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Studies with Inorganic Ion-exchange Membranes. I. Effect of Binding Material on the Permeation of Electrolyte Solutions across Titanium Tungstoarsenate Membranes

S. K. SRIVASTAVA,* Satish KUMAR,† and Surendra KUMAR
Department of Chemistry, University of Roorkee, Roorkee-247 667, India

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A comparative study of permeability for various electrolytes is made on parchment-, polystyrene-, and Araldite based membranes of titanium tungstoarsenate at 20, 25, 30, and 35 °C. At any given temperature the order of permeability increase is $K^+>Na^+>Li^+$ for 1:1 electrolytes and $Ba^{2+}>Ca^{2+}>Mg^{2+}$ for 2:1 electrolytes. Permeability values are higher for parchment-based than polystyrene-based membranes. The diffusion of these electrolyte solutions across Araldite based membrane is almost negligible. Thermodynamic parameters of diffusion process, *viz.*, $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta F^{\neq}$ have been evaluated at 25 °C by applying the theory of absolute reaction rates. $\Delta S^{\neq}$ values are negative for all the cations for both the membranes except that of Li^+ which is positive for parchment-based membranes. $\Delta F^{\neq}$ values are higher for the polystyrene-based than parchment-based membranes.

Inorganic ion-exchange membranes are of vital importance in analytical chemistry[1—6] and also as the models for biological membranes. Literature survey on this topic reveals that a lot of work has been done in the last two decades on the characterization and membrane properties of this class of membranes by various research groups.[7—13] Most of the reports made in this direction deal with the membranes prepared by keeping the same binder but different membrane materials and almost no attempt has been made so far to investigate the effect of binding material on membrane properties by selecting the same membrane material but different binding materials.

We have also been working on the electrochemical properties of inorganic ion-exchange membranes and their possible applications as ion-selective electrode.[14—16] In this communication we report the effect of binding material on the permeability and thermodynamic parameters of the diffusion process, *viz.* $\Delta S^{\neq}$, $\Delta H^{\neq}$, $\Delta F^{\neq}$, across titanium tungstoarsenate membranes with parchment, polystyrene and Araldite as binding material for their preparation.

Experimental

Titanium(IV) chloride (B.D.H), sodium arsenate heptahydrate (E. Merck) and sodium tungstate (AnalR) were used as such. The specimen of Araldite was obtained from Cibatul Limited, India (composition not known). All other chemicals used in this investigation were also of A.R. grade.

Preparation of Titanium Tungstoarsenate. Titanium tungstoarsenate is prepared by adding 0.25 M (1 M=1 mol dm^{-3}) titanium(IV) chloride solution to a mixture of 0.25 M sodium arsenate and 0.25 M sodium tungstate in the volume ratio 2:1:1. The pH of the mixture and titanium(IV) chloride solution was adjusted to one. The precipitate thus obtained was allowed to stand for 24 h at room temperature. It was then washed by decantation with distilled water and afterwards with 2 M nitric acid. The gel, dried at 50 °C, broke down to small particles when immersed in distilled water. The conditions mentioned above are optimum one for the preparation of a stable gel showing good sorption property.

A 0.2 g amount of the exchanger material was dissolved in concentrated sodium hydroxide solution and filtered. The residue, titanium hydroxide was dissolved in sulfuric acid and titanium was determined by hydrogen peroxide method, In the filtrate, arsenic was estimated by Volhard's thiocyanate method and tungsten by gravimetry as barium tungstate. The values obtained are Ti=9.51%, W=40.03%, and As=19.98% (the ratio Ti:W:As=1:4:2). The exchange capacity of the material is 0.86 meq g^{-1} (univalent ion) as reported earlier.[17]

Preparation of Membranes Using Different Binding Materials. The homogeneous membranes of titanium tungstoarsenate could not be prepared. Heterogeneous membranes of these compounds employing three different support materials (*i.e.* parchment paper, polysterene and Araldite) were prepared and found to be quite satisfactory.

(i) Preparation of Parchment Paper Impregnated Membrane: The membrane was prepared by impregnated parchment paper with titanium tungstoarsenate. The paper was first soaked in distilled water and then tied carefully on an open glass cylinder. A 0.25 M titanium(IV) chloride (pH=1) solution was filled inside the paper container which was then suspended in a beaker containing a mixture of sodium arsenate and sodium tungstate (prepared by mixing 0.25 M solution each in volume ratio 1:1 at pH=1) for 12 h. The parchment was then taken out and washed repeatedly with distilled water to remove the adsorbed electrolytes. The solutions of titanium(IV) chloride and mixture of sodium arsenate and sodium tungstate were then interchanged and paper was immersed again for another 12 h. The white membrane thus obtained was repeatedly washed with distilled water for complete removal of adsorbed electrolytes.

(ii) Preparation of Polystyrene-based Membrane: Polystyrene granules were heated in a glass tube in a concentrated sulfuric acid bath at 200 °C. The molten mass was allowed to cool down to room temperature and the polystyrene rod, thus obtained was ground to a 50 mesh sieve product. Membranes were obtained by mixing polystyrene and exchanger material in the ratio 1:5 by weight and heating the mass in a die kept in a metallurgical specimen mount press at 110 °C under a pressure of 6000—7000 psi. The optimum quantity of polystyrene to be added was determined by trial. Membranes with 20% polystyrene content were quite stable and did not show any dispersion in salt solutions.

(iii) Preparation of Araldite-based Membranes: A homogeneous mixture of 0.6 g titanium tungstoarsenate and 0.4 g

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† Institute of Paper Technology, Saharanpur.

of Araldite (minimum amount of binder necessary for a stable membrane) was uniformly spread over a piece of filter paper, which was then pressed gently with the help of a glass plate and left to dry overnight. After drying, the membrane of 1.5 cm in diameter was cut manually with the help of a razor and filter paper was also removed from the membrane surface. A large number of membranes were thus prepared and the one which did not have any cracks and was quite smooth and had a thickness of 2 mm was selected for subsequent investigations.

Determination of Permeability. The constant flow method, recommended by Willis,[18] was emplyed for permeability measurements. All experiments were performed with 0.05 M metal chloride solutions and the flow of water as well as solution was maintained at 50 ml h^{-1}. The conductivity of the lower half cell solution was measured at various time intervals. An increase in initial stages and then a constant value of conductance were observed in almost one hour time. The equilibrium conductance was corrected for conductance of water flowing through the lower half cell.

The concentration of the solution flowing through the lower half cell was computed from calibration curves drawn for this purpose by plotting conductance against concentration. For the evaluation of thermodynamic parameters of diffusion process, the permeability of salt solutions was determined at four tempertures, *viz.* 20, 25, 30, and 35 °C.

Results and Discussion

Permeability of a membrane may be defined as the amount of solute diffusing across it in unit time and unit concentration gradient. The data on permeability of various electrolyte solutions at different temperatures across the parchment- and polystyrene-based membranes are given in Table 1. The permeability across Araldite-based membrane of this compound was found to be negligible and no diffusion of the electrolyte was observed even when the experiments were performed with salt solutions tagged with radioactive isotopes. Thermodynamic parametres for the diffusion process across the membranes, as computed from permeation data at 25 °C, are given in Table 2.

Permeabilities of various electrolytes across the membranes having different binders show the following order:

Parchment-based membranes > Polystyrene-based membranes > Araldite-based membranes.

The diffusion of various salt solutions across the parchment- and polystyrene-based membranes follow the order:

$$K^+ > Na^+ > Li^+ \text{ and } Ba^{2+} > Ca^{2+} > Mg^{2+}$$

The permeation of an electrolyte through a membrane depends upon the charge and size of the diffusing ion, charge on the membrane matrix and its porosity. Over and above this, another factor of prime importance is the exchange capacity of the membrane material and the nature of binder used (in the case of heterogeneous membranes).

The fixed charge on the membrane matrix acts in two ways, firstly it excludes the co-ions from the membrane phase due to electrostatic repulsion and secondly it increases the mobility of counter ions in the membrane phase. Thus the fast moving chloride ions would be exluded from the membrane phase whereas the slow moving cations such as Li$^+$, Na$^+$, and Ca^{2+} *etc.* would be attracted towards it. The next two steps in the process of diffusion are the entry of cations into the membrane phase by ion exchange and their diffusion to the other side, through the pores of the membrane.

TABLE 1. PERMEABILITY OF UNIVALENT AND BIVALENT METAL CHLORIDES THROUGH TITANIUM TUNGSTOARSENATE MEMBRANES AT DIFFERENT TEMPERATURES

Electrolyte	Parchment-based TWA membrane Permeability/μmol h^{-1}				Polystyrene-based TWA membrane Permeability/μ mol h^{-1}			
	20 °C	25 °C	30 °C	35 °C	20 °C	25 °C	30 °C	35 °C
LiCl	23.20	30.35	41.50	58.30	1.30	1.70	1.84	2.32
NaCl	38.20	46.25	55.00	62.75	1.64	1.99	2.23	2.50
KCl	82.00	89.00	103.50	121.00	1.99	2.32	2.81	3.27
$BaCl_2$	36.10	42.20	47.75	53.00	0.43	0.45	0.51	0.55
$CaCl_2$	23.10	27.60	31.15	36.20	0.15	0.20	0.24	0.29
$MgCl_2$	8.25	11.15	14.10	17.75	0.05	0.07	0.08	0.99

TABLE 2. ACTIVATION ENERGY AND OTHER THERMODYNAMIC PARAMETERS FOR ELECTROLYTE DIFFUSION THROUGH TITANIUM TUNGSTOARSENATE MEMBRANES AT 25 °C

Electrolyte	Parchment-based TWA membrane				Polystyrene-based TWA membrane			
	E_a	$\Delta H^{\ddagger}$	$\Delta F^{\ddagger}$	$\Delta S^{\ddagger}$	E_a	$\Delta H^{\ddagger}$	$\Delta F^{\ddagger}$	$\Delta S^{\ddagger}$
	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
LiCl	44.98	42.50	37.73	16.00	25.01	22.53	40.46	−60.16
NaCl	23.96	21.48	36.67	−50.97	19.55	11.07	40.07	−77.18
KCl	19.49	17.01	35.00	−60.37	25.53	23.05	39.69	−55.84
$BaCl_2$	19.40	16.92	36.90	−67.05	12.31	9.83	43.72	−113.72
$CaCl_2$	21.13	18.65	37.99	−64.89	31.53	29.05	44.60	−58.18
$MgCl_2$	36.76	34.28	40.24	−20.00	36.47	33.99	48.35	−48.18

This eventually leads to the setting up of an electrical double layer across the membrane and gives rise to equilibrium conditions.

The passage of ions through membranes also depends on the charge and hydration of ions. Multivalent ions will experience a greater electrostatic force than the univalent one. Ions undergoing hydration would affect the permeability in two ways: Firstly by virtue of their size and secondly due to the extent to which the electrical forces of the membrane can pierce through the hydration shell. The position of ions in Holfmeister series should therefore influence the diffusion process and the order of diffusion should be:

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ \text{ and } Ba^{2+} > Ca^{2+} > Mg^{2+}$$

The order of permeability observed with the membranes under discussion, is in agreement with the sequence mentioned above.

It is observed that permeability increases with temperature. Applying Boltzmann distribution law to hydration-dehydration dynamic equilibrium, it can be concluded that at higher temperature considerably higher fraction of the total number of ions would be dehydrated and would possess the excess energy E_a required for permeation. The slope of log P *vs.* $1/T$ (Figs. 1 and 2) gives the activation energy E_a for the process of diffusion and the values obtained for these membranes are listed in Tables 1 and 2.

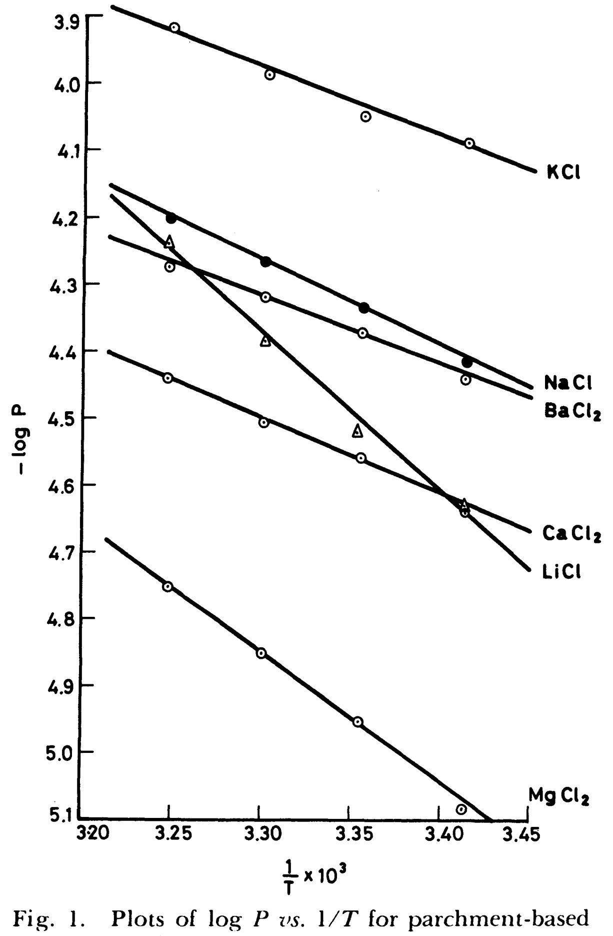

Fig. 1. Plots of log P *vs.* $1/T$ for parchment-based TWA membrane.

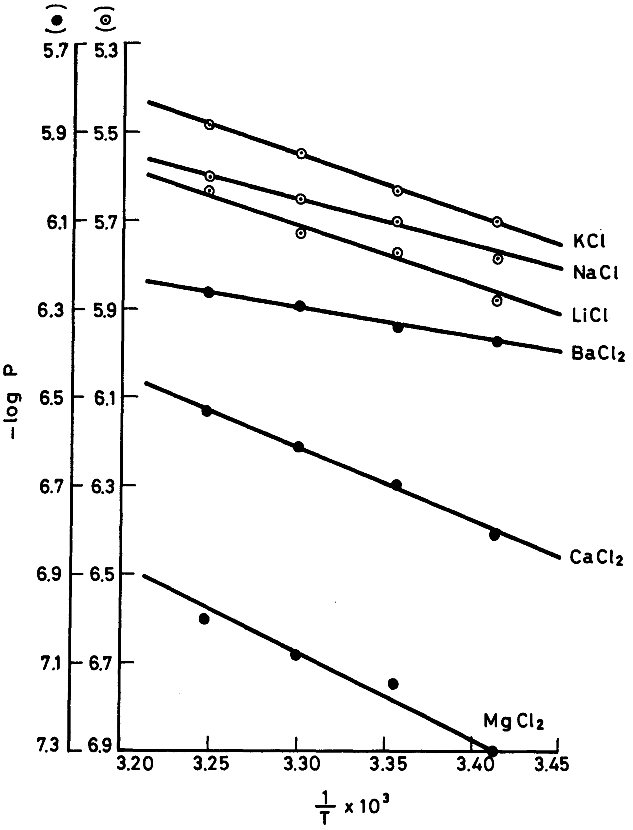

Fig. 2. Plots of log P *vs.* $1/T$ for polystyrene-based TWA membrane.

The theory of absolute reaction rate has been applied to diffusion processes in membranes by several investigators.[19–21] According to Zwolinski *et al.*[19] the permeability P' (cm s^{-1}) is given by the expression

$$P' = \left(\frac{\lambda^2 kT}{\delta h}\right)\exp(-\Delta F^{*}/RT)$$

where λ is the average distance between two equilibrium positions during the diffusion process, δ is the thickness of the membrane, while other symbols have their usual thermodynamic meanings. The value of free energy of activation can be calculated provided λ is known. This distance can be taken to be the same as the hopping distance, (3×10^{-8} cm) determined by Lai and Mortland.[22]

The ΔH^{*}, enthalpy of activation is related to E_a by the equation:

$$\Delta H^{*} = E_a + RT$$

and ΔS^{*}, the entropy of activation, can be calculated by Gibbs-Helmholtz equation:

$$\Delta F^{*} = \Delta H^{*} - T\Delta S^{*}$$

The values of ΔS^{*}, ΔF^{*}, and ΔH^{*} calculated on the basis of expressions given above are tabulated in Table 2.

It is observed that the values of entropy of activation are generally negative except for lithium in the case of parchment-based membrane of this compound which exhibits a positive entropy of activation. Similar observations have also been reported by other workers in the case of parchment based ion-exchange membranes.[23] According to Zwolinski *et al.*[19] the values of ΔS^* indicate the mechanism of flow and a large positive ΔS^* is interpreted to reflect the breakage of bonds while low and negative values of entropy of activation indicate that activation is accompanied by a decrease in entropy and this would be possible only if the activated state involved formation of some bonds between the diffusing ion and the membrane material.

According to zone activation theory of Barrer and coworkers[24,25] for permeation of gases through polymer membranes, a high entropy value means either the existence of a large zone of activation or the reversible loosening of ordered segments of the membrane structure on permeation.

The positive value of ΔS^* obtained for Li^+ in the case of parchment-based membrane of this compound indicates that the diffusion of this ion across the membrane generates a greater region of disorder. The negative ΔS^* for other species imply two things:

(i) The permeating ions are partially immobilized in the membrane structure or interfacial region as the activated state involves in the formation of a bond between the diffusing ion and membrane material.

(ii) Permeation across membrane is not the only step which guides the rate, besides other factors are also operative.

A perusal of Table 2 reveals that the energy of activation (E_a) and enthalpy of activation (ΔH^*) values for the diffusion of cations are higher in the case of parchment based membrane except for K^+ and Ca^{2+} ions. The values of ΔF^* are higher for polystyrene-based than the parchment-based membranes for all the cations. ΔF^* may be interpreted as the work involved for the permeating species in overcoming the energy barrier during diffusion. Thus the values (Table 2) reveal that diffusion across polystyrene-based membrane involves more work than the parchment-based membrane of this exchanger material. The data on ΔS^* is higher for parchment-based membrane than polystyrene-based membrane. Higher values of permeability observed across the parchment-based membrane also support the above view-points.

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