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Transport of ions across peritoneal membrane

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Abstract

The electrical conductance of ions across the peritoneal membrane of young buffalo (approximately 18–24 months old) has been recorded. Aqueous solutions of NaF, $NaNO_3$, NaCl, Na_2SO_4, KF, KNO_3, KCl, K_2SO_4, $MgCl_2$, $CaCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_3$, $CoCl_2$, and $CuCl_2$ were used. The conductance values have been found to increase with increase in concentration as well as with temperature (15 to 35 °C) in these cases. The slope of plots of specific conductance, κ, versus concentration exhibits a decrease in its values at relatively higher concentrations compared to those in extremely dilute solutions. Also, such slopes keep on increasing with increase in temperature. In addition, the conductance also attains a maximum limiting value at higher concentrations in the said cases. This may be attributed to a progressive accumulation of ionic species within the membrane. The κ values of electrolytes follow the sequence for the anions: $SO_4^{2-}>Cl^->NO_3^->F^-$ while that for the cations: $K^+>Na^+>Ca^{2+}>Mn^{2+}>Co^{2+}>Cu^{2+}>Mg^{2+}>Cr^{3+}>Fe^{3+}$. In addition, the diffusion of ions depends upon the charge on the membrane and its porosity. The membrane porosity in relation to the size of the hydrated species diffusing through the membrane appears to determine the above sequence. As the diffusional paths in the membrane become more difficult in aqueous solutions, the mobility of large hydrated ions gets impeded by the membrane framework and the interaction with the fixed charge groups on the membrane matrix. Consequently, the membrane pores reduce the conductance of small ions, which are much hydrated. An increase in conductance with increase in temperature may be due to the state of hydration, which implies that the energy of activation for the ionic transport across the membrane follows the sequence of crystallographic radii of ions accordingly. The Eyring's equation, $\kappa=(RT/Nh)\exp[-\Delta H^*/RT]\exp[\Delta S^*/R]$, has been found suitable for explaining the temperature dependence of conductance in the said cases. This is apparent from the linear plots of $\log[\kappa Nh/RT]$ versus $1/T$. The results indicate that the permeation of ions through the membrane giving negative values of ΔS^* suggest that there may be formation of either covalent linkage between the penetrating ions and the membrane material or else the permeation may not be the rate-determining step. On the one hand, a high ΔS^* value associated with the high value of energy of activation, E_a, for diffusion may suggest the existence of either a large zone of activation or loosening of more chain segments of the membrane. On the other hand, low value of ΔS^* implies that converse is true in such cases, i.e., either a small zone of activation or no loosening of the membrane structure upon permeation.

Keywords: Transport of ion; Thermodynamic parameter; Entropy of activation; Free energy of activation; Activation energy; Peritoneal membrane

1. Introduction

Tremendous amount of work has been done in the measurement of electromotive force of ion transport across artificial as well as biomembranes. Few membranes are prepared by extracting the constituents of biomembranes, e.g., monolayer and bilayer lipid membranes (BLM), which have been employed in such studies in recent years [1–6]. Similarly, some of the complex membranes have also been reported earlier [7–13]. The permeation of ions across the membranes, having the rate limiting 'gate mechanism,' at their surfaces, is known [14–17] to depend upon the (i) size of the pores lined by charges, (ii) on water/fluid soluble carrier molecules as well as (iii) on the homogeneous dielectric medium. The permeation of ions across a natural or artificial membrane seems to follow similar mechanisms.

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In addition, the membrane structure and the boundary conditions at the membrane/electrolyte interface determine the selective nature of ion diffusion/permeation.

In case the permeant molecules are hydrophilic groups in the membrane, the permeability is facilitated [18,19] through the formation of hydrogen bonds with water. In such cases the 'hole' type and the 'alignment' type diffusion mechanisms have been reported [20] for the permeation of ions. These mechanisms find support from the electrical resistance data of several membranes [21]. Attempts have also been made [22–24] to explain the process of permeation of ions in terms of binding energetics of ion–protein and ion–water interactions. It has been proposed [25,26] that a penetrating ion forms an activated complex, which is composed of channel sites, a cation and an anion. The anionic channel site attracts and retains a cation as short lived associated ion-pairs, which may either decay by dissociation of anion or of anion–cation pairs. As reported recently [27] the prokaryotes regulate the fluidity of their membranes by varying the number of double bonds and the length of their fatty acyl chains.

Attempts have been made to understand the process of diffusion in terms of collision-, jump-, carrier-, and solvent drag mechanisms. In pursuance of such an attempt, two classes of allosteric proteins, channels, and pumps have been identified in conferring biomembrane permeability. Channels enable ions to flow rapidly through the membranes in a thermodynamically downhill direction. Pumps, by contrast, use a source of free energy such as ATP or light to drive the uphill transport of ions and molecules. Channels may be either voltage-gated or ligand-gated. The best examples are acetylcholine for ligand-gated channels while sodium and potassium channels for those of the voltage-gated. Out of these two, the voltage-gated channels play a pivotal role in the transport of ions through membranes. The gating charges [28], the opening of sodium channels [29], the sensitivity to voltage [30–32], and the potassium channels' voltage sensors [33–35] have recently been reported. The breakthrough in the biochemical study of potassium channel came through the genetic studies of mutant fruit flies that shake violently when subjected to anaesthesia with ether [35]. The permeability of potassium channels for K^+ is 100-fold in comparison to Na^+. The potassium channel avoids closely embracing the Na^+ ions, giving Na^+ no choice but to stay hydrated and be impermeable [35–37].

The transport of ions across a membrane may be active or passive. It is noteworthy that active transport requires a coupled input of free energy: The channels control the diffusion of ions on either side of a membrane. The transport of ions through the membrane channels (i.e., K^+ or Na^+ channels) falls under the group of passive transport devices. However, such a passive transport device cannot transport a large gradient of Na^+/K^+ ions generated and the fuel molecules concentrated in the cell [38]. These processes are carried out by the active transport systems. It is to be pointed out that whether a transport process is active or passive depends upon the change in free energy of the transported species.

It may further be noted that ATP hydrolysis drives the pumping of Na^+ and K^+ ions across the membrane. It is an established fact that most animal cells have a high concentration of K^+ and a low one of Na^+ ions relative to the external medium. These ionic gradients are generated by a specific transport system that is called Na^+- K^+ pump, because the movement of these ions are linked. The Na^+-K^+ gradient in animal cells controls cell volume, renders nerve and muscle cells electrically excitable, and controls the active transport of sugars and amino acids. In 1957, Jens Skou discovered an enzyme that hydrolyses ATP only if Na^+ and K^+ are present in addition to Mg^{+2}. He named this enzyme as Na^+-K^+-ATPase [38,39]. One of the most important features of the pump is that ATP is not hydrolysed unless Na^+ and K^+ ions are transported. In other words, the system is coupled so that ATP is not wasted [38–43]. In addition, a symporter carries the transported species in the same direction across a membrane, whereas an antiporter carries them in opposite directions [44–49]. The L-type Ca^{+2} channels in heart have been extensively studied [50–54].

Thus, the selective nature of biomembranes in respect of permeability of ions, as well as of the mechanism of diffusion of varied nature involving "gates," "channels,' etc. as stated above, enthused curiosity to look into some of aspects of diffusion across the peritoneal membrane. In addition, there is a twofold equally important reason for selecting this membrane for the present investigation. First of all, it is easily available, and secondly, it has found its application/utility in the peritoneal dialysis in treating the patients of uremia.[1]

2. Materials and methods

The salts, NaF, $NaNO_3$, NaCl, Na_2SO_4, KF, KNO_3, KCl, K_2SO_4, $MgCl_2$, $FeCl_3$, $CrCl_3$, $CuCl_2$, $CoCl_2$, $MnCl_2$,

[1] The ethacryline acid and furosemide have been found to affect the Na^+-transfer across the human peritoneal membrane. It has been observed that the mesothelial cells of the parietal peritoneum react with the pharmacological agents with altered transport properties. In addition, the cause and the control on regulating the sodium and potassium losses during the peritoneal dialysis; the transfer of chromium dialyzate to the blood during the peritoneal dialysis; the water transport across the peritoneal membrane necessitated in different clinical problems; the role of ascites and phospholipase A_2 in understanding the changes in peritoneal permeability in acute experimental pancreatitis, etc. are some of the aspects highlighting the importance of such studies involving the peritoneal membrane. Similarly, the limit of concentration for diffusion/uptake of ions through the membrane may determine the physiologic function of the membrane in the permissible range of variations in ionic concentration up to the tolerance level of these biomembranes vis-à-vis the toxicity level of these ions.

Table 1
Values of specific conductance (mS cm^{-1}) of aqueous solution of NaF, $NaNO_3$, NaCl, Na_2SO_4, KF, KNO_3, KCl, K_2SO_4, $MgCl_2$, $FeCl_3$, $CrCl_3$, $CuCl_2$, $CoCl_2$, $MnCl_2$, and $CaCl_2$ across peritoneal membrane as functions of concentration (mol/l) and temperature (°C)

Temperature (°C)	Electrolyte (mol/l)							
	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2
NaF								
15	0.085	0.095	0.195	0.492	0.734	1.87	3.60	5.10
20	0.086	0.10	0.225	0.574	0.772	2.99	4.50	6.13
25	0.088	0.11	0.249	0.622	0.933	3.73	5.40	7.16
30	0.089	0.12	0.285	0.772	1.24	4.48	6.40	8.04
35	0.090	0.13	0.345	0.921	2.34	4.98	7.23	8.83
$NaNO_3$								
15	0.088	0.109	0.299	0.640	0.986	2.49	4.40	6.03
20	0.090	0.115	0.325	0.723	1.04	3.73	5.49	6.93
25	0.091	0.136	0.373	0.862	1.32	4.48	6.56	8.24
30	0.094	0.184	0.448	0.996	2.60	4.86	7.52	8.43
35	0.095	0.226	0.498	1.72	3.49	5.98	8.52	10.02
NaCl								
15	0.128	0.179	0.373	0.747	1.49	4.48	6.89	9.21
20	1.32	0.197	0.407	0.815	1.72	4.87	7.72	9.84
25	0.155	0.246	0.467	0.996	2.95	6.30	9.53	10.80
30	0.160	0.279	0.528	1.42	3.49	7.29	10.20	11.20
35	0.172	0.295	0.621	2.28	4.73	8.32	10.70	12.20
Na_2SO_4								
15	0.179	0.249	0.597	1.04	2.79	4.98	8.44	10.40
20	0.204	0.299	0.659	1.51	3.54	6.27	9.96	10.70
25	0.224	0.345	0.723	2.54	4.49	6.96	10.30	11.30
30	0.249	0.408	0.786	3.79	5.39	7.75	11.00	12.10
35	0.269	0.498	0.896	4.94	6.48	8.80	11.80	13.00
KF								
15	0.095	0.132	0.320	0.597	0.933	1.95	4.98	6.19
20	0.096	0.140	0.345	0.689	1.07	3.20	5.60	6.72
25	0.097	0.149	0.373	0.772	1.32	3.73	6.40	7.50
30	0.098	0.165	0.448	0.869	1.79	4.48	7.47	8.64
35	0.103	0.189	0.472	0.996	2.62	5.38	8.53	9.40
KNO_3								
15	0.102	0.140	0.373	0.747	0.932	2.99	7.47	9.12
20	0.104	0.154	0.448	0.845	1.28	4.48	8.28	9.79
25	0.109	0.166	0.482	0.933	1.60	4.77	8.90	10.10
30	0.115	0.179	0.527	1.07	1.95	5.43	9.28	10.50
35	0.121	0.205	0.560	1.28	2.99	5.60	10.00	11.10
KCl								
15	0.128	0.179	0.498	0.896	1.54	4.98	8.30	10.10
20	0.143	0.195	0.527	0.996	1.66	5.33	9.26	11.10
25	0.145	0.213	0.560	1.09	2.45	5.60	9.86	11.40
30	0.154	0.234	0.640	1.32	2.99	6.40	10.50	11.70
35	0.166	0.264	0.700	1.79	3.80	7.43	11.10	12.20
K_2SO_4								
15	0.140	0.264	0.540	1.12	2.19	5.60	9.96	12.00
20	0.149	0.295	0.600	1.28	2.74	6.14	11.10	12.60
25	0.154	0.333	0.660	1.79	3.50	6.60	11.60	13.10
30	0.179	0.373	0.726	2.46	4.48	7.39	12.40	13.80
35	0.213	0.448	0.814	3.83	5.42	8.46	13.40	14.60
$MgCl_2$								
15	0.132	0.204	0.448	0.896	1.49	4.50	7.32	8.43
20	0.140	0.224	0.492	0.974	1.68	4.92	7.96	9.01

Table 1 (*continued*)

Temperature (°C)	Electrolyte (mol/l)							
	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2
$MgCl_2$								
25	0.149	0.264	0.515	1.09	2.04	5.25	8.46	9.43
30	0.154	0.272	0.546	1.38	2.49	6.00	9.20	10.00
35	0.166	0.302	0.605	1.57	3.20	6.65	10.10	11.60
$FeCl_3$								
15	0.160	0.249	0.521	0.996	1.79	4.98	7.93	9.04
20	0.172	0.279	0.560	1.19	2.23	5.37	8.30	9.42
25	0.179	0.315	0.622	1.61	2.69	5.77	9.00	10.01
30	0.204	0.358	0.669	2.19	3.23	6.40	9.79	10.80
35	0.224	0.401	0.747	3.00	4.67	6.79	10.07	11.10
$CrCl_3$								
15	0.179	0.299	0.589	1.12	2.24	5.46	8.34	9.73
20	0.187	0.345	0.640	1.38	2.99	5.89	8.90	10.20
25	0.213	0.400	0.679	1.60	3.82	6.69	9.49	10.70
30	0.224	0.438	0.728	2.39	4.88	7.40	10.30	11.60
35	0.242	0.553	0.802	3.20	5.37	8.21	10.90	12.00
$CuCl_2$								
15	0.187	0.320	0.614	1.21	3.20	6.22	9.00	10.20
20	0.204	0.353	0.659	1.56	3.78	7.00	9.90	11.00
25	0.224	0.372	0.700	2.19	4.40	7.89	10.60	11.70
30	0.230	0.410	0.747	2.84	5.00	8.39	11.50	12.30
35	0.240	0.440	0.800	3.60	6.04	9.47	12.00	13.20
$CoCl_2$								
15	0.249	0.373	0.727	2.04	4.67	7.23	9.82	10.90
20	0.253	0.412	0.768	2.62	5.29	7.86	10.60	11.70
25	0.262	0.458	0.836	3.60	5.97	8.96	11.20	12.30
30	0.283	0.513	0.912	4.32	6.64	9.53	11.70	12.30
35	0.300	0.549	1.54	5.02	7.19	10.30	12.50	13.40
$MnCl_2$								
15	0.280	0.418	0.853	3.94	5.42	8.30	10.30	11.20
20	0.300	0.451	0.854	4.49	6.10	8.76	10.80	11.70
25	0.313	0.470	0.904	5.02	6.53	9.60	11.50	12.30
30	0.324	0.522	0.950	5.68	7.22	10.30	12.20	13.00
35	0.342	0.564	1.02	6.49	8.10	11.10	13.00	14.10
$CaCl_2$								
15	0.373	0.516	0.922	4.96	7.00	9.86	11.80	12.60
20	0.382	0.549	1.04	5.90	7.80	10.60	12.40	13.20
25	0.402	0.602	1.32	6.48	8.21	11.10	12.80	13.50
30	0.413	0.630	1.84	7.02	8.90	11.90	13.50	14.20
35	0.434	0.683	2.21	8.01	9.81	12.80	14.40	15.30

and $CaCl_2$ of analytical grade reagents (BDH), were used after the usual purification for preparing their aqueous solutions in triply distilled water. The peritoneal membrane of buffalo removed immediately after the slaughter of relatively young (aged between 18–24 months) animal from the local abattoir was preserved in ice-cold Ringer's solution of about 7.4 pH in order to prevent the decay of membrane tissues. The Ringer's solution had the following composition in grams/litre: NaCl (8.0), KCl (0.20), $CaCl_2$ (0.20), $MgCl_2$ (0.10), $NaHCO_3$ (1.0), NaH_2PO_4 (0.05) and glucose (1.00).

The membrane piece of adequate/desired size was washed several times with double-distilled water to remove any traces of ions of Ringer's solution. It was then placed between the two halves of the cell compartment provided with platinum electrodes. After filling the two halves of the cell compartment with each of the electrolytic solutions of desired concentration, the conductances/resistances were recorded with the help of an LCR bridge (Elico, Hyderabad) using mono-, di-, and trivalent metal salts (NaF, $NaNO_3$, NaCl, Na_2SO_4, KF, KNO_3, KCl, K_2SO_4, $MgCl_2$, $CaCl_2$, $MnCl_2$, $CuCl_2$, $CoCl_2$, $CrCl_3$ and $FeCl_3$). The cell assembly

was immersed in a thermostated bath of ±0.01° thermal stability maintained at 25 °C.

3. Results and discussion

The specific conductance values (Table 1) of aqueous solutions of NaF, $NaNO_3$, NaCl, Na_2SO_4, KF, KNO_3, KCl, K_2SO_4, $MgCl_2$, $FeCl_3$, $CrCl_3$, $CuCl_2$, $CoCl_2$, $MnCl_2$ and $CaCl_2$ were recorded across the peritoneal membrane of young buffalo in order to examine the ionic diffusion across the biomembrane. The overall behaviour of specific conductance of these electrolytes as a function of concentration and temperature is displayed by taking one of the representative plots shown in Fig. 1 for the NaF solutions. The remaining 14 plots (not shown here) based on the data contained in the table have also exhibited a similar behaviour. The conductance values have been found to increase with increase in concentration as well as temperature (15°–35 °C) in all the cases. These results are in accord with those found for the pericardial membrane in respect of their conductance behaviour with varying electrolytic concentrations [55]. Such a similarity in the behaviour of these biomembranes is understandable as they regulate the diffusion of ionic/solvated-ionic entities as well as those of water molecules in the maintenance of ionic/fluid equilibria around the protected organs through these membranes.

An examination of these plots shows that their slope values ($d\kappa/dc$ in which κ and c stand for the specific conductance and concentration, respectively) decrease at relatively higher concentrations compared to those of extremely dilute solutions. Also, such slopes keep on increasing with increase in temperature as one may envisage. The best-fit plots[2] (Fig. 1) were obtained by considering all the data points. For more details, each of the plots at different temperatures was analysed by linearly fitting the maximum number of data points to regression equation and connecting the linear plot with the minimum number of ignored points with dotted line. For example, in the case of NaF at 15 °C, the best-fit plot was obtained by considering all the data points except the last one for 0.2 mol/l concentration (Table 1 for NaF), which was ignored from the simple linear fit or best-fit. The relevant parameters thus obtained were: A (intercept)=0.0529, B (slope)=35.64, R=0.999, S.D.=0.048, N (number of data points)=7, and P was less than 0.0001. In case, in addition to ignoring the specific conductance value at 0.2 M, the value at 0.01 M was deleted altogether, the intercept value was improved a little bit. That is, it decreased from 0.05 to 0.03, a value a little bit closer to zero (since the intercept should have been zero). Furthermore, when polynomial of order 2 was applied in best fitting all the data points except those for 0.01 and 0.2 M concentrations, the intercept value turned out to be 0.0215; again approaching somewhat closer to zero. However, if all (except that at 0.01M) the data points were considered in the best-fit using a polynomial of order 2, the intercept value was found to be −0.029. This plot also represented a rapid decrease in the conductance values with further increase in concentration (i.e., >0.2 mol/l). This is exactly what one may seem to envisage at much higher concentrations when pores seem to be either blocked or saturated for diffusion or, in other words, less pores of adequate size may be available for diffusion. Similarly, the data points at 20, 25, 30 and 35 °C were examined. A similar behaviour was noted in all the cases except that the last two data points of higher concentrations were ignored for obtaining the best-fit linear plots. Similarly, the plots of $NaNO_3$, NaCl, Na_2SO_4, KF, KNO_3, KCl, K_2SO_4, $MgCl_2$, $FeCl_3$, $CrCl_3$, $CuCl_2$, $CoCl_2$, $MnCl_2$ and $CaCl_2$ were examined in which the last two or three data points were ignored for obtaining the best-fit linear plots. In general, the ignored data points indicate the fast decreasing trend in the values of specific conductance at higher concentrations. An examination of Table 1 shows that the specific conductance not only increases with an increase in the electrolyte concentration but also attains a maximum limiting value at higher concentrations. Such a trend has been observed in all the above electrolytic solutions. This may be attributed to a

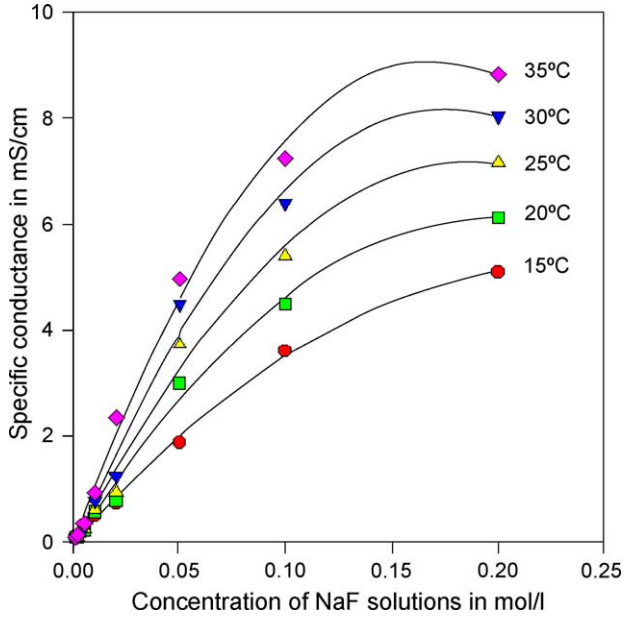

Fig. 1. Second-order best-fit of specific conductance vs. [NaF].

[2] Coefficients for the second-order best-fit plots of specific conductance versus [NaF] by taking all the data points at 15, 20, 25, 30, and 35 °C using Sigma plots are given below. Similar plots and their corresponding coefficients may also be given for the remaining 14 electrolytic solutions:

(°C)	b[0]	b[1]	b[2]
15	0	44.1864056694	−92.9321917815
20	0	58.7329148273	−123.5492574656
25	0	75.0248781429	−196.3879978024
30	0	91.6071872847	−257.481567679
35	0	107.8232146633	−319.9005043712

progressive accumulation of ionic species within the membrane. The tendency to attain a limiting value seems to be due to the fact that an electrically neutral pore, which is specific for a particular ion, is unlikely to contain more than one type of ion. Consequently, at high electrolyte concentration, the pore saturates and the conductance approaches a limiting value. Also, since the biomembranes possess protein, which acts as a carrier, the latter picks up ion on one side and then returns for more ions. In such a mode, the flow of ions through the membrane reaches a limiting value at higher concentrations as stated above, thereby decreasing the slope values since all the carriers in the membrane get themselves bound to the ions. The values of specific conductance of the above electrolytes follow the sequence for the anions: $SO_4^{2-}>Cl^->NO_3^->F^-$ whereas for the cations the sequence is: $K^+>Na^+>Ca^{2+}>Mn^{2+}>Co^{2+}>Cu^{2+}>Mg^{2+}>Cr^{3+}>Fe^{3+}$. In addition, the diffusion of ions depends upon the charge on the membrane and its porosity. The membrane porosity in relation to the size of the hydrated species diffusing through the membrane appears to determine the above sequence. Several probable structures of water molecules under the condition of a given temperature may play an important role in determining the size of the hydrated ions [56]. As the diffusional paths in the membrane become more difficult in aqueous solutions, the mobility of large hydrated ions gets impeded by the membrane framework and the interaction with the fixed charge groups on the membrane matrix. Consequently, the membrane pores reduce the conductance of small ions, which is much hydrated. This is in accord with the earlier reported significance of the factors like pore size, hydration, etc., in understanding the process of permeation through such biomembranes [14–17]. An increase in conductance with increase in temperature may be due to the state of hydration, which implies that the energy of activation [obtained from the linear plots[3] of log κ versus $1/T$ using Arrhenius equation (Fig. 2) for the ionic transport across the membrane follows the sequence of crystallographic radii of ions accordingly.

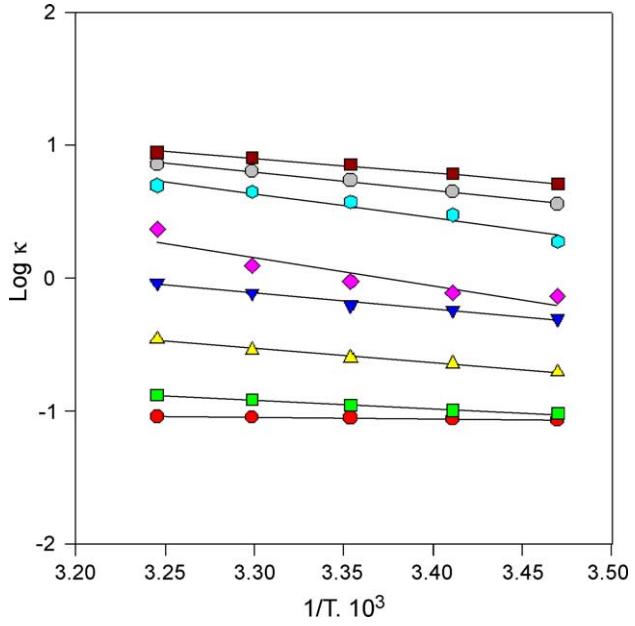

Fig. 2. First-order best-fit plots of log κ versus $1/T$ for [NaF].

Table 2
Entropy-, enthalpy-, energy-, and free-energy of activation for conductance of NaF (mol/l) solutions across peritoneal membrane

NaF (M)	ΔS^* (cal mol^{-1} deg^{-1})	ΔH^* (kcal mol^{-1})	E_a (kcal mol^{-1})	ΔG^* (kcal mol^{-1})
0.001	−29.39	1.42	2.01	10.18
0.002	−29.17	1.26	1.85	9.96
0.005	−28.35	1.20	1.79	9.65
0.010	−27.60	0.94	1.53	9.17
0.020	−26.92	0.73	1.32	8.76
0.050	−25.85	0.42	1.01	8.13
0.100	−25.53	0.35	0.94	7.96
0.200	−25.47	0.17	0.76	7.76

According to Eyring, the pores in the membranes may be considered as a sequence of energy barriers over which the ion has to jump in order to cross the barriers in the process of diffusion/transport of ions. The Eyring's equation, $\kappa=(RT/Nh)\exp[-\Delta H^*/RT]\exp[\Delta S^*/R]$,based on the theory of absolute reaction rates, has been used to explain the said process. κ, R, T, N, h, ΔH^* and ΔS^* stand as usual for the specific conductance, gas constant, temperature in Kelvin, Avogadro's number, Planck's constant, enthalpy of activation, and entropy of activation, respectively. This equation has been found to be suitable for explaining the temperature dependence of conductance in the said cases as apparent from the linear plots of $\log[\kappa Nh/RT]$ versus $1/T$ (not shown here). The $\Delta H^*/R$ and $\Delta S^*/R$ were obtained, respectively, from the slope and intercept values of these plots. The free energy of activation, ΔG^* , and the activation energy, E_a, were obtained by using their respective relations: $\Delta G^*=\Delta H^*-T\Delta S^*$ and $E_a=\Delta H^*+RT$. The relevant parameters for all the electrolytes are not given here for brevity; nevertheless, Table 2 displays their representative case. However, they are given in Table 3 in a condensed form as discussed below. These results indicate that the permeation of ions through the membrane giving negative values of ΔS^* suggests that there may be formation of either covalent linkage between the penetrating ions and the membrane

[3] Coefficients for the first-order best-fit plots of Log κ vs. $1/T$ for NaF solutions shown in Fig. 2 are given below.

$b[0]$	$b[1]$	r^2
−0.6725095899	−114.7481588649	0.9838627224
1.1352142883	−623.6095518263	0.9904055755
2.9651171617	−1060.4892830961	0.9851013215
3.8231991318	−1193.0881560691	0.9771920213
7.2089567865	−2137.0660685311	0.8533302219
6.68239962	−1832.2491815662	0.9342544413
5.2509648618	−1349.716312762	0.9928005501
4.3922246964	−1058.4283279	0.9867318732

Table 3
Averaged ΔS^* (cal mol^{-1} deg^{-1}) values for each concentration of each of the remaining electrolytes: $NaNO_3$, NaCl, Na_2SO_4, KF, KNO_3, KCl, K_2SO_4, $MgCl_2$, $FeCl_3$, $CrCl_3$, $CuCl_2$, $CoCl_2$, $MnCl_2$, and $CaCl_2$ and the range of variation in their values of ΔH^* (kcal mol^{-1}), E_a (kcal mol^{-1}), and ΔG^* (kcal mol^{-1})

mol/l	ΔS^*	ΔH^*	E_a	ΔG^*
0.001	−28.76	1.57–2.12	2.16–2.71	10.29–10.51
0.002	−28.25	1.47–1.80	2.06–2.39	10.09–10.06
0.005	−27.60	1.25–1.26	1.84–1.85	9.58–9.24
0.010	−26.62	0.96–1.22	1.55–1.81	9.10–8.84
0.020	−26.07	0.80–1.00	1.39–1.59	8.78–8.58
0.050	−25.55	0.50–0.95	1.09–1.54	8.19–8.46
0.100	−25.27	0.42–0.65	1.01–1.24	7.98–8.13
0.200	−25.13	0.25–0.60	0.84–1.19	7.80–8.05

material or else the permeation may not be the rate-determining step. On the one hand, a high ΔS^* value associated with the high value of E_a for diffusion may suggest the existence of either a large zone of activation or loosening of more chain segments of the membrane. On the other hand, low value of ΔS^* implies either a small zone of activation or no loosening of the membrane structure upon permeation. Based on these considerations, Schuler et al. [57] found negative values of ΔS^* for the diffusion of sugar through the colloidal membrane. They proposed that in the case of ions, the small values of ΔS^* may be interpreted as due to the interstitial permeation of the ionic species with the partial immobilisation in the membrane. It means the small zone of disorder; while Tien and Ting [58], who found negative values for the permeation of water through a very thin bilayer membrane, suggested that the solution–membrane interface and not the membrane itself may be the rate-determining intermediary for permeation. Consequently, the negative ΔS^* values may be considered as due to the partial immobilisation of ions and their interaction with the membrane fixed charge groups.

Thus, in general, the specific conductance of ions across the biomembrane varies almost linearly with concentration in the lower concentration range. However, sometimes due to the age factor some of the pores are fully or partially blocked either as a result of fat deposition or damage caused by some physiological malfunctioning of the system as observed from the nonlinear portion of such plots (Fig. 1). Similarly, a higher salt concentration apparently seems to be responsible for either damaging or partially blocking the normal available pores of the membrane, as a consequence of which less number of ions is allowed to diffuse across the biomembrane. This is apparent from the decreasing trend in the slope values of the said plots. Such a deduction is reinforced further in view of the values of the computed parameters. An examination of Table 2 shows that the values of ΔS^* increase while those of ΔH^*, E_a, and ΔG^* decrease with successive increases in electrolyte concentration from 0.001 to 0.2 mol/l. In addition, these values lie in the range −29.39 to −25.47 cal mol^{-1} deg^{-1}, 1.42 to 0.17 kcal/mol, 2.01 to 0.76 kcal/mol, and 10.18 to 7.76 kcal/mol, respectively, in the case of NaF. A similar trend in their behaviour has also been observed in other electrolytes too. Consequently, in view of such a similarity in their overall behaviour, the values of ΔS^* for conductance of the remaining 14 electrolytic [namely $NaNO_3$, NaCl, Na_2SO_4, KF, KNO_3, KCl, K_2SO_4, $MgCl_2$, $FeCl_3$, $CrCl_3$, $CuCl_2$, $CoCl_2$, $MnCl_2$, and $CaCl_2$ (mol/l)] solutions have been averaged for each of the eight concentrations. The averaged values thus obtained are found to be very close to those of the individual values as they differ from each other by only fractional values in most of the cases. In addition, the decreasing trend in the values of ΔH^*, E_a, and ΔG^* as well as in their range of variation with concentration has been found to be very close to those of the above corresponding values of NaF as observed from their condensed form given in Table 3. It is noteworthy that the measurements of resistance, capacitance and impedance of the said electrolytic solutions across this membrane [59] lend support to the deductions based on the conductance measurements.

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