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Ionic permeability of polymeric membranes: part 1—steady state transport of binary electrolytes through polyethylene films

E. E. Oguzie · A. I. Onuchukwu · U. J. Ekpe

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Abstract This paper describes a simplified model of the diffusion process based upon a linear idealization of Fick's law. Ion permeation through polyethylene films was investigated using a conductometric technique at 28°C. The electrolytes studied were KCl, NaCl, LiCl, $MgCl_2$, $CaCl_2$ and $AlCl_3$. The initial concentration gradient was established by introducing 0.01 mol dm^{-3} of electrolyte on one side of the membrane and deionized water on the other side. The results show that the PE membranes have a negative surface charge and exhibit selective permeability to the various cations, with very high selective affinity for Li^+. The selectivity sequence was in the order $K^+ < Na^+ \ll Li^+$ for the monovalent cations and $Al^{3+} < Ca^{2+} < Mg^{2+}$ for the multivalent ions, suggesting dependence on the crystallographic, rather than hydrated radius of the cations. Permeation rates calculated from the evaluated transport parameters using a mathematical model based on Fick's law showed good agreement with the experimental values.

Keywords Polyethylene membrane · Ionic diffusion · Selectivity · Fick's law · Modelling

1 Introduction

Evaluation of the ionic permeabilities of polymer membranes in equilibrium solutions of electrolytes is of immense importance for the theory of membrane processes as well as the practice of the various membrane-separation techniques. Separation between different components is effected by the difference in transport rates through the membrane; hence some mechanism must exist in the membrane which is responsible for improving the transport of one component while impeding the transport of the other. Membranes may be classified as either porous or dense (non porous). Porous membranes discriminate among penetrating components according to their sizes, whereas non porous membranes discriminate according to chemical affinities between components and the membrane material. However some controversy exists on the distinction between porous and non porous membranes, since actual membrane structures are in practice neither entirely porous nor dense, and the so called non porous membranes may in fact be very finely microporous, with some minute pores of diameter in the order of tenths of nanometers [4, 12]. Permeation can thus occur both through the material of the membrane and through the porous network. Nevertheless, porous membranes are best characterized by their separating mechanism as are non porous ones.

A very important and fundamental means by which a penetrant can be transported through a non-porous membrane involves dissolving of the permeate species into the membrane at its upstream surface, followed by activated diffusion down its concentration gradient to the downstream face of the membrane and then dissolution into the adjacent fluid phase. This is the solution-diffusion model [4, 11, 14]. Separation of different components is related directly to their relative transport rate within the membrane,

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E. E. Oguzie (✉) · A. I. Onuchukwu
Electrochemistry and Materials Science Research Laboratory,
Department of Chemistry, Federal University of Technology,
Owerri PMB 1526, Nigeria
e-mail: oguziemeka@yahoo.com

U. J. Ekpe
Department of Pure and Applied Chemistry, University
of Calabar, Calabar PMB 1115, Nigeria

which is determined by their diffusivity and solubility in the membrane phase. Preferential permeability may be as a result of a number of different interactions such as ionic–ionic, ionic–dipole, dipole–dipole etc [4].

Ionic diffusion in charged membranes constitutes a complex phenomenon where many effects are simultaneously present. Separation is mainly achieved by exclusion of ions of the same charge as the membrane charge and, to a much lesser extent, by the pore size [1]. Membrane conductivity thus depends on the electrostatic interaction between the counter-ions and the fixed charges; the relative sizes of the mobile ions and the membrane structural properties and characteristics. Separation of ionic species is linked to hydrated ion sizes which produce hydration rejection patterns, or coulombic interactions which produce charge rejection patterns. A number of studies involving the transport of ionic species through polymeric membranes have been reported. Tischenko et al. [13] studied the electrical resistance and diffusion permeability of microporous polyethylene membranes modified with polypyrrole and polyaniline in solutions of electrolytes. Ding et al. [22] studied electrokinetic phenomena of a polyethylene microfilteration membrane in solutions of NaCl, KCl, $MgCl_2$, Na_2SO_4 and $MgSO_4$. They observed that the membrane had a weak negative charge due to specific sorption of ions and the valence of the cations had a significant influence on the surface charge density of the membrane.

In this paper, a simplified model is proposed for the permeation of ionic species through polymer membranes in the absence of an applied electric field. The experimental data was adapted from conductometrically determined permeation fluxes of different electrolytes through polyethylene film membranes. The transport characteristics and selectivity of the studied membranes were also determined and are discussed vis-à-vis some existing theories.

2 Experimental

2.1 Materials

All chemicals were BDH grade, used as received without further purification. Standard solutions of the 1:1 electrolytes LiCl, NaCl, KCl; 2:1 electrolytes $MgCl_2$, $CaCl_2$, and 3:1 electrolyte $AlCl_3$ were prepared using deionised water of known conductivity. Calibration curves for all experiments were obtained using the standard addition technique.

The membrane chosen was a dense polyethylene film (LDPE) supplied by the Polymer Laboratory of the Department of Polymer and Textile Engineering, Federal University of Technology, Owerri. The density was $0.917\ g\ cm^{-3}$, with the volume fraction of crystalline phase in the range 45–50% [18]. Films of thickness 6.5 and 15.0 μm, denoted PE-1 and PE-2 were used. The membranes were cut into circular discs of diameter 4.5 cm and pre-treated by a procedure similar to that of Djong-Gei [8] and Yeager et al. [24]. The treatment did not include expansion of the membranes by boiling in the solvent. Membranes were soaked in ethanol for about 30 min, washed thoroughly with warm water and then stored in deionised water prior to use in diffusion experiments. Total soaking time was never less than 48 h.

2.2 Transport measurements

The apparatus for diffusion measurements consists of a glass bi-cell with two compartments separated by the membrane. The LDPE films were fixed between the two half cells using silicone sealant. The exposed membrane area was $1.77\ cm^2$ and the volume of each half cell was 40 ml. The assembly was clamped together using Perspex end plates. At the start of all experiments the initial electrolyte concentration in C_1 was 0.01 M while C_2 contained only deionized water of known conductivity so that $[C_2] = 0$. The contents of both compartments were stirred throughout the experiment using specially fabricated glass stirrers. The whole set up was temperature controlled in a water thermostat maintained at 28°C. Solute concentration was monitored conductometrically in both cells and the signals were recorded at 30-min intervals progressively for 180 min. No appreciable change in conductivity was noted within the 3-h period in the feed solution (C_1) and so the concentration was assumed to be constant. Conductivity changes were thus monitored only in the permeate solution (C_2) and the concentration of this solution at any given time was estimated from a calibration curve. All experiments were repeated at least three times. The diffusion runs using membrane PE-1 and KCl were repeated five times to assess the reproducibility of the method.

3 Results and discussion

3.1 Membrane permeability

Permeation rates were determined from conductivity changes of permeate-side solution (C_2). The conductometric technique is generally acceptable for monitoring the transport of single binary electrolytes through flat membranes [7, 15]. Figure 1 illustrates the rate of change in $[C_2]$ for various electrolytes diffusing through membrane PE-1. The values for LiCl have been divided by ten in order to appear on the same scale as the other data. Figure 2 shows similar plots for PE-2, where the results for the 1:1 electrolytes LiCl, NaCl and KCl are plotted

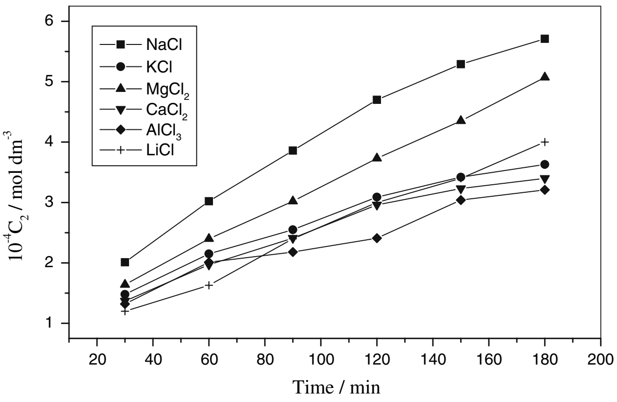

Fig. 1 Change in C_2 concentration with time for permeation of various electrolytes through PE-1

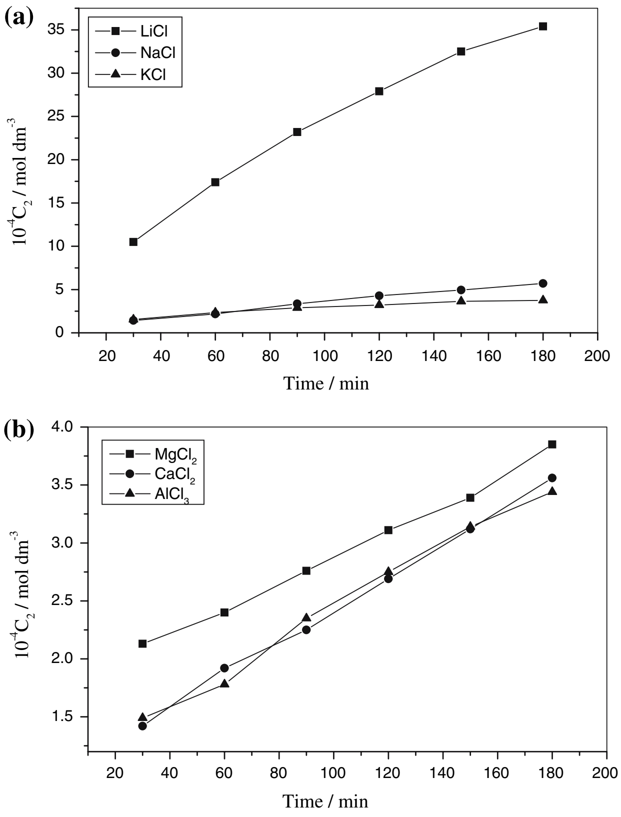

Fig. 2 Change in C_2 concentration with time for permeation of (**a**) 1:1 and (**b**) 2:1 electrolytes through PE-2

separately (2a) from those of the 2:1 and 3:1 electrolytes (2b). The plots depict a linear increase in [C_2] with time for all the electrolytes. The slight non linearity displayed in some of the plots can be attributed to inhomogeneities inherent in the membrane structure. In addition, it was difficult to maintain the apparatus at a constant rate of stirring, which could also lead to the existence of local concentration gradients that are dependent on local fluid velocities.

Experimental conditions were adapted so that the steady-state approximation of Fick's law was applicable. The conditions include a high, constant concentration of diffusing species on one side of the membrane and negligible concentration on the other side (i.e. $C_1 \gg C_2$), as well as limited time span for the experiment. Under these conditions a linear concentration gradient can be assumed and the flux (J) of diffusing species is constant and can be evaluated from [3]:

$$J = \frac{\Delta C}{\Delta t} \cdot \frac{V}{A} \mathrm{mol\,cm^{-2}\,min^{-1}} \tag{1}$$

where V is the volume of permeate solution, A the exposed area of the membrane and $\Delta C/\Delta t$ is the slope of the concentration versus time curve. The electrolyte permeability coefficient P_s can then be determined from Fick's law. The results shown in Fig. 3 reveal that significant variation in the permeation fluxes of the different electrolytes through the LDPE membranes. This implies that the membranes show preference to one counter-ion over the other, resulting in selective ion exchange and different permeation rates of electrolytes having the same co-ion but different counter-ions. The observed order of the permeation rates was: $\mathrm{KCl} < \mathrm{NaCl} \ll \mathrm{LiCl}$ for the 1:1 electrolytes and $AlCl_3 < CaCl_2 < MgCl_2$ for the others. Also the fluxes were generally found to be higher in the thinner PE-1 membrane.

Polyethylene membranes are known to carry a negative charge due to specific sorption of ions [6], which implies that Cl^- ions are excluded from the membrane phase while the counter ions are attracted. The next two steps are the entry of the cations into the membrane phase, swollen by sorbed water from the pre-treatment process and diffusion of these ions to the other side through the membrane. The numerical values of the membrane charge density were not determined experimentally in the present study. However

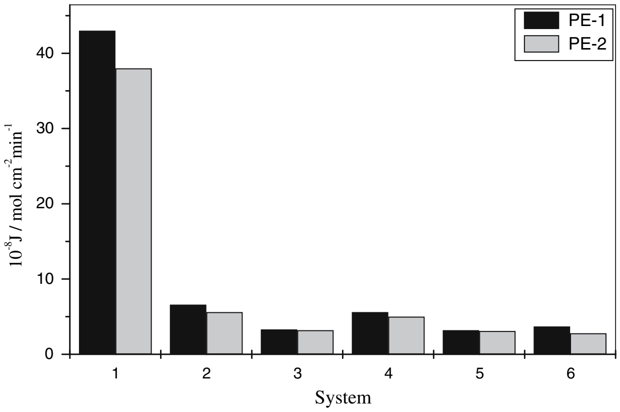

Fig. 3 Permeation fluxes of various electrolytes through membranes PE-1 and PE-2 at 28°C. (1 = LiCl; 2 = NaCl; 3 = KCl; 4 = $MgCl_2$; 5 = $CaCl_2$; 6 = $AlCl_3$)

De Korosy [5] observed that the crystalline structure of polyethylene is such that the active sites are concentrated on the surface of the crystallites and on the intercrystalline material between the platelets. Thus, the charge distribution is such that charge sites are closer together and exert an appreciable net effect, which plays a vital role in the ion transport properties of PE membranes.

As stated previously, separation of ionic species is correlated to hydrated ion sizes which produce hydration rejection patterns, or coulombic interactions which produce charge rejection patterns. The former effect governs separation by porous polymer membranes, where ionic permeability often decreases linearly as the hydrated ionic radii increase [2, 10, 16]. This can be considered in terms of the inverse dependence between mobility and ionic radius in aqueous solutions since the environment in the pore solution is similar to that in the external liquid phase and the pore sizes are much larger than the ionic sizes and as such will not significantly influence the permeation process. In such cases, water-ion interactions determine the membrane permeability and the normal selectivity sequence $K^+ > Na^+ > Li^+$ for alkali cations or $Ba^{2+} > Ca^{2+} > Mg^{2+}$ for alkaline earth cations should be the outcome. Our results with the studied PE films show that the permeation rates of the monovalent cations increased in the order $K < Na \ll Li$ and that of the multivalent ions $Al^{3+} < Ca^{2+} < Mg^{2+}$. This trend is the opposite of the normal trend of ionic mobility in aqueous solution, indicating that the normal selectivity sequence was reversed in the membrane phase. The observed sequence is evidence that membrane-ion interactions determine the permeability, as opposed to water-ion interactions. The high permeability of the membranes to the lithium ion means that the naked (unhydrated) ions are the predominant permeating species in the membrane phase and the permeation speed, hence selectivity, is regulated by the crystal radii of the cations. All these are indications that pore transport did not play a significant role in the permeation process. According to Mafe et al. [16], ion transport in dense membranes is governed by coulombic interactions which produce charge rejection patterns as observed in this study. A number of reasons have been suggested to account for such phenomena. Varela et al. [23] noted that the smaller cations like Li^+ may not move with their entire hydration sphere and can thus move faster than the bigger ones through the polymer matrix. This may also be considered in line with Mullin concept that the hydration of the membrane material may provide a favourable water environment for particular ions so that they step into the pores away from the water molecules with which they were already associated before entering the membrane phase [2]. The permeability of smaller ions is thus favoured once they have left their rigid hydration shell. However, in order to obtain a quantitative relation between the ease of penetration and the ion size, it is necessary to know the electrostatic force which acts between the ions and the material of the membrane. The conductivity in the membrane surface is due to the mobile counter-ions around the membrane fixed charges, hopping between neighbouring charge sites. The less hydrated ions interact more strongly with the membrane charge and their transport is impeded compared to the more hydrated ones, whose interaction with the membrane charge would be considerably weaker due to the larger effective hydrated radius, giving rise to higher surface mobility. This, as well as the ease of penetration of the smaller unhydrated ions through the membrane matrix, accounts for the high permeation flux of Li^+ ions.

A plot of permeability coefficient P_s versus the crystallographic radii of the cations is given in Fig. 4 for both PE-1 and PE-2, while Fig. 5 illustrates the variation of permeability coefficient with ionic charge. For the series of isoelectronic ions Na^+, Mg^{2+}, Al^{3+}, the multivalent ions are seen to permeate at a slower rate despite their smaller size. This is because multivalent counter ions have greater interaction with the membrane charge. Such interactions usually give rise to two different electrochemical phenomena due to multivalent ion adsorption. One is the reduction in the effective surface charge density and conductivity of the membrane, while the other is the change in membrane permselectivity. The former effect is usually observed with membranes where the charge sites are relatively far apart, such that a highly charged counter ion will not find sufficient neighbours and will bind to one or two charged sites, still retaining some of its free charge. This results in surface charge reversal and the membrane changes the sign of its permselectivity. Consequently, the ions that were formerly co-ions will now begin to invade

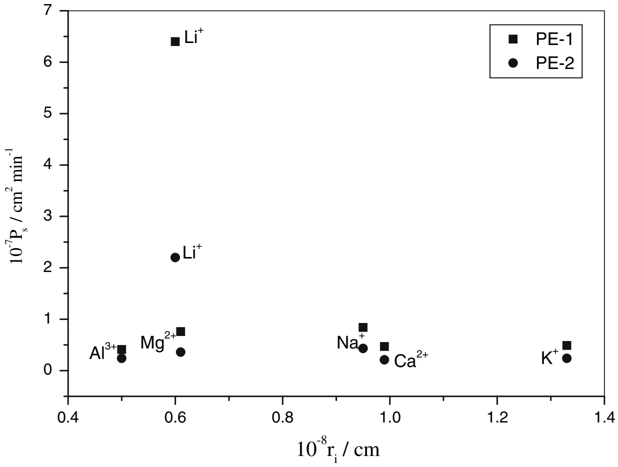

Fig. 4 Variation of permeability coefficient with crystallographic radii

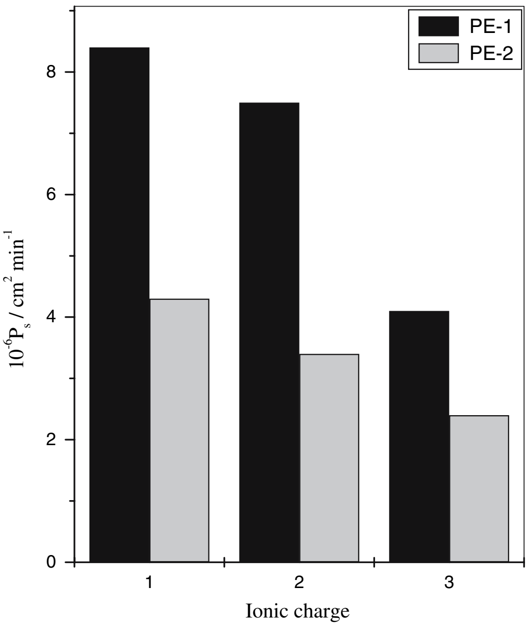

Fig. 5 Variation of permeability coefficient with ionic charge (1 = Na^+; 2 = Mg^{2+}; 3 = Al^{3+})

the membrane to neutralize the free charges of the now fixed primary counter ions. On the other hand, for membranes where the charged sites are closer together, a highly charged counter-ion can be bound to several sites simultaneously and although the resulting increase in membrane resistance reduces conductivity, membrane selectivity is less affected. This represents the scenario in this study and further corroborates the proposed charge distribution of the PE membranes.

Table 1 shows the breakthrough time t_b, which characterizes ionic arrival on the permeate side of the membrane (solution C_2). According to Onuchukwu et al. [19], t_b is related to the permeability coefficient P_s by the equation:

$$t_b = \frac{0.758l^2}{\pi^2 P_s} \tag{2}$$

Table 1 Breakthrough time for various ions through membranes PE-1 and PE-2

Ion	t_b/s	
	PE-1	PE-2
Li^+	0.1	0.2
Na^+	0.5	1.2
K^+	1.0	2.1
Mg^{2+}	0.5	1.4
Ca^{2+}	1.0	2.2
Al^{3+}	0.8	2.5

where π is a constant and l and P_s retain their previous meanings. The results imply a strong dependence of t_b on membrane thickness, l, as well as ionic radius, exhibiting a similar trend as observed for the permeate flux.

3.2 Mathematical modelling of ion transport

Development of mathematical models constitutes an important step towards understanding the behaviour and predicting the performance of membrane systems. Both statistical and continuum methods have been used to model mass transport of ionic species [17, 20]. Although some of the models are, in principle, rigorous enough to describe transport with sufficient accuracy, they are not feasible to rapid evaluation in practice due to their complexity, but demand lengthy computations. We propose a method based on the use of a mathematical model of the diffusion process, which makes it possible to predict permeation rates on the basis of information obtained under specified hydrodynamic conditions. The present report describes a mathematical model of the diffusion process based upon a linear idealization of Fick's law [9] so that behaviour that cannot be sufficiently modelled using Fick's law will be apparent. For simplicity the model approach introduces a number of assumptions: the electrolyte is completely dissociated, the effects of ion–ion and ion–dipole interactions and the electroosmotic permeability are not taking into consideration.

The following solution to the differential equation of Fick's first law which has also been previously used to describe membrane–solute equilibration and subsequent membrane permeation under a concentration gradient [21] was slightly modified and adapted for this study by the equation:

$$C_2 = C_1\left[1 - \exp\left(\frac{-P_s A t}{V l}\right)\right] \tag{3}$$

where C_2 again represents the lower concentration of diffusing species (permeate side, mol dm^{-3}) and C_1 the higher concentration (feed side, mol dm^{-3}); P_s is the effective species permeability coefficient for the membrane material (cm^2 min^{-1}); A is the exposed membrane surface area (cm^2); l is the membrane thickness (cm) and t is time (min). This equation was found to be generally inappropriate for modelling the experimental data in our study.

Usually for ideal Fickian diffusion, P_s depends only on temperature; however, when there are specific interactions between the polymer and the penetrant and the polymeric matrix is swollen by the penetrant, P_s also depends on the local penetrant concentration, as well as temporary fluctuations in both the concentration of the feed solution and the stirring rate. Under such conditions the expression representing Fick's equation with a constant permeability coefficient does not fit the experimental permeation rates well and one is faced with a mathematical problem. An approximate numerical solution for C_2, the concentration of diffused ions, was suggested as follows [7]:

$$C_2^{i+1} = C_2^i + \Delta C_2^i \tag{4}$$

where the change in concentration of diffused species over the time interval ΔC_2^i is approximated from the governing differential equation by;

$$\Delta C_2^i = \frac{P_s A \Delta t^i}{Vl}(C_2^i - C_1^i) \tag{5}$$

Δt_1^i is the magnitude of the time-step. Superscripts *i* and *i* + 1 refer to parameter values at specific time-step intervals. Equation 6 was found to be a fairly appropriate model for describing ionic diffusion through the studied LDPE membranes. Table 2 compares the observed and calculated permeation fluxes through PE-1 and PE-2. The fluxes derived from the conductometrically determined changes in the concentration of the test solution C_2 are referred to as the observed permeation fluxes (Obsd.), whereas the values calculated from model equation are designated as calculated (Calc). The corresponding plot for NaCl through PE-2 is shown in Fig. 6. Similar plots for $MgCl_2$ through PE-1 and $CaCl_2$ through PE-2 are given in Figs. 7 and 8 respectively. The values agree reasonably well, demonstrating the usefulness of this model. The deviations observed can be attributed to experimental errors.

Table 2 Observed and calculated permeation fluxes

Electrolyte	J/mol cm^{-2} min^{-1}			
	PE-1		PE-2	
	Obsd.	Calc	Obsd.	Calc
LiCl	42.5	37.5	37.7	31.5
NaCl	5.63	5.58	6.60	6.42
KCl	3.25	3.23	3.28	3.53
$MgCl_2$	5.04	5.24	5.61	5.70
$CaCl_2$	3.12	3.07	3.16	3.19

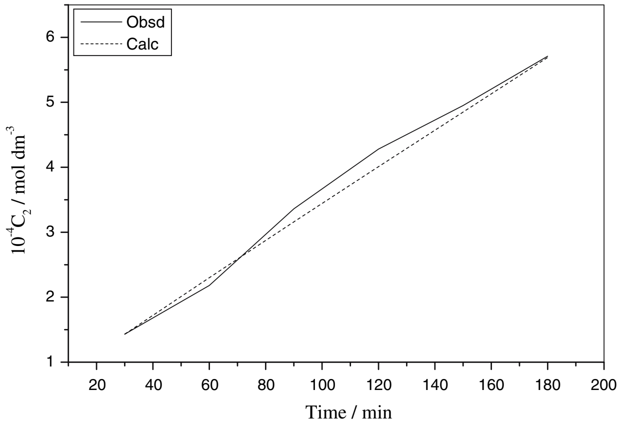

Fig. 6 Observed and calculated permeation rates for Na^+ through PE-1

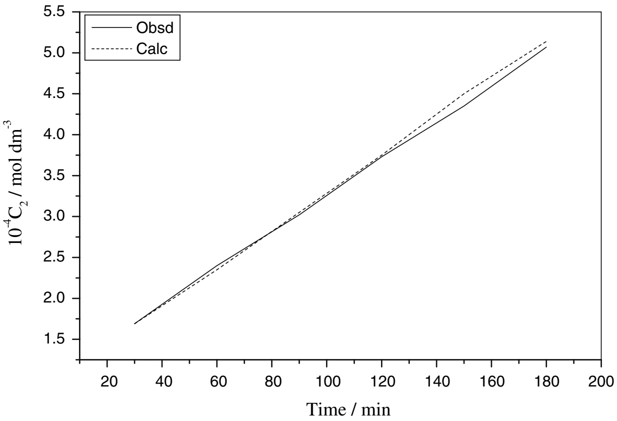

Fig. 7 Observed and calculated permeation rates for Mg^{2+} through PE-1

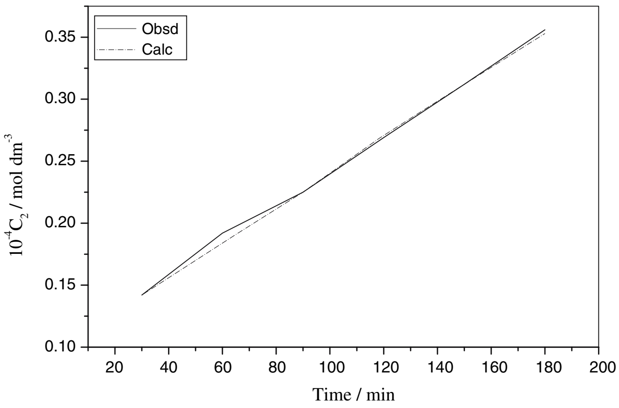

Fig. 8 Observed and calculated permeation rates for Ca^{2+} through PE-2

4 Conclusions

The studied PE films have negative surface charge due to adsorption of ions and exhibit selective cation permeability in the order: K < Na ≪ Li for the monovalent cations and $Al^{3+} < Ca^{2+} < Mg^{2+}$ for the multivalent cations. Membrane selectivity was dependent on the crystallographic radii of the permeating ions. The permeation process was adequately described by a mathematical model based upon a linear idealization of Fick's first law.

References

1. Baker RW (2004) Membrane technology and applications. Wiley, New York

2. Beg NM, Siddiqi FA, Shyam R, Altaf I (1979) J Electroanal Chem 98:231
3. Bratin P, Tomckeweiz M (1982) J Electrochem Soc 129:2469
4. Bruschke H (1995) Pure Appl Chem 6:67
5. De Korosy FD (1982) Biochem Bioenerg 9:391
6. Ding N, Wang XL, Wang J (2006) Desalination 192:18
7. Divine CE, McCray JE (2004) Environ Sci Tech 38:1849
8. Djong-Gie O (1985) J Appl Electrochem 15:231
9. Fialova K, Petrychkovych R, Sharma M, Uchytil P (2006) J Memb Sci 275:166
10. Inone H (2004) J Memb Sci 228:209
11. Izak P, Bartovska L, Friess K, Sipek M, Uchytil P (2003) J Memb Sci 214:293
12. Kontturi K, Murtomaki L (1996) J Control Release 41:177
13. Koryta J (1982) Ions, electrodes and membranes. Wiley, New York
14. Koter S, Kujawski W (2002) Pol J Chem 76:1637
15. Leaist DL (1989) Electrochim Acta 34:371
16. Mafe S, Jose MA, Ramirez P (2002) Phys Chem Chem Phys 5:376
17. McLaughin BD (1984) J Electroanal Chem 172:1
18. Oguzie EE (2005) Investigation and modelling of ionic diffusion through synthetic membrane. Ph.D. Thesis, University of Calabar, Nigeria
19. Onuchukwu AI, Trasatti SP, Trasatti S (1984) Corros Sci 36:1815
20. Orazem ME, Newman J (1984) J Electrochem Soc 131: 2569
21. Stanford WE, Shropshire RG, Solomon DK (1996) Water Resour Res 32:1635
22. Tischenko GA, Dybal J, Stejskal J, Kudela V, Bleha M, Rosova EY, Elyashevich GK (2002) J Memb Sci 196:279
23. Varela H, Bruno RL, Torresi RM (2003) Polymer 44:5369
24. Yeager HL, O'Dell B, Twardowski Z (1982) J Electrochem Soc 129:85