \quad (2)$$

According to Zabolotsky model the specific electro-conductivity of the membrane ( $\kappa_m$ ) may be corre-



**Figure 5** Electro-conductivity of membranes in sodium butyrate solution. % Resin loading I, 40%; II, 50%; III, 60%; IV, 70%.

lated to the conductivity of the joint gel phase ( $\bar{\kappa}$ ) and of the solution ( $\kappa$ ) by the equation

$$\kappa_m = (f_1 \bar{\kappa}^{-\alpha} + f_2 \kappa^\alpha)^{1/\alpha} \quad (3)$$

$$\text{or } \kappa_m^\alpha = (f_1 \bar{\kappa}^\alpha + f_2 \kappa^\alpha) \quad (4)$$

where  $\alpha$  is the structural parameter and reflects the reciprocal arrangement of the phase elements that are the joint gel and inter gel phases of the membrane. When  $\alpha \ll 1$  eq. (4) becomes

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

$$\text{Hence, } \ln \kappa_m = f_1 \ln \bar{\kappa} + f_2 \ln \kappa \quad (6)$$

Equation (6) indicates that  $\ln \kappa_m$  varies linearly with  $\ln \kappa$  and Zabolotsky et al. showed that this linear relationship is maintained up to  $\alpha \leq 0.2$ .

Again they have described the joint gel phase as a reciprocal combination of pure gel phase and inert gel phase. The pure gel phase contains the ionogenic groups and hence it is the hydrophilic part of the matrix whereas the inert gel phase is the polymeric binder part of the membrane.

$$\text{Hence } f_1 = f'_1 + f_{in} \quad (7)$$

where  $f_1$ ,  $f'_1$  and  $f_{in}$  are the volume fraction of joint gel, pure gel, and inert gel phases, respectively. By knowing the composition of the membranes and the densities of the resin and inert binder, the  $f_{in}$  can be calculated. Zabolotsky et al. introduced another parameter  $\beta$  characterizing the arrangement of the pure gel and the inert binder in the joint gel phase.  $\beta$  may be derived from the equation

$$\bar{\kappa} = \left(\frac{f'_1}{f_1}\right)^{1/\beta} \cdot \bar{\kappa}' \quad (8)$$

$$\text{Or } \ln \bar{\kappa} = \frac{1}{\beta} \ln \left(\frac{f'_1}{f_1}\right) + \ln \bar{\kappa}' \quad (9)$$

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

Equation (9) shows that the plot of  $\ln \bar{\kappa}$  versus  $\ln \left(\frac{f'_1}{f_1}\right)$  is a straight line. From the slope of the curves and the intercepts, the values of  $\beta$  and the values of  $\bar{\kappa}'$  can be found out.

### Isoconductance point

Consider the Figures 2–5. The intersection points of  $\kappa_m$  versus  $C$  (lines I, II, III, and IV) and  $\kappa$  versus  $C$  graphs (line S) are known as isoconductance points.

TABLE II  
Isoconcentration and Isoconductance Values

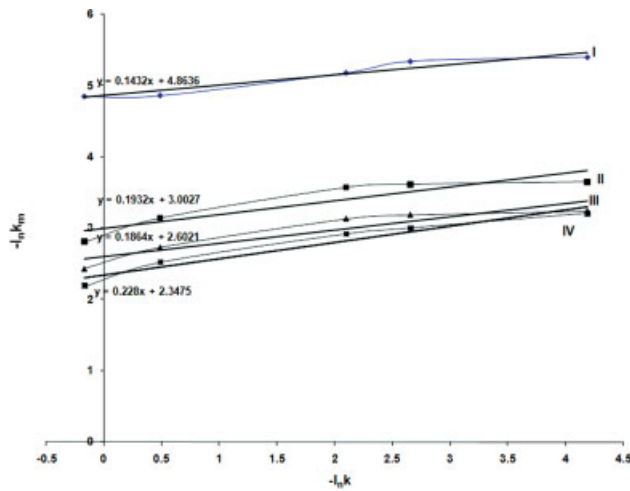
Resin content (%)	Mono-carboxylate anion	$C_{iso}$ (equiv/m <sup>3</sup> )	$\kappa_{iso}^m \times 10^3$ (mho/m)
40	Formate	0.314	4.36
	Acetate	0.224	3.299
	Propionate	0.177	2.054
	Butyrate	0.177	1.80
50	Formate	1.806	26.359
	Acetate	0.595	7.988
	Propionate	0.595	8.101
	Butyrate	0.617	6.217
60	Formate	2.807	40.085
	Acetate	0.805	10.503
	Propionate	0.711	9.136
	Butyrate	0.782	8.397
70	Formate	3.228	45.498
	Acetate	1.643	21.329
	Propionate	1.225	15.540
	Butyrate	1.247	13.710

The concentration of the solution at isoconductance point is known as isoconcentration  $C_{iso}$  and the membrane conductance is known as isoconductance  $\kappa_{iso}^m$ . The isoconductance points of different membranes in four different mono-carboxylate salt solutions are shown in Figures 2–5. The different  $C_{iso}$  and  $\kappa_{iso}^m$  values are presented in Table II.

According to Zabolotsky's model at isoconductance point  $\kappa_{iso}^m = \bar{\kappa} = \kappa$ . Hence the conductivities of the joint gel phase  $\bar{\kappa}$  may be achieved from this data. From the tabulated data it is observed that for all the blend ratios the specific conductivities of the joint gel phase ( $\bar{\kappa}$ ) decreases in the order  $\bar{\kappa}$  formate >  $\bar{\kappa}$  acetate >  $\bar{\kappa}$  propionate >  $\bar{\kappa}$  butyrate. This is because the ionic conductance is proportional to the ionic mobility and ionic mobility of formate > acetate > propionate > butyrate. Similarly for any particular counter ion, the specific conductance of the joint gel phase  $\bar{\kappa}$  (or the isoconductance) of the membranes, increase with the increase in resin loading. Hence, for any specific external electrolyte solution it is observed that  $\bar{\kappa}_{70} > \bar{\kappa}_{60} > \bar{\kappa}_{50} > \bar{\kappa}_{40}$ . The behavior may be explained in the same way as in the case of membrane conductance.

### Volume fraction $f_1$ , $f_2$ , and exchange capacity $Q$

Zabolotsky's model states that at isoconductance point that is at  $C_{iso}$ , the  $\kappa_{iso}^m = \bar{\kappa} = \kappa$  and the values of  $\kappa_m$  depends slightly on  $\alpha$ . In the range  $0.1 C_{iso} < C < 10 C_{iso}$  the dependence of  $\ln \kappa_m - \ln \kappa$  may be approximated by a linear relationship up to  $|\alpha| = 0.2$  as shown in eq. (6). The dependence of  $\ln \kappa_m$  and  $\ln \kappa$  for different mono-carboxylate solutions at different blend ratios are shown in Figures 6–9 and their dependence may be approximated by linear

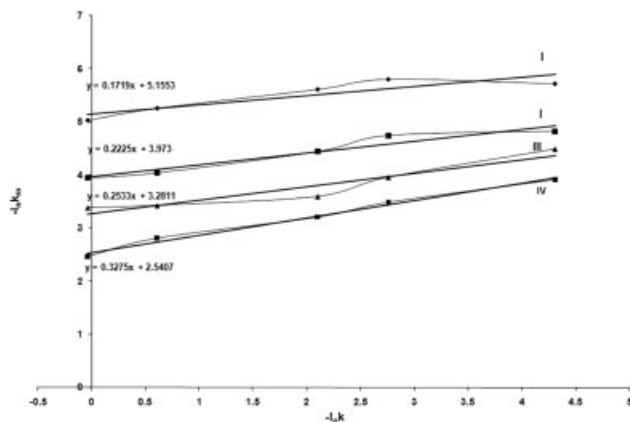


**Figure 6**  $\ln \kappa_m$  versus  $\ln \kappa$  in sodium formate solution. % Resin loading I, 40; II, 50; III, 60; IV, 70. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

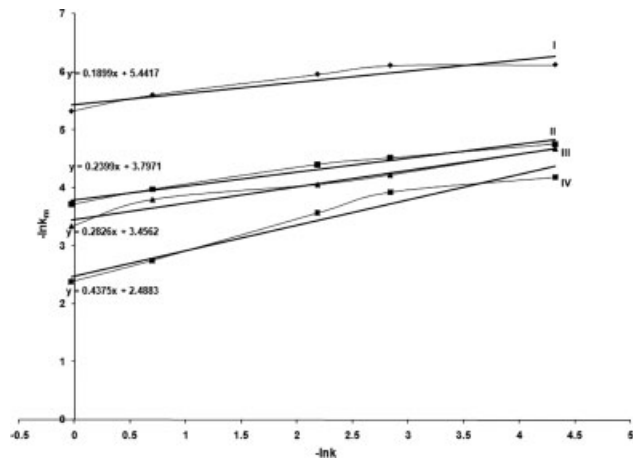
relationship indicating that, for these series of membranes studied here  $|\alpha| \leq 0.2$ .

The values of  $f_2$  that is the volume fraction of the intergel phase is evaluated from the slope of the graphs. The volume fraction of the joint gel phase has been evaluated with the help of eq. (2) and the values of  $f_1$  and  $f_2$  are presented in Table III.

The values of  $f_1$  depend upon three different factors like size of the counter-ions in the pure gel phase, relative exchange affinity of the active sites towards the counter ion, and the swelling behavior of the pure gel phase. The predominant values of  $f_1$  compared to  $f_2$  clearly indicate that  $f_1$  plays a dominant role in the selective transport of ions through the membranes. In most of the cases, the values of  $f_1$  is found to be highest in the case of formate ions followed by acetate, and for propionate and butyrate the  $f_1$  values are approximately equal. Formate ion



**Figure 7**  $\ln \kappa_m$  versus  $\ln \kappa$  in sodium acetate solution. % Resin loading I, 40; II, 50; III, 60; IV, 70.

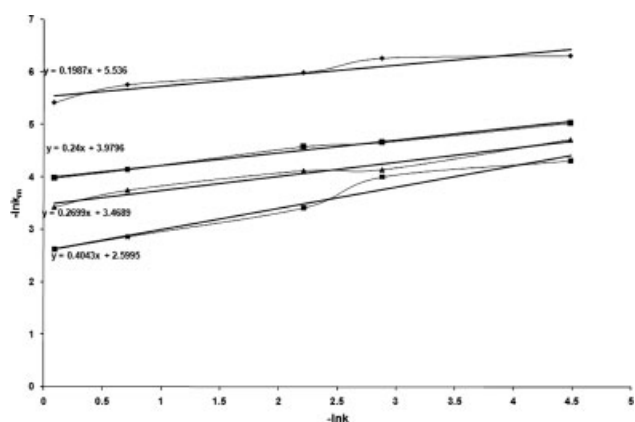


**Figure 8**  $\ln \kappa_m$  versus  $\ln \kappa$  in sodium propionate solution. % Resin loading I, 40; II, 50; III, 60; IV, 70.

being smallest in size has more penetrability through the membranes, which is reflected in comparatively higher values of  $f_1$ . Increase in resin content increases the value of  $f_2$ . Joint gel phase is a combination of pure gel phase and inert gel phase. The pure gel phase consists of the resin bearing the active functional groups. Increase in the resin content results to more hydrophilicity in the membranes and hence and the more swelling tendency of the membrane is reflected in the higher values of the volume fraction of the intergel phases. The ion exchange capacity of the joint gel phase may be derived by the equation

$$\bar{Q} = \left( \frac{Q_0}{f_1} \right) \quad (10)$$

where,  $Q_0$  is the average exchange capacity of the membrane. Having the values of  $f_1$ , the  $\bar{Q}$  values have been calculated with the help of eq. (10) and reported in Table III. It is observed that for any



**Figure 9**  $\ln \kappa_m$  versus  $\ln \kappa$  in sodium butyrate solution. % Resin loading I, 40; II, 50; III, 60; IV, 70.

TABLE III  
Diffusion Coefficient of Anions Through the Joint Gel Phase of Anion Exchange Membranes

Resin content (%)	Mono-carboxylate anion	$f_2$	$f_1$	$\bar{Q} = Q_0/f_1$ (equiv/m <sup>3</sup> )	$\bar{D} \times 10^{12}$ (m <sup>2</sup> /s)
40	Formate	0.1432	0.8568	1451.1	0.813
	Acetate	0.1719	0.8281	1501.7	0.594
	Propionate	0.1899	0.8101	1535.1	0.362
	Butyrate	0.1987	0.8013	1551.9	0.314
50	Formate	0.1932	0.8068	1645.5	4.333
	Acetate	0.2225	0.7775	1707.9	1.265
	Propionate	0.2314	0.7686	1727.6	1.268
	Butyrate	0.2400	0.7600	1747.2	0.962
60	Formate	0.1864	0.8136	1702.1	6.371
	Acetate	0.2533	0.7467	1855.5	1.531
	Propionate	0.2826	0.7174	1931.3	1.279
	Butyrate	0.2699	0.7301	1897.7	1.197
70	Formate	0.2280	0.7720	1929.8	6.378
	Acetate	0.3275	0.6725	2215.3	2.604
	Propionate	0.4375	0.5625	2648.5	1.587
	Butyrate	0.4043	0.5957	2500.9	1.483

external electrolyte solution  $\bar{Q}$  values increase with increase in resin loading. This is because with increase in resin loading the active sites and the homogeneity in the membranes also increase, ref. 19.

#### Counter ion diffusion coefficient, $\bar{D}$

The diffusion coefficient of the counter ions ( $\bar{D}$ ) in the joint gel phase is calculated by using the following equation

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

where  $R$  is the universal gas constant,  $T$  is the absolute temperature, and  $F$  is Faraday number. The values are presented in Table III. For any particular resin loading, the counter ion diffusion coefficient in the membrane decreases in the order formate > acetate > propionate > butyrate which is in accordance with their ionic mobility. The diffusion coefficient increases with increase in resin loading in the membrane. Butyrate being bulkier in nature compared to formate is expected to experience more hindrance in their diffusion through the membrane. Increase in resin loading imposes more functional sites for transportation of ions and hence makes the diffusion of any counter ion much more facile (Fig. 10).

#### Evaluation of $f'_1$ and $\beta$

By knowing the composition of the membranes that is the resin : binder ratio and with the help of the density of anion exchange resin and the inert binder PVC, the  $f_{in}$  that is the volume fraction of inert gel phase for different anion exchange membranes have been calculated (Table IV).  $f'_1$ , the volume fraction of

the pure gel phase was calculated with the help of eq. (7).

As the pure gel phase is expected to consist only of the ion exchange resin, hence the volume fraction of the pure gel phase increases with increase in resin loading (Table IV). For any particular resin loading the  $f'_1$  values are least when butyrate is the counter ion and highest for the formate. A plot of the values of  $\ln \bar{\kappa}$  versus  $\ln \frac{f'_1}{f_1}$ , for membranes varying in their blend ratios in different monocarboxylate solutions exhibits linear relationship proving the validity of eq. (10). A representative graph for acetate ion is shown in Figure 11.

The values of  $\beta$  and  $\bar{\kappa}'$  for different counter ions are given in Table V. It is seen from the Table V that the values of  $\beta$  is almost constant that is  $0.38 \pm 0.04$  for all the heterogeneous membranes in equilibration with different counter ions studied here. This indi-

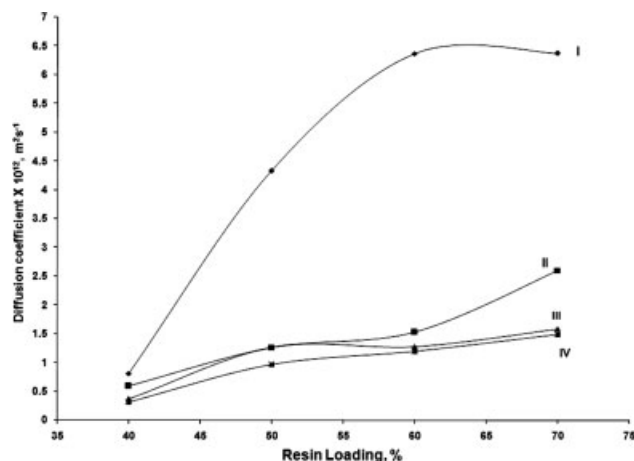


Figure 10 Variation of diffusion coefficient with resin loading. I, sodium formate; II, sodium acetate; III, sodium propionate; IV, sodium butyrate.



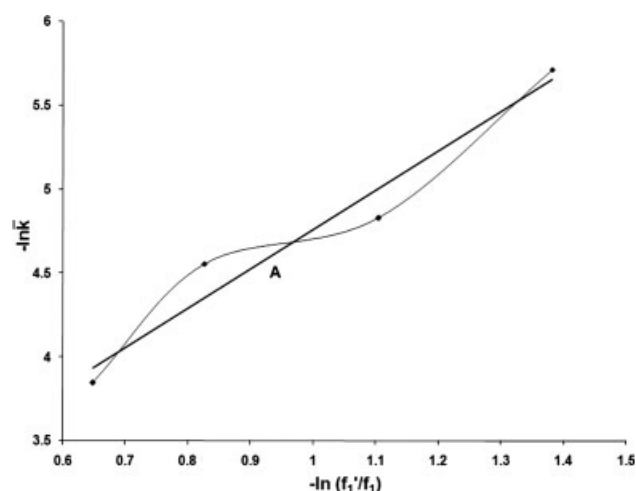
**TABLE IV**  
The Values of  $f_1$  and  $f_{in}$  of Anion Exchange Membranes in Different Mono-carboxylate Salt Solutions

Resin loading	$f_{in}$	Mono-carboxylate anion	$f_1$	$f_1' = f_1 - f_{in}$	$f_1'/f_1$
40	0.62	Formate	0.8568	0.2368	0.276
		Acetate	0.8281	0.208	0.251
		Propionate	0.8101	0.1901	0.235
		Butyrate	0.8013	0.1813	0.226
50	0.52	Formate	0.8068	0.2868	0.355
		Acetate	0.7775	0.2575	0.331
		Propionate	0.7686	0.2486	0.323
		Butyrate	0.7600	0.2400	0.316
60	0.42	Formate	0.8136	0.3936	0.484
		Acetate	0.7467	0.3267	0.4375
		Propionate	0.7174	0.2974	0.414
		Butyrate	0.7301	0.3101	0.424
70	0.32	Formate	0.7720	0.4520	0.585
		Acetate	0.6725	0.3525	0.523
		Propionate	0.5625	0.2425	0.431
		Butyrate	0.5957	0.2757	0.463

cates that the relative distribution of pure gel phase and inert gel phase in the joint gel phase does not vary much at different blend ratios of resin and PVC. Hence a series of heterogeneous ion exchange membranes composed of the same binder material and ion exchange resins may be synchronized by a simple heterogeneity factor. At the same time, it is also observed that the conductivity of the pure gel phase is much higher with formate as the counter ion than the other three counter ions studied here.

## CONCLUSION

- Heterogeneous anion exchange membranes prepared from PVC and ion exchange resin in different blend ratios possess good dimensional sta-



**Figure 11** Variation of joint gel phase conductivity  $\kappa$  with the ratio of the pure gel phase fraction ( $f_1'$ ) to the joint gel phase ( $f_1$ ) one.

**TABLE V**  
Data for  $\beta$  and  $\bar{\kappa}'$

Counter ion	$\beta$	$\bar{\kappa}' \times 10^2$
Formate	0.34	29.0
Acetate	0.42	8.9
Propionate	0.34	16.0
Butyrate	0.38	9.5

bility, mechanical strength, and electrochemical properties.

- The solution conductance in  $\text{HCOONa} > \text{CH}_3\text{COONa} > \text{CH}_3\text{CH}_2\text{COONa} > \text{CH}_3\text{CH}_2\text{CH}_2\text{COONa}$  at any particular solution concentration.
- At any particular solution concentration membrane conductance increases with increase in resin loading.
- For membranes having the same resin loading membrane conductance in  $\text{HCOONa} > \text{CH}_3\text{COONa} > \text{CH}_3\text{CH}_2\text{COONa} > \text{CH}_3\text{CH}_2\text{CH}_2\text{COONa}$ .
- The specific conductivities of the joint gel phase decreases in the order  $\bar{\kappa}$  formate  $>$   $\bar{\kappa}$  acetate  $>$   $\bar{\kappa}$  propionate  $>$   $\bar{\kappa}$  butyrate.
- For any specific carboxylate  $\bar{\kappa}_{70} > \bar{\kappa}_{60} > \bar{\kappa}_{50} > \bar{\kappa}_{40}$ .
- For any particular resin loading the diffusion coefficient in membrane for formate  $>$  acetate  $>$  propionate  $>$  butyrate.
- For such anionic membranes  $|\alpha| = 0.2$ .
- The values of heterogeneity factor  $\beta$  for the membranes is  $0.38 \pm 0.04$ .
- The specific conductivity of the pure gel phase is highest for formate as the counter ion.

## NOMENCLATURE

- $W_1, W_2, W_3, W_C$  Weight of empty bottle, empty bottle + air dried membrane, empty bottle + dry membrane, and air dried membrane, respectively (g)
- $V, V_1, V_e$  Volume of aliquot taken for titration, titre volume of 0.1N  $\text{AgNO}_3$  and volume of 1N  $\text{KNO}_3$  taken for equilibrium (mL)
- $E_c$  Membrane capacity (equiv/kg)
- $Q_0$  and  $\bar{Q}$  Ion exchange capacity of membrane and the joint gel phase respectively (equiv/m<sup>3</sup>)
- $S$  Strength of  $\text{AgNO}_3$  (N)
- $\rho$  Density of the membrane (kg/m<sup>3</sup>)
- $\delta$  Membrane thickness (cm)
- $A$  Membrane area (cm<sup>2</sup>)

$R_m$	Membrane resistance (ohm)
$\kappa, \kappa_m, \kappa, \kappa', \kappa_{iso}^m$	Specific conductance of solution, membrane, joint gel phase, pure gel phase, and membrane conductance at isoconductance point, respectively (mho/cm)
$f_1, f_2, f_{in}, f_1'$	Volume fraction of the joint gel, intergel, inert gel, and pure gel phase, respectively
$\alpha, \beta$	Structural parameters
$F$	Faraday constant
$R$	Gas constant (J/mol/K)
$\lambda_0$	limiting equivalent conductance (m <sup>2</sup> s/mol)
$T$	Temperature (K)
$C_{iso}$	Isoconcentration (equiv/m <sup>3</sup> )

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