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Studies on the Membrane Permeability of Silver and Cadmium Ferro- and Ferricyanides

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The permeability and membrane potential of various electrolytes, through parchment supported silver and cadmium ferro- and ferricyanide membranes was investigated. The order of permeability was found to be:

$$Cl^- > NO_3^- > SO_4^{-2} > FeCy_6^{-3} > FeCy_6^{-4}$$

while membrane potential was of the reverese order. The magnitude of permeability and potential values, decreases or increases respectively, with potassium ferro- or ferricyanide treated membranes. The relation $y=ax^{1/n}$ where x and y represents permeability and potential respectively, and a and n are constants, proposed earlier has been found to be valid for these membranes also. The energy of activation for the diffusion process for various electrolytes was found to lie between 4 to 10 kcal/mol. The potential values determined at varying concentrations of electrolytes, showed that the values increase with dilution. The electronegative character of the membranes, have got a profound influence on the movement of the anions. When the concentration of the electrolyte within the pores are higher, the repulsion of the fixed charges are reduced by screening, that is, at higher concentrations the selectivity of the membrane is decreased to an appreciable extent, resulting thereby in a marked decrease in membrane potential and increase in the permeability values.

The problem of the transport of charged or uncharged particles across different types of membranes is intrinsically a complex one. Various theories[1-7] have been put forward from time to time to explain the experimental results but none of them is good enough to give a clear understanding of the real mechanism involved. We during the course of our studies on the permeability of alkali metal salts on the metal ferrocyanide membranes,[8] could find a simple relationship between permeability, membrane potential and adsorption by considering the transport phenomenon across the artificially prepared, parchment supported membranes.

The present communication deals with the permeability data of various electrolytes for silver and cadmium ferro and ferricyanide membranes, the energy of activation of the diffusion process, membrane potential and ionic mobilities of the diffusing anions.

Experimental

All the four membranes, namely, silver ferro- and ferri- and cadmium ferro- and ferricyanides were prepared by the method of interaction recommended by Weiser.[9] The membranes were prepared by impregnating the parchment paper with the gel. The parchment paper was first soaked in distilled water for two hours and then tied carefully on the mouth of a beaker. The various solutions taken inside and outside the beaker, for different membranes and the time for deposition were as follows:

The four above mentioned membranes when viewed under the microscope showed a very uniform deposit throughout the surface. All the membranes were kept in doubly distilled water in dark.

Apparatus and Experimental Procedure. The diffusion experiments were carried out following the method of Austin, Hartung and Willis[10] based on the constant flow principle. This gave very accurate and reproducible data for diffusion rates. The sallent

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[1] R. Schlögl, *Discussions Faraday Soc.*, No. 21 (1956).

[2] Wiebenga, *Rec. Trav. Chim.*, **65**, 273 (1946).

[3] A. J. Staverman, *Trans. Faraday Soc.*, **48**, 176 (1952).

[4] T. Teorell, *Proc. Soc. Expt. Biol. Med.*, **33**, 282 (1935); *J. Gen. Physiol.*, **19**, 917 (1936); *Trans. Faraday Soc.*, **33**, 1053 (1937); *Z. Electrochem.*, **55**, 293 (1951).

[5] J. S. Mackie and P. Meares, *Proc. Roy. Soc.*, **A232**, 498 (1955).

[6] H. Davison and J. F. Danielli, The Permeability of Natural Membranes (Cambridge, 1943, Chapter 21 and Appendix A).

[7] B. J. Zwolinsky, H. Eyring and C. Reese, *J. Phys. Chem.*, **53**, 1426 (1949).

[8] W. U. Malik, A. Hasan and A. K. Bhattacharya, *J. Indian Chem. Soc.*, **32**, 501 (1955); W. U. Malik and S. A. Ali; *Kolloid-Z.* **175**, 139 (1961); W. U. Malik and F. A. Siddiqi, *J. Colloid Sci.*, **18**, 161 (1963); W. U. Malik and F. A. Siddiqi, *Proc. Ind. Acad. Sci.*, **56**, 206 (1962).

[9] H. B. Weiser, *J. Phys. Chem.*, **34**, 335, 1826 (1930).

[10] A. T. Austin, E. J. Hartung and G. M. Willis, *Trans. Faraday Soc.*, **40**, 520 (1944).

features of this apparatus being (i) considerable increased size of the membrane, (ii) decrease in the actual volume of the permeability cell, enabling equilibrium to be reached more quickly; (iii) stirring of the lower half of the cell; and lastly (iv) more rigid control of all the essential parts of the apparatus, of the rates of flow, and of the hydrostatic pressure on either side of the membrane.

The membrane was obtained in the form of a circular disc 50 mm in diameter. The membrane was washed several times with doubly distilled water to remove all the adsorbed ions before carrying out the diffusion experiments with a particular electrolyte. The hydrostatic pressure on each side of the membrane was kept equal by maintaining the flow of electrolyte and conductivity water across the membrane. The analysis of the effluent coming out of the lower half cell was made conductometrically by a W. T. W. type L. B. R. bridge. By knowing the rate of flow and concentration of the effluent coming out of the lower half cell, (from concentration conductance curves) the permeability in millimoles per hour was determined at 10, 15, 20, 25 and 30°C. The results in the form of plots between log p against $1/T$ (p and T being permeability and absolute temperature respectively) are given in Figs. 1, 2, 3 and 4.

Permeability of Various Electrolytes through Pre-treated Membranes. The effect of pre-treated membranes on the permeability of various electrolytes was studied by soaking the membranes in solutions of their respective constituent ions (0.2 M) for 24 hr.

The results are summarized in Tables 2A and 2B.

Membrane Potential. The method used for the determination of membrane potentials was that of Michaelis[11] for concentration potential; the potential difference of the concentration cell,

$$\mathrm{Hg}\mid \mathrm{Hg_2Cl_2}\mid \mathrm{sat.KCl}\parallel \underset{E_1}{\mathrm{Electrolyte}(C_1)}\mid \underset{E}{\mathrm{Membrane}}\mid$$

$$\mathrm{Electrolyte}\ (C_2)\parallel \underset{E_2}{\mathrm{sat.\ KCl}}\mid \mathrm{Hg_2Cl_2}\mid \mathrm{Hg}$$

measured on a low range Tinsley potentiometer (Type 3387). The same electrolyte was taken on both sides of the membrane and the concentration ratio C_1/C_2 was kept equal to 10 throughout. The dilute side always remained positive.

Freshly prepared membranes were employed for potential determinations. The membrane potential measurements were also carried out with pre-treated membranes as was done previously in permeability experiments. The variation in potential with time was determined. The experiments were repeated with fresh solutions of electrolyte and the maximum potential attained was recorded. The results in the form of plots between reciprocal of permeability and membrane potentials are given in Fig. 5. Figures 6A, 6B, 6C depict the relationship between membrane potential and concentration.

In order to have a better insight of the electrical nature of the membranes, the investigations were carried out by soaking the membrane first with 0.2 M solutions of potassium ferro- or ferricyanide (similar to permeability measurements) for 24 hr and the membrane potentials were then determined. The results are shown in Table 3.

TABLE 3.

Electrolyte	Membrane potential, V		
	Cadmium ferrocyanide	Cadmium ferricyanide	Silver ferrocyanide
KCl	0.198	0.033	—
KNO_3	0.028	0.036	0.027
CH_3COOK	0.033	0.040	0.030
K_2SO_4	0.035	0.043	0.034
K_3FeCy_6	—	0.047	0.037
K_4FeCy_6	0.043	—	0.041
NaCl	—	0.037	—
$NaNO_3$	0.028	0.042	0.024
CH_3COONa	0.038	0.045	0.034
Na_2SO_4	0.040	0.048	0.035

The above membranes were then soaked in 0.2 M $CdCl_2$ (in the case of Cadmium ferro- and ferricyanide) solution and 0.2 M $AgNO_3$ solution (in the case of silver ferrocyanide (membrane) for 24 hr. The maximum membrane potential (in volts) developed was measured for different electrolyte using 0.1 M and 0.01 M solutionsin each case. The results are given in Table 4.

TABLE 4.

Electrolyte	Membrane Potential, V		
	Cadmium ferrocyanide	Cadimium ferrocyanide	Silver ferrocyanide
KCl	0.019	0.033	—
KNO_3	0.027	0.036	0.026
CH_3COOK	0.032	0.039	0.029
K_2SO_4	0.033	0.042	0.032
K_3FeCy_6	—	0.047	0.036
K_4FeCy_6	0.041	—	0.040
NaCl	—	0.037	—
$NaNO_3$	0.026	0.041	0.022
CH_3COONa	0.038	0.044	0.033
Na_2SO_4	0.040	0.048	0.034

Mobility of Anions in Presence of the Membrane. The results of permeability and membrane potential revealed that the mobility of anions decreases due to the negative change of the membrane which is increased due to anionic adsorption. The electrochemical nature of the membrane and its influence on the mobility of anions was studied by finding out the mobility following the equation given by Willis[12] in the case of cupric ferrocyanide membranes.

$$E=\frac{\dfrac{U}{Zc}-\dfrac{V}{Za}}{U+V}\,\frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln\frac{f_1c_1}{f_2c_2}$$

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11) L. Michaelis, *Kolloid-Z*, **62**, 1 (1933); L. Michaelis and T. Fijita, *Biochem-Z.*, **142**, 398 (1923); *Z. Physik Chem.*, **110**, 266 (1924).

12) G. M. Willis, *Trans. Faraday Soc.*, **38**, 171 (1942).

where E is the membrane potential, c_1 and c_2 are the concentrations of the electrolyte solutions in g·equiv. per litre, f_1 and f_2 are corresponding activity coefficients, Z_c and Z_a are the valencies and U and V are the mobilities of cations and anions respectively. If U is taken as unchanged by the membrane then V may be calculated from the equation, and then would be called the apparent mobility.

The apparent mobilities of anions were calculated for cadmium ferrocyanide and ferricyanide and silver ferrocyanide membranes both for the treated and untreated ones, the concentration ratio C_1/C_2 was kept equal to 10 and the value of mobility U for K and Na was taken to be equal to 74.5 and 50.9 respectively. The results are shown in Figs. 7A, 7B, and 7C (plots between $\log 1/c$ and apparent mobility *i e.*, V)

Results and Discussion

Permeability. The two main factors, which may be considered to determine the permeability of ions through membranes are (i) charge on the membrane pores, due to either adsorption or ionization which act as barrier to the diffusing ions according to Meyer and Sievers[13] and Teorell[4]; (ii) sieve action whereby screening of ions according to their size takes place, larger ions diffusing out more slowly than the smaller ones and *vice versa* according to Collander,[13] Willis,[14] and Sollner.[14] The permeability data on uni-, bi-, tri- and tetra-valent potassium and sodium salts at different temperatures with the membranes under investigation go to show that the first factor plays a more dominant role in the diffusion process, than the second one.

Considering the permeability of different anions for the membranes under study, it is seen that the order of permeability is as follows:

$$\mathrm{Cl^- > NO_3^- CH_3COO^- > SO_4^{2-} > FeCy_6^{3-} > FeCy_6^{4-}}$$

The above sequence indicates that the free diffusion of ions is greatly restricted due to the interposition of the membrane and no where the order of free diffusion *viz.*,

$\mathrm{FeCy_6^{4-} > SO_4^{2-} > Cl^- > NO_3^-}$, is realised.

Assuming that the factors like area and thickness of the membrane are equally operative in all the cases, the only factor which is most likely to control the diffusion process is the physicochemical nature of the membrane material *vis-a-vis* the electrolyte employed. From the purely physical point of view, adsorption may be considered as an important factor controlling the permeability phenomenon. Adsorption studies carried out on these precipitates give the following order:

$$\mathrm{FeCy_6^{4-} > FeCy_6^{3-} > SO_4^{2-} > Cl^-}$$

This order is just the reverse of the permeability, exhibiting the interdependence of diffusion and adsorption processes. Furthermore the difference in permeability values of the untreated and pretreated membranes lend support to the role of

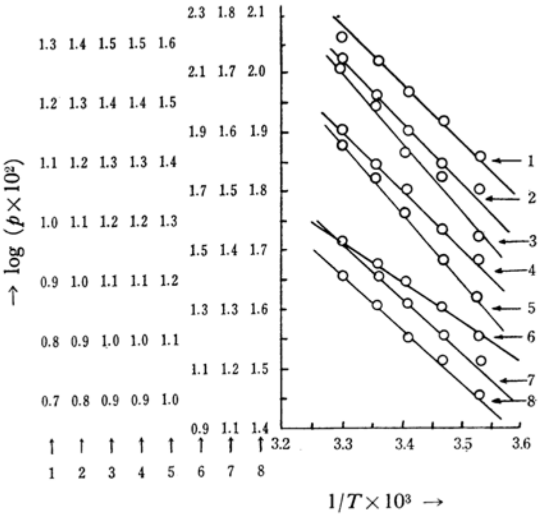

Fig. 1. The variation in permeability with temperature in the presence of different electrolytes with cadmium ferrocyanide membrane.

1, $\mathrm{K_4FeCy_6}$ 2, NaAc 3, KAc 4, $\mathrm{Na_2SO_4}$ 5, $\mathrm{K_2SO_4}$ 6, $\mathrm{KNO_3}$ 7, $\mathrm{NaNO_3}$ 8, KCl

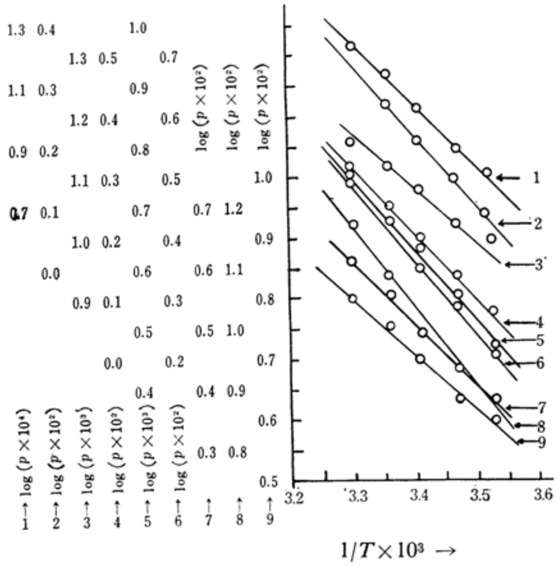

Fig. 2. The variation in permeability with temperature in the presence of different electrolytes with cadmium ferricyanide membrane.

1, $\mathrm{K_3FeCy_6}$ 2, NaAc 3, KAc 4, $\mathrm{Na_2SO_3}$ 5, $\mathrm{K_2SO_4}$ 6, $\mathrm{KNO_3}$ 7, $\mathrm{NaNO_3}$ 8, KCl 9, NaCl

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[13] K. H. Meyer and J. F. Sievers, *Helv. Chim. Acta*, **19**, 649 (1936); *Trans. Faraday Soc.*, **33**, 1073 (1937); **23**, 795 (1940).

[14] R. Collander, *Kolloid-Beih*, **19**, 72 (1924); *ibid.*, **20**, 273 (1925).

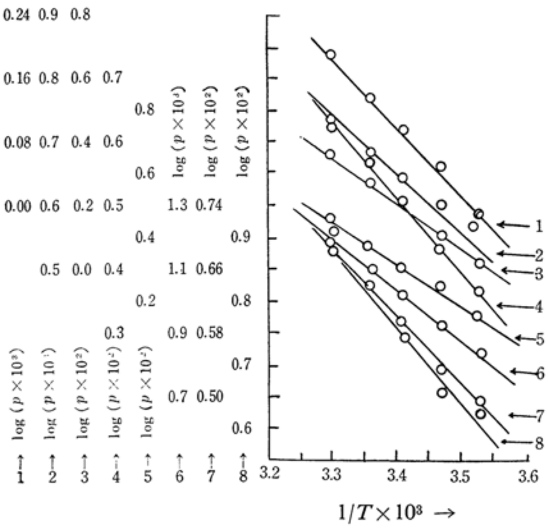

Fig. 3. The variation in permeability with temperature in the presence of different electrolytes with silver ferrocyanide membrane.

1, K_4FeCy_6 2, K_3FeCy_6 3, NaAc 4, KAc
5, Na_2SO_4 6, K_2SO_4 7, $NaNO_3$ 8, KNO_3

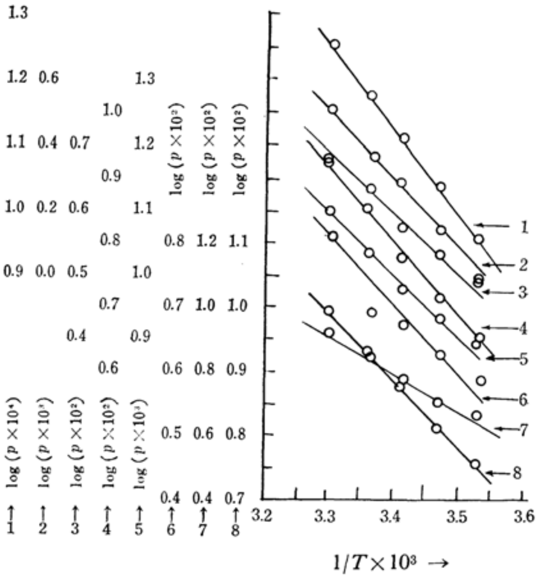

Fig. 4. The variation in permeability with temperature in the presence of different electrolytes with silver ferricyanide membrane.

1, K_4FeCy_6 2, K_3FeCy_6 3, NaAc 4, KAc
5, Na_2SO_4 6, K_2SO_4 7, $NaNO_3$ 8, KNO_3

adsorption. Thus with potassium ferrocyanide and ferricyanide treated membranes, the rate of diffusion is retarded to such a great extent that diffusion rate of SO_4^{2-} becomes nearly half to that of the original. Moreover, the permeability ratio of uni- and bi-valent ions, say NO_3^- by SO_4^{2-}, increases on passing from the untreated to the pre-treated membranes. To explain this behaviour, it may well be assumed that the stronger adsorption of ferrocyanide and ferricyanides by the membrane surface results in restricted movement of anions, and that the retardation would be more marked with the bivalent sulphate than the univalent nitrate.

The relative adsorbability of the different membranes for similar ions is also of some significance in understanding the permeability phenomenon. The adsorption studies show that the order is cadmium ferricyanide>silver ferrocyanide >silver ferricyanide>cadmium ferrocyanide. This observation namely, greater the adsorption capacity, lesser the permeation is self-explanatory, since membranes showing greater adsorption capacity would clogg the pores to a greater extent resulting in restricted movement of ions through them. Similar behaviour has been reported by other workers in this laboratory, while working with chromic, cobalt(II), manganese(II) ferrocyanide and ferricyanide membranes.(8)

The results for permeability show strong dependence upon the temperature. From the temperature coefficient as determined by plotting $\log p$ (p being permeability) against $1/T$ (T being the absolute temp.) the energy of activation of the diffusion process, *i. e.*, E was calculated from the slope which is equal to $E/2.303R$ (Figs. 1—4). The values of E_A in kcal per mole as determined from the graph for different membranes are shown in Table 5.

The value of the E_A *i. e.*, energy of activation for the free diffusion of KCl (0.2 M) reported in literature is 3.6 kcal/mol(10) and is smaller than that calculated above. In the case of K_2SO_4 the values found given in the table are also higher. These results (for KCl and K_2SO_4) confirm the values of Tolliday, Woods and Hartung(16) who got 5.1 kcal/mol for KCl and 5.9 kcal/mol for K_2SO_4. It can thus be concluded that the membrane barrier is electrical in nature, and, therefore the activation energy of the ions must exceed in the process of diffusion as compared to that of the free diffusion.

Membrane Potential The results described in the preceeding pages may be discussed in view of the theories put forward by Michaelis,(11) Meyer and Sievers(13) and also by Teorell.(4) Michaelis held the view that the selective permeability and potential of collodion membranes are due to preferential ion adsorption modifying differential diffusion rates. Willis(12) extended this theory to cupric ferrocyanide membrane and Sollner(15) showed the behaviour of collodion membranes to electrolyte is mainly due to surface charges fixed on the membrane matrix.

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15) K. Sollner, *J. Phys. Chem.*, **49**, 265 (1945); K. Sollner and H. P. Gregor, *J. Am. Chem. Soc.*, **67**, 346 (1945).

16) J. D. Tolliday, E. F. Woods and E. J. Hartung, *Trans. Faraday Soc.*, **45**, 148 (1949).

Meyer and Siever's quantitative theory (*loc. cit.*) of membrane behaviour postulates a number of fixed charges on the membrane pores due to either adsorption or ionization. They held the view that an equilibrium is set up between the mobile ions in the membrane phase and those in the bulk of the solution. Ionic selectivity of the membrane and the effect of concentration was very beautifully demonstrated in the case of cupric ferrocyanide membranes by Willis (*loc. cit.*).

The results on the membrane potential studies on silver ferrocyanide and cadmium ferrocyanide and ferricyanide show that the order is

$$FeCy_6^{4-} > FeCy_6^{3-} > SO_4^{2-} > NO_3^{-} > Cl^{-}$$

for the potassium salts (0.1 and 0.01 M). Similar type of order was found to hold good for sodium salts *i. e.* $SO_4^{2-} > NO_3^{-} > Cl^{-}$. Different concentration ranges (0.1 and 0.01 to 0.0025 M) were taken and it was found that in all the cases the order remains practically the same.

Another interesting feature of these studies is that the potential values increase with time, at first rapidly attaining a maximum value after a certain interval of time, and then falls off slowly for all the electrolytes used. Although this behaviour was found to hold good for all the cases; the time required for the attainment of maximum potential was different with different electrolytes. Moreover, it was highly dependent upon the concentration of the electrolyte used, the concentrated solution giving maximum potential value in a shorter time and *vice versa*. These results indicate that the ions are preferentially being adsorbed at the surface of the membrane making it progressively more electronegative in character. Once this saturation stage is reached, the membrane assumes charge stability and similar potential value could be realised for the entire diffusion process. The membrane having once acquire a charge stability in this manner, can be employed with different lots of solutions of a particular electrolyte without waiting for the potential to reach the maximum value.

Weiser[9] has explained the differential behaviour of cupric ferrocyanide membranes towards Cl^-, SO_4^{2-}, $FeCy_6^{3-}$ and $FeCy_6^{4-}$ ions on the basis of adsorption. The complete impermeability of $FeCy_6^{4-}$ was due to the complete irreversible adsorption whereby clogging of the pores of the membrane walls takes place.

Willis[12] and also Tolliday, Woods and Hartung[16] after extensively studying the behaviour of cupric ferrocyanide membrane has shown that the membrane potential is due to preferential ionic adsorption on the membrane surface. The extensive investigation on metallic ferrocyanide and ferricyanide gels[8] and membranes carried out by Malik and coworkers,[17] have shown that the adsorption plays a prominent role in the permeability of electrolytes, through metallic ferrocyanide and ferricyanide membranes. As already stated the order of adsorption of the electrolyte is: $FeCy_6^{4-} > FeCy_6^{3-} > SO_4^{2-} > Cl^-$, which is quite similar to the membrane potential order. Similarly the permeability order was found to be the reverse of the potential order.

A close relationship between permeability and potential is also observed from the plots of reciprocal of permeability against membrane potential (for K^- salts). From these curves (Fig. 5) an empirical relationship of the form $y = ax^{1/n}$ where a and n are constants and x and y represents permeability and potential can be put forward. The values of the constants a and n are given in Table 8.

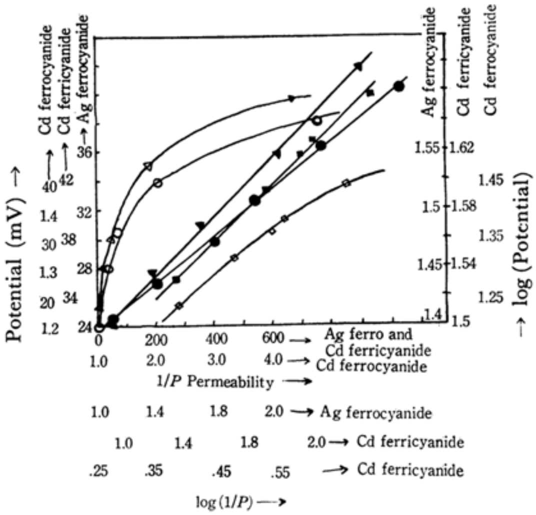

Fig. 5. The variation in membrane potential with reciprocal of the permeability through silver ferrocyanide (▲, △) cadmium ferricyanide (●, ○) and cadmium ferrocyanide (■, □) membranes for potassium salts.

TABLE 8

	a	n
Cadmium ferrocyanide	7.85	1.0
Cadmium ferricyanide	26.97	12.3
Silver ferrocyanide	18.43	7.8

A better insight into the physico-chemical behaviour of these parchment supported membrane is made available by comparing the results of membrane potential at different concentrations of the electrolyte. From membrane potential values the mobilities of anions relative to cations were calculated by means of the equation given by

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17) W. U. Malik, A. Hasan and A. K. Bhattacharya, *J. Indian Chem. Soc.*, **32**, 501 (1955); W. U. Malik and S. A. Ali, *Kolloid-Z.*, **175**, 139 (1961); W. U. Malik and F. A. Siddiqi, *J. Colloid Sci.*, **18**, 161 (1963); W. U. Malik and F. A. Siddiqi, *Proc. Ind. Acad. Sci.*, **56**, 206 (1962).

Willis[12] in the case of cupric ferrocyanide membrane.

The values of the mobilities of anions calculated from the equation are likely to be influenced by the following factors.

(i) The mobility of anion in the free solution.
(ii) The chances of entry of anions in the pores.
(iii) The valency of the anion.
(iv) The various factors which are operative in the movement of anions in the pores.

The clogging of the pores by the adsorbed ions would greatly influence the factors (iii) and (iv). If the pores are clogged to a great extent, the electrical forces (electrostatic nature of the membrane which is negative) would be playing a great role, as well as the size of the anions (sieving effect) will influence the entry inside the pores. In the free solution and at infinite dilution the mobilities are of the following order:

$$\mathrm{FeCy_6}^{4-} > \mathrm{SO_4}^{2-} > \mathrm{Cl}^- > \mathrm{NO_3}^-$$

The mobilities calculated from potential measurements are:

$$\mathrm{Cl}^- > \mathrm{NO_3}^- > \mathrm{SO_4}^{2-} > \mathrm{FeCy_6}^{3-} > \mathrm{FeCy_6}^{4-}$$

which is quite different from the order of mobility in the free solution. The tetravalent $\mathrm{FeCy_6}^{4-}$ has got the least mobility which is due to the maximum adsorption resulting in the greatest electrostatic repulsion. The pre-treated membranes (potassium ferrocyanide treated in the case of cadmium and silver ferrocyanide membranes and potassium ferricyanide in the case of cadmium ferricyanide membrane) have got high potential value (*vide* Table 3) showing that the electrical

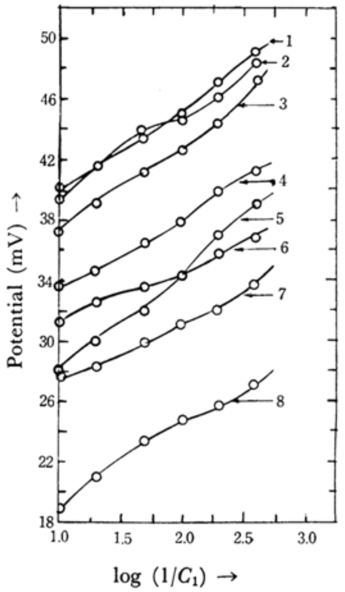

Fig 6(A). The variation in membrane potential with concentration in presence of different electrolytes through cadmium ferrocyanide membrane.

1, Na_2SO_4 2, K_4FeCy_6 3, CH_3COONa
4, K_2SO_4 5, $NaNO_3$ 6, CH_3COOK
7, KNO_3 8, KCl

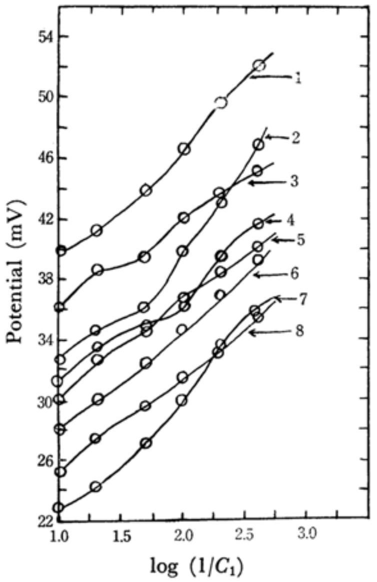

Fig. 6(B). The variation in membrane potential with concentration in presence of different electrolytes through cadmium ferricyanide membrane.

1, K_3FeCy_6 2, Na_2SO_4 3, CH_3COONa
4, K_2SO_4 5, $NaNO_3$ 6, KNO_3 7, NaCl
8, CH_3COOK 9, KCl

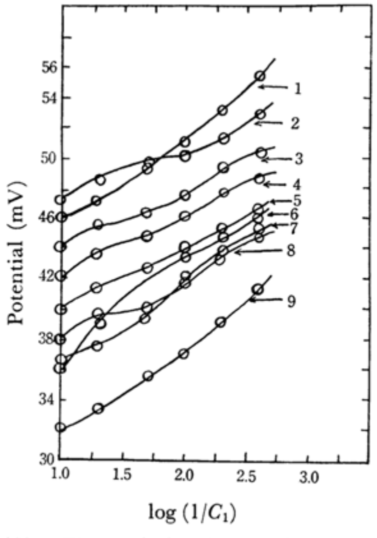

Fig. 6(C). The variation in membrane potential with concentration in presence of different electrolytes through silver ferrocyanide membrane.

1, K_4FeCy_6 2, Na_2SO_4 3, K_3FeCy_6
4, CH_3COONa 5, K_2SO_4 6, CH_3COOK
7, $NaNO_3$ 8, KNO_3

forces are greatly enhanced due to adsorption. If these pre-treated membranes are again treated with the metal ions (Ag^+ in the case of silver ferrocyanide membrane and Cd^{2+} in the case of cadmium ferrocyanide and ferricyanide membranes) the potential again decreases (*vide* Table 4) showing thereby that the additional charge developed was compensated by the metal ion treatment. The fact that the electrostatic nature of the membrane controls the diffusion process is further substantiated from the results on potential values determined at varying concentrations of electrolyte. (0.1 and 0.01 M to 0.0025 and 0.00025 M). In Figs. 6A, 6B, and 6C, the membrane potential are drawn as a function of concentration. The plot of log $1/C_1$ (C_1 being the higher concentration $C_1/C_2=10$) against potential shows that as the concentration is decreased, the potential increases. In the higher concentration ranges, the increase in potential is sharp, gradually decreasing at lower concentrations. In Figs. 7A, 7B and 7C the apparent mobilities of anions in the membrane have been plotted against log $1/C_1$ (C_1 being the higher concentration). It is seen that the mobilities of anions decreases as the concentration is lowered the fall being rapid in higher concentration ranges. These results can be explained in the light of the theory developed by Willis.[12] An adsorptive layer is formed on the surface of the membrane. Within the pores of the membrane, there would be a diffuse ionic atmosphere extending from the negatively charged walls. The thickness of this atmosphere depends on the electrolyte concentration in contact with the membrane. At a particular concentration an equilibrium will be set up between the fixed ions in the pores and those in the bulk of the solution. These ions namely $FeCy_6^{3-}$ (in the case of cadmium ferricyanide membrane) tend to keep out the ions of the same sign (Cl^-, SO_4^{2-}, $FeCy_6^{3-}$, $FeCy_6^{4-}$). The thickness of ionic atmosphere would be maximum when the electrolyte solution is very dilute. An increase in the ionic atmosphere would therefore, result in great repulsion of anions (descending part of the curves of log $1/C_1$ against mobility). At these concentration ranges the mobility of anions have got lowest values. As the concentration increases, the ionic atmosphere decreases, which leads to increase in the values of mobilities (ascending part of the curves of log $1/C_1$ against mobility). High enough concentration of electrolyte leads to the

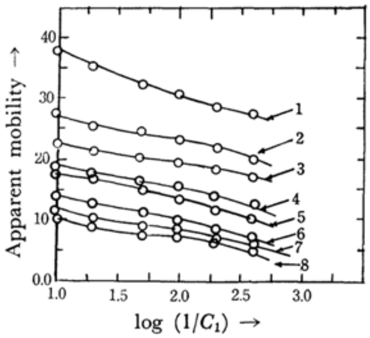

Fig. 7(A). The variation in apparent mobility with concentration in the presence of different electrolytes with cadmium ferrocyanide membrane.

1, KCl 2, KNO_3 3, CH_3COOK
4, $\frac{1}{2}K_2SO_4$ 5, $NaNO_3$ 6, $\frac{1}{4}K_4FeCy_6$
7, CH_3COONa 8, $\frac{1}{2}Na_2SO_4$

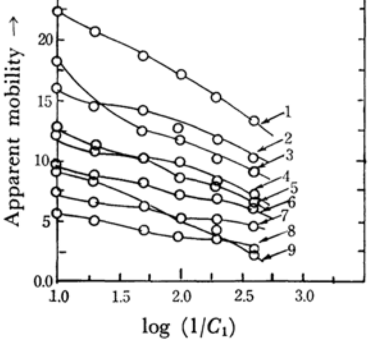

Fig. 7(B). The variation in apparent mobility with concentration in the presence of different electrolytes with cadmium ferricyanide membrane.

1, KCl 2, CH_3COOK 3, KNO_3
4, $\frac{1}{2}K_2SO_4$ 5, NaCl 6, $NaNO_3$
7, CH_3COONa 8, $\frac{1}{2}Na_2SO_4$ 9, $\frac{1}{4}K_4FeCy_6$

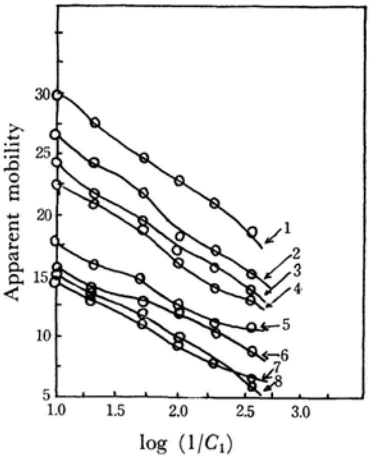

Fig. 7(C). The variation in apparent mobility with concentration in the presence of different electrolytes with silver ferrocyanide membrane.

1, KNO_3 2, CH_3COOK 3, $\frac{1}{2}K_2SO_4$
4, $NaNO_3$ 5, $\frac{1}{3}K_3FeCy_6$ 6, CH_3COONa
7, $\frac{1}{2}Na_2SO_4$ 8, $\frac{1}{4}K_4FeCy_6$

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18) W. W. Kittelberger, *J. Phys. Chem.*, **53**, 392 (1949).

reduction of ionic atmosphere to a minimum value and at this point the effect of the membrane vanishes and the potential developed approaches that for free diffusion.

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