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MEMBRANE PERMEABILITY OF HEAVY WATER

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SUMMARY

Hydrodynamic permeability, thermoosmotic permeability and thermoosmotic pressures of liquid H_2O and ^2H_2O have been measured and heats of transport estimated. Similar measurements have been made for solutions of KCl in H_2O and ^2H_2O using a copper ferrocyanide impregnated membrane. The permeability of ^2H_2O is approximately 60 % that of H_2O. This is also the case for solution of KCl in ^2H_2O and H_2O. It appears that the difference in permeability arises on account of the difference in the mobility of H^+ and $^2H^+$.

Isothermal permeability of H_2O and ^2H_2O vapour through porous ceramic has been measured. Thermoosmotic pressure has been measured and heats of transport estimated. The permeability characteristics differ mainly on account of difference in molecular weights.

INTRODUCTION

Biological processes are known to be significantly affected by heavy water. It has been suggested that heavy water may influence the factors regulating protein synthesis or cause changes in the conformation of certain macromolecules involved in such synthesis at the microsomal level[1]. In the squid giant axon immersed in ^2H_2O a prolongation of the spike potential has been observed[2]. ^2H_2O is known to affect the conduction velocity in isolated frog nerve[3]. The pharmacological action of ^2H_2O has also been studied[4]. Effects of heavy water on living cells have been recently studied by KATZ.[5] ^2H_2O probably affects the osmotic properties of the living cell. KATZ has studied cultures of algae and other microorganisms in deuterium oxide[6]. Water permeability for lipid bilayer membrane has been studied recently[7].

The reason for the pronounced effect of ^2H_2O on biological processes is not clear. Table I gives a comparative idea of the properties of water and heavy water. It can be seen that viscosity, ionic mobility and autoprotolysis constant are significantly different in H_2O and ^2H_2O. Of these, viscosity and ionic mobilities would influence the osmotic and permeation properties.

It is difficult to ascertain which of these is instrumental in vitally affecting the biological processes. However, experimental studies with artificial membranes may yield some useful information to serve as a guide. The present investigation was undertaken in this hope. For this purpose permeation properties of (1) H_2O and ^2H_2O vapour, (2) liquid H_2O and ^2H_2O and (3) solutions of KCl in H_2O and ^2H_2O have

TABLE I

PROPERTIES OF HEAVY WATER

Properties	*Units*	H_2O	^2H_2O
Molecular weight		18.016	20.006
Density at 25°	g/cm^3	0.99704	1.104625
Dielectric constant		81.5	80.7
Refractive index at 20°		1.333	1.2382
Viscosity at 10°	mP	13.10	16.85
Ionic mobility 18° (K^+)	$cm^2 \cdot \Omega^{-1}$	64.2	54.2
Ionic mobility of cation	$cm^2 \cdot \Omega^{-1}$	315.2	213.7
Autoprotolytic constant at 25°		$1 \cdot 10^{-14}$	$3 \cdot 10^{-15}$

been studied. The transport of electrolyte solution was studied just to ascertain the role of ions in water transport.

Natural membrane transport is a complex phenomenon. Theoretical studies are difficult since the pore size is comparable to molecular size and the channels have complex geometry and complex surface characteristics. Experimental studies are equally difficult. However, transport studies on artificial membrane, controlling (i) the nature of the barrier (ii) the nature of the medium and (iii) the nature of the permeant species, can yield extremely useful information. With this end in view, studies with H_2O and ^2H_2O have been undertaken.

EXPERIMENTAL

Materials

Heavy water was obtained from Bhabha Atomic Research centre (India). It was 99.4 % pure. Its purity was checked by density measurements. Conductivity water was prepared by double distillation of water from $KMnO_4$ solution.

Membranes

For the study of thermoosmosis of vapour, a porous ceramic was used as a membrane as described earlier[8]. However, for the study of thermoosmosis of liquids a modified membrane was used. In earlier[9] studies on thermoosmosis, cellophane membranes were used. The possibility of deformation of the membrane when higher pressure differences were applied affected the reliability of the results. We selected pyrex sinter (G_4) for the present investigation since it is sufficiently strong to withstand high pressure. However, as such it does not exhibit any thermoosmosis[10]. This is due to the fact that the pore size is much larger than that required for thermoosmosis to occur. The size of the pores was reduced by impregnating the membrane with copper ferrocyanide in the following manner.

0.05 M copper sulphate and potassium ferrocyanide were kept on the two sides of the membrane for about 4 h. Sufficient copper ferrocyanide was deposited in the pores to reduce the pore size so that thermoosmosis really occurred.

Experimental procedure

Experimental techniques for the measurement of the thermoosmosis of vapour and liquid were the same as described earlier[8,9]. The temperature difference was estimated with the help of copper constantan thermocouples placed in contact with the two faces of the membrane. For liquids, volume flow was measured by noting the rate of advancement of fluid in a capillary. Thermoosmotic pressure was measured with a cathetometer. During thermoosmotic permeability and thermoosmotic pressure measurements, occasional formation of bubbles in the experimental cell vitiated the results. This difficulty could, however, be avoided by degassing the liquid prior to use.

RESULTS AND DISCUSSION

Using methods of thermodynamics of irreversible processes, it can be shown that for a non-ideal binary mixture, the mass flows J_1 and J_2 of Components 1 and 2 and heat flow J_q may be written as follows[11]:

$$J_1 = L_{11}X'_1 + L_{12}X'_2 + L_{1q}X_q \tag{1}$$

$$J_2 = L_{21}X'_1 + L_{22}X'_2 + L_{2q}X_q \tag{2}$$

$$J_q = L_{q1}X'_1 + L_{q2}X'_2 + L_{qq}X_q \tag{3}$$

where

$$X_q = -\frac{\Delta T}{T^2}$$

$$X'_1 = -v_1\frac{\Delta P}{T} - \left(\frac{\partial \mu_1}{\partial C_1}\right)_{T,P}\frac{\Delta C_1}{T}$$

$$X'_2 = -v_2\frac{\Delta P}{T} - \left(\frac{\partial \mu_2}{\partial C_1}\right)_{T,P}\frac{\Delta C_1}{T}$$

L_{ik}, L_{qi} and L_{qq} are phenomenological coefficients. X'_1, X'_2 and X_q are "forces". Components 1 and 2 have mass fractions C_1 and C_2 and partial specific volumes v_1 and v_2. It is supposed that the two subsystems (liquid or gas), one on each side of the membrane, are themselves uniform and homogeneous; the Δ's refer to differences existing across the membrane. From Eqns. 1–3 it can be shown[11] that

$$\left(\frac{\Delta P}{\Delta T}\right)_{J=0} = -\frac{C_1Q_1^* + C_2Q_2^*}{vT} \tag{4}$$

where Q^*_1 and Q^*_2 are the heats of transport of Components 1 and 2, respectively, and are related to phenomenological coefficients. v is the mean specific volume of the mixture, which is given by

$$v = v_1C_1 + v_2C_2 \tag{5}$$

For pure components we have similar results and

$$\left(\frac{\Delta P}{\Delta T}\right)_{J_i=0} = -\frac{(Q_i^*)_0}{v_iT}$$

where $(Q^*_i)_0$ is the heat of transport of pure Component i.

The separation ΔC_1 corresponding to fixed ΔT can also be obtained by solving Eqns. 1 and 2 after appropriate substitution. Thus,

$$\frac{\Delta C_1}{\Delta T} = \frac{C_2(v_1Q_2^* - v_2Q_1^*)}{(\partial\mu_1/\partial C_1)_{T,P}vT} \tag{6}$$

It is obvious that ΔC_1 will depend on the magnitude of quantity $v_1Q^*_2 - v_2Q^*_1$.

The total material flow $J = J_1 + J_2$ which can be easily measured, is given by following phenomenological equation obtained on adding Eqns. 1 and 2

$$J = -L'_{11}\left(\frac{\Delta P}{T}\right) - L'_{12}\left(\frac{\Delta C_1}{T}\right) - L'_{13}\left(\frac{\Delta T}{T^2}\right) \tag{7}$$

where

$$L'_{11} = \{(L_{11}v_1 + L_{12}v_2) + (L_{21}v_1 + L_{22}v_2)\}$$

$$L'_{12} = \left\{(L_{11} + L_{21})\left(\frac{\partial\mu_1}{\partial C_1}\right)_{T,P} + (L_{12} + L_{22})\left(\frac{\partial\mu_2}{\partial C_1}\right)_{T,P}\right\}$$

$$L'_{13} = (L_{1q} + L_{2q})$$

When $\Delta C_1 = 0$ and $\Delta T = 0$,

$$J = -L'_{11}\left(\frac{\Delta P}{T}\right) \tag{8}$$

L'_{11} for pure components and mixtures was estimated from the slope in Fig. 1 where J has been plotted against P.

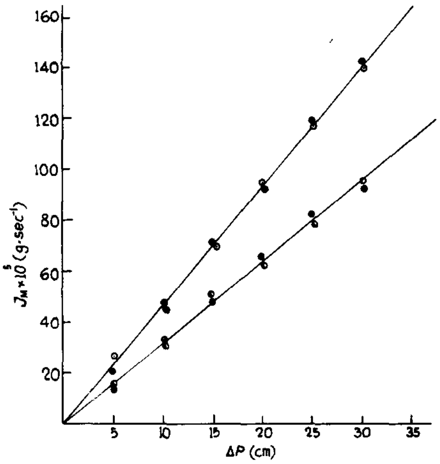


Fig. 1. Dependence of solvodynamic permeability on pressure difference for water + heavy water system. ⊙, water; ⊗, heavy water; ●, KCl in water; ◐, KCl in heavy water.

We shall first comment on the nature of flow. When the flow is viscous, J would be given by

$$J = -\frac{n\pi v^4}{8\eta l}\cdot\Delta P\cdot d \tag{9}$$

where η is the viscosity, d is the density of the liquid, v is the radius and n is the number of pores. On the other hand, when the flow is diffusive[12]

$$J = -\frac{D\varepsilon v}{RTl}\cdot d\cdot\Delta P \tag{10}$$

where D is diffusion coefficient, ε is fractional void volume and l is the thickness of the membrane. On comparing Eqns. 8 and 10, we have for diffusive flow

$$L'_{11} = \frac{D\varepsilon}{Rl} \tag{11}$$

Eqns. 8 and 9 yield

$$L'_{11} = \frac{dTn\pi r^4}{8\eta l} \tag{12}$$

The values of L'_{11} for pure components and electrolyte solutions as estimated from the experimental data can be used to differentiate between two types of flows. Thus for the same membrane L'_{11}/D would be constant and independent of the nature of the permeant if the flow is diffusive while $L'_{11}\,\eta\,/d$ would be constant if the flow is viscous. The values of these quantities are given in Table II.

TABLE II

VALUES OF DIFFERENT COEFFICIENTS

Substance	$L'_{11}/D \times 10^2$ ($g \cdot cm \cdot degree \cdot erg^{-1}$)	$L'_{11}\eta/d \times 10^9$ ($sec \cdot erg \cdot degree \cdot poise \cdot cm^2$)
Water	1.10	2.37
Heavy water	0.85	1.62
KCl in water	1.00	2.39

Since L'_{11}/D and $L'_{11}\eta/d$ are practically constant, it is difficult to differentiate between diffusive and viscous flow. However, if the values of L'_{11} were available at different temperatures it could have been possible to differentiate between the two since $L'_{11}\eta/d$ would alone vary with temperature.

The hydrodynamic permeability for ^2H_2O as well as for solutions of KCl in ^2H_2O is only 60 % of the corresponding values for water. This is true for thermo-osmotic permeability also. The values of the coefficients are given in Table III.

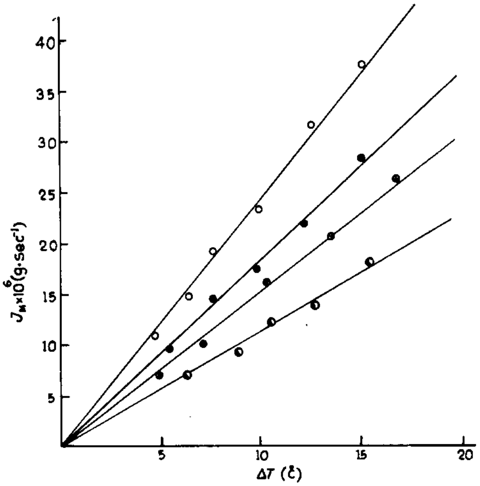
TABLE III

THERMOOSMOSIS OF ELECTROLYTES IN H_2O AND ^2H_2O

Substance	$L'_{11} \times 10^5$ ($cm \cdot g \cdot erg^{-1} \cdot sec^{-1} \cdot degree$)	L'_{13} ($g \cdot sec^{-1} \cdot degree$)	$(L'_{13}/L'_{11})v \times 10^3$ (cal/g)	$Q^* \times 10^3$ (cal/g)
Water	0.144	0.244	4.05	3.87
Heavy water	0.086	0.152	3.79	3.70
KCl in water	0.148	0.178	3.00	3.10
KCl in ^2H_2O	0.084	0.108	2.92	2.89

The data on thermoosmotic flow are plotted against temperature difference in Fig. 2. L'_{13} was estimated from the slope. Thermoosmotic pressure has been plotted in Fig. 3. The slope yields Q^*. The internal consistency of the data was checked in the following manner. If $\Delta C_1 = 0$ Eqn. 7 yields

$$J = -L'_{11}\left(\frac{\Delta P}{T}\right) - L'_{13}\left(\frac{\Delta T}{T^2}\right) \tag{13}$$



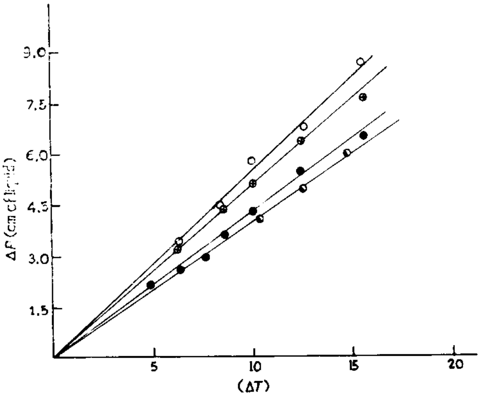


Fig. 2. Dependence of thermoosmotic permeability on temperature difference for water + heavy water system. ⊙, water; ⊗, heavy water; ●, KCl in water; ◐, KCl in heavy water.

Fig. 3. Dependence of thermoosmotic pressure on temperature difference for water + heavy water system. ⊙, water; ⊗, heavy water; ●, KCl in water; ◐, KCl in heavy water.

Under these circumstances

$$\left(\frac{\Delta P}{\Delta T}\right)_{J=0} = -L'_{13}/L'_{11}T \tag{14}$$

so that

$$Q^* = -vL'_{13}/L'_{11} \tag{15}$$

Eqn. 15 is confirmed by the data recorded in Table III.

In order to assess whether any ΔC is developed during the experiment, the density of the mixture on the two sides of the membrane in the thermoosmosis cell was measured, after the steady state was reached. The changes in the density were within experimental error. Further similar determinations of the density were made when the flow was allowed to take place for several hours under pressure gradient. Again the difference of density of the two sides of the membrane was found to be negligible. Both the experiments showed that ΔC_i is negligible.

The permeability of H_2O and ^2H_2O is unaffected when KCl is dissolved. This only shows that the transport mechanism is unaffected. On the other hand, thermoosmotic permeability and heats of transport are found to be considerably different. In other words, heat transported per unit mass flow for the pure solvents and solutions of the electrolytes differ considerably. It is surprising to note that this change is observable even in case of 0.1 M KCl. This simply points to the fact that interactions of ions with the solvent is an important factor. The ratio of L'_{13}, L'_{11} for liquid H_2O and ^2H_2O are as follows,

$$\frac{(L'_{13})_{H_2O}}{(L'_{13})_{^2H_2O}} = 1.61 \text{ and } \frac{(L'_{11})_{H_2O}}{(L'_{11})_{^2H_2O}} = 1.67$$

Further,

$$\frac{(L'_{13})_{H_2O}}{(L'_{13})_{KCl\ in\ H_2O}} = 1.37 \text{ and } \frac{(L'_{13})_{^2H_2O}}{(L'_{13})_{KCl\ in\ ^2H_2O}} = 1.40$$

We will now discuss the results on thermoosmosis of vapours. Isothermal permeabilities of H_2O and ^2H_2O vapour were experimentally determined. Values of L'_{11} for H_2O and ^2H_2O vapour had similar magnitude within experimental error. The difference in the values of heat of transport appears to be due to molecular weight only. Heat of transport for gaseous water and heavy water for the same magnitude of mean free path is found to be related as follows,

$$\frac{Q^*_{^2H_2O}}{Q^*_{H_2O}} = \frac{M_{H_2O}}{M_{^2H_2O}} = 0.92$$

where M is molecular weight.

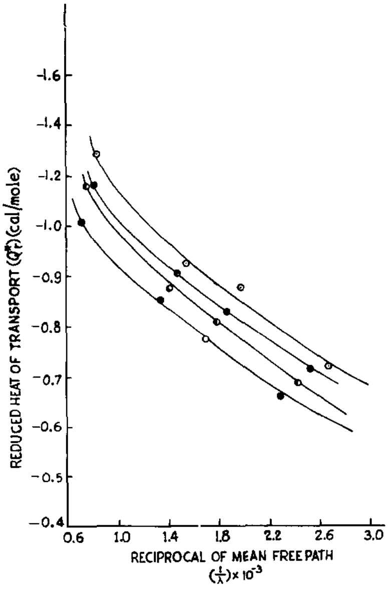
For an ideal membrane and an ideal gas

$$Q^* \rightarrow -RT/2M \text{ as } a/\lambda \rightarrow 0$$

and

$$Q^* \rightarrow 0 \text{ as } a/\lambda \rightarrow \infty$$

where a is the radius of the capillary and λ is the mean free path. Heat of transport Q^* was calculated from Eqn. 4. The reduced heat of transport $Q^*_r = Q^*$ $(RT/2M)$ is plotted against $1/\lambda$ in Fig. 4. Thus the heat of transport ranges between 0 and $-RT/2M$. Q^* for ^2H_2O and H_2O are 13.2 ± 0.2 and 10.1 ± 0.1 cal/g at 72°, respectively.



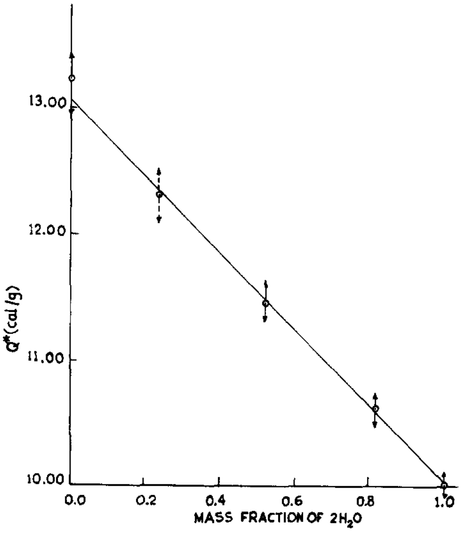


Fig. 4. Dependence of reduced heat of transport against $1/\lambda$ for water.

Fig. 5. Dependence of heat of transport against composition of heavy water for water + heavy water system.

These values are positive and markedly different from the ideal values. It is obvious that during transport work has to be done in counteracting interaction between the molecules and between the molecules and surface of capillaries. For liquid water and liquid heavy water, heats of transport are considerably reduced as compared to vapour.

As expected the heat of transport of a mixture is a linear function of concentration[13] of ^2H_2O as shown in Fig. 5. Using values of heat of transport for H_2O and ^2H_2O given in Table IV, $\Delta C_1/\Delta T$ is estimated to be $3.82 \cdot 10^{-4}$ when $C_1 = 0.2237$ using Eqn. 6. This shows that enrichment of heavy water could be accomplished by thermo-osmosis.

TABLE IV

HEAT OF TRANSPORT OF H_2O AND ^2H_2O VAPOURS AND THEIR MIXTURES

Mass fraction of water (H_2O)	ΔT	T	ΔP *(cm Hg)*	Q^* *(cal/g)*
1.00	80.0°	74.0°	0.270	13.2 ± 0.2
0.78	80.0°	72.0°	0.260	12.2 ± 0.2
0.47	80.0°	72.0°	0.250	11.4 ± 0.1
0.19	80.0°	72.0°	0.237	10.5 ± 0.1
0.00	80.0°	73.0°	0.232	10.1 ± 0.1

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