Biophysical Chemistry 4 (1976) 305–308

ANOMALOUS OSMOSIS THROUGH A MODEL MEMBRANE CONSTRUCTED WITH POTASSIUM POLYSTYRENESULFONATE SOLUTION

Masayasu TASAKA and Sueo NAGASAWA *
Department of Industrial Chemistry, Faculty of Engineering,
Shinshu University, Wakasato, Nagano, Postal Code 380, Japan

It is reported that anomalous osmosis can be observed through liquid membranes which are made by placing a potassium polystyrenesulfonate solution between two inert cellophane membranes. No anomalous osmosis is observed with pure water instead of polyelectrolyte solution.

1. Introduction

Permeation of water through a membrane is observed if two solutions of different concentration of an electrolyte are separated by a membrane. However, the permeation velocity of a solvent is not proportional to the difference of chemical potential of water or to that of osmotic pressure on both sides of the membrane if the membrane is a charged membrane such as oxidized collodion, interpolymer membrane of collodion and polystyrenesulfonic acid, etc. Sometimes it appears to be accelerated by an unknown factor. In some cases, moreover, the flow of water occurs against the chemical potential gradient of water (negative osmosis). Many reports have been published to discuss the cause for the "anomalous" osmosis through charged membranes [1–5]. Some authors, including one of the present authors (M.T.), showed that the anomalous osmosis can be caused by strong interaction between flow of ions and that of water. That is, the cross terms in the phenomenological equations for fluxes of ions and water may be so high that the flow of solute retards the flow of water [5–7].

This paper presents additional data using a polyelectrolyte solution as a model membrane. Since the membrane phase is a solution, any abnormal pressure distribution in the direction of flow as was assumed in various papers [4,8,9] cannot be assumed in this case.

2. Experimental

Half of the cell used for the measurements of solvent flow is shown in fig. 1. The thickness of the solution part (E) is 0.3 cm. Deformation of the cellophane membranes due to osmotic pressure was prevented by mounting a pair of plastic supports (C) with an effective area of 0.88 cm^2. Two samples of potassium polystyrenesulfonate (KPSS) solutions were used. The degree of sulfonation of sample M-1 is about 50% and its concentration is about 0.07 g/cm^3. Thus, the concentration of fixed charges in the membrane phase X is 2×10^{-4} eq/cm^3. The concentration of the other sample M-2, the degree of sulfonation of which is undetermined, is about 0.2 g/cm^3. Besides, pure water was also employed instead of KPSS solution for refer-

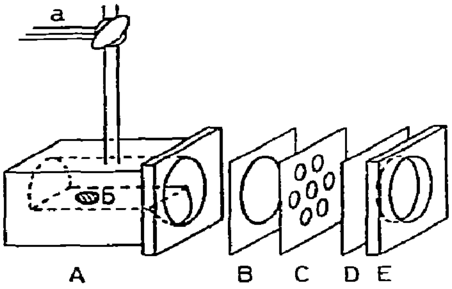

Fig. 1. Half of the decomposed cell. A, compartment for salt solution; B, rubber gasket; C, plastic support; D, cellophane; E, compartment for polyelectrolyte solution; a, capillary; b, magnetic strirrer tip.

---

* Present address: Water Re-use Promotion Center, Akasaka 2-3-4, Minato-Ku, Tokyo, Postal Code 107, Japan.

ence. We denote those model membranes by M-1 (0.07 g/cm^3 KPSS), M-2 (0.2 g/cm^3 KPSS), and M-3 (H_2O), respectively.

The rate of volume flow was determined from movement of the liquid meniscus in a capillary (a). The rate of water transport, expressed in mol cm^{-2} min^{-1}, was calculated from the rate of volume flow. The bulk solutions of electrolyte (A) on both sides of the model membrane were stirred by a pair of magnetic stirrer tips (b).

The diffusion potential (membrane potential) $\Delta\psi$ was measured in the same cells. The transference number of cation t_+ were calculated from

$$-\Delta\psi = (2t_+ - 1)(RT/F)\ln(a''_\pm/a'_\pm), \qquad (1)$$

where R is the gas constant, F the Faraday constant, T the temperature, and $a''_\pm$ and $a'_\pm$ are the mean activities of salt on both sides of the membrane. The transference numbers in M-1 and M-2 are plotted against the lower concentration of KCl, c', with concentration ratio $c''/c' = 2$ in fig. 2.

3. Results

The velocities of water transport, J_0, through M-1 with ratio of KCl concentration $r = 5$ and 10 and through M-2 with $r = 10$ are plotted against the lower concentration, c', in fig. 3 ($r = c''/c'$). The data for M-1 and M-2 clearly show the features of anomalous osmosis, i.e., the N-shape dependence of J_0 on the logarithmic concentration of electrolyte as through collodion based membranes [1–5]. In fig. 3, the data for M-3 with $r = 10$ are also shown for comparison with the data for M-1 and M-2. No anomalous osmosis is observed. The data for M-3 may correspond to the data for an untreated collodion membrane [5] or the oxyhemoglobin membrane at the isoelectric state [3].

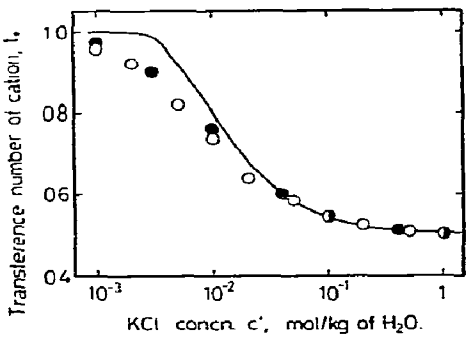

Fig. 2. The dependence of transference number on electrolyte concentration, c', for M-1 (○) and M-2 (●). The solid line is calculated from eq. (3) for M-1.

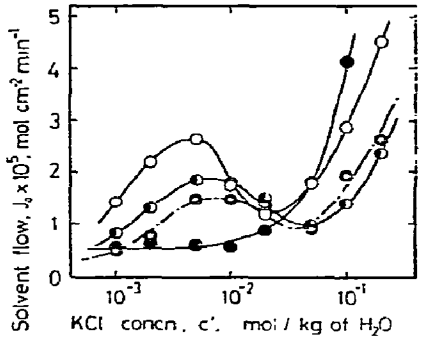

Fig. 3. Solvent flows through M-1, M-2, and M-3. Electrolyte: KCl. M-1: ◐, $r = 5$; ○, $r = 10$. M-2: ◎, $r = 10$. M-3: ●, $r = 10$.

4. Discussion

In fig. 2 the transference number of cation decreases from 1.0 to 0.5 because of the increase of coion in membranes with increasing concentration of KCl. If the membrane phase can be approximated as a polyelectrolyte solution and the effect of water flux on membrane potential is negligible, the membrane potential appearing on both sides of the membrane is given by [10]

$$-\Delta\psi = \frac{RT}{2F}\ln\left(\frac{\bar{c}''_-(\bar{c}'_- + \phi X)}{\bar{c}'_-(\bar{c}''_- + \phi X)}\right) + \frac{RT}{F}\left(\frac{l_+ - l_-}{l_+ + l_-}\right)$$
$$\times \ln\left(\frac{\bar{c}''_- + \phi X l_+/(l_+ + l_-)}{\bar{c}'_- + \phi X l_+/(l_+ + l_-)}\right), \qquad (2)$$

where ϕ is a parameter expressing the non-ideality of the solution in the membrane and l_i is the mobility in the membrane phase. The concentration of coion in polyelectrolyte solution can be calculated assuming the Donnan membrane equilibrium between polyelectrolyte solution and external solutions. Assuming that $l_{K^+} = l_{Cl^-}$, from eqs. (1) and (2) the mean transference number of K^+ ion, t_{K^+}, is given by

$$t_{\mathrm{K}^+} = \frac{1}{2}\left\{1 + \ln\left(\frac{\bar{c}''_-(\bar{c}'_- + \phi X)}{\bar{c}'_-(\bar{c}''_- + \phi X)}\right) / 2\ln\left(\frac{a''_\pm}{a'_\pm}\right)\right\} . \qquad (3)$$

From studies in polyelectrolyte solutions, it can be speculated that ϕ is about 0.1 to 0.5 [11,12]. The calculated values of t_+ for membrane M-1 assuming $\phi = 0.1$ is shown by a solid line in fig. 2. The agreement between the theory and experiments is satisfactory.

As was discussed in detail in a previous paper [5], the anomalous osmosis occurs due to the interaction between the flux of salt and that of water. Water permeates through the membrane from the dilute solution to the concentrated solution by osmotic force and the permeation coefficient is a constant independent of electrolyte concentration and membrane fixed charges. The electrolyte permeates from the concentrated solution to the dilute solution due to concentration difference. The permeability coefficient of electrolyte, which is defined by the flux of electrolyte per unit difference of electrolyte concentration, is dependent upon the electrolyte concentration and the concentration of membrane fixed charges [10].

Because of the strong interaction between both fluxes, the flow of water is markedly affected by the flux of electrolyte. If the membrane has no fixed charges, that is, in M-3, the flow of water does not show any abnormal behaviour though there is an interaction between them since the transference number t_+ is kept constant (≈ 0.5) in the whole range of electrolyte concentrations. The flow of water is approximately proportional to the difference of concentration on both sides of membrane. If J_v is plotted against concentration in a semi-logarithmic plot, therefore, it shows monotonous increase as the concentration of KCl increases (see M-1 in fig. 3).

If the membrane has fixed charges, however, the transference number of cation t_+ is almost unity at low concentrations of electrolyte but decreases sharply as the concentration of electrolyte increases. If t_+ is close to unity, the flux of KCl is almost completely stopped, whereas if t_+ is close to 0.5, the electrolyte permeates through the membrane as if the membrane has no charges. This increase of electrolyte flux causes the decrease of water flux because of the strong interaction between both fluxes. It was shown in a quantitative way by using interpolymer membranes that the maximum in fig. 3, i.e., the anomalous osmosis is caused by this effect of electrolyte flux on water flux. In this paper it is pointed out that such anomalous osmosis is observed not only through membranes having rigid structures but also through membranes having solution structures.

In some papers [4,8] the anomalous osmosis is explained by the change of pressure difference inside the membrane as concentration of electrolyte increases. At both interfaces between the outer solutions and the polyelectrolyte solution, there must be an osmotic pressure difference. The osmotic pressure difference may be calculated from

$$\Delta\pi = RT \sum_i \phi_i \Delta c_i \, , \qquad (4)$$

where ϕ_i is the osmotic coefficient of the ith species dissolved in the solution. In the present case, however, no pressure difference can be set up inside the membrane phase, since the phase is a uniform solution. That is, the pressure distribution in the direction of flow cannot reach any equilibrium state or steady state. Therefore, the anomalous osmosis through the model membrane constructed with polyelectrolyte solution cannot be explained by the abnormal pressure difference inside the membrane.

Acknowledgement

The authors wish to thank Professor M. Nagasawa of Nagoya University for many helpful discussions.

References

[1] J. Loeb, J. Gen. Physiol. 1 (1919) 717.

[2] F.E. Bartel and D.C. Carpenter, J. Phys. Chem. 27 (1923) 101.

[3] E. Grim and K. Sollner, J. Gen. Physiol. 40 (1957) 887.

[4] Y. Toyoshima, Y. Kobatake and H. Fujita, Trans. Faraday Soc. 63 (1967) 2828.

[5] M. Tasaka, Y. Kondo and M. Nagasawa, J. Phys. Chem. 73 (1969) 3181.

[6] O. Kedem and A. Katchalsky, J. Gen. Physiol. 45 (1961) 143.

[7] W. Dorst, A.J. Staverman and R. Caramazza, Rec. Trav. Chim. 83 (1964) 1329.

[8] R. Schlögl, Z. Phys. Chem. (Frankfurt am Main) 3 (1955) 73.

[9] E. Riande, Physics of Electrolytes, ed. J. Hladik, Vol. 1 (Academic Press, London, 1972) ch. 11.

[10] M. Tasaka, N. Aoki, Y. Kondo and M. Nagasawa, J. Phys. Chem. 79 (1975) 1307.

[11] A. Katchalsky, Z. Alexandrowicz and O. Kedam, Chemical Physics of Ionic Solutions, eds. B.E. Conway and R.G. Barradas (Wiley, New York, 1966) ch. 15.

[12] M. Nagasawa, Polyelectrolytes, ed. E. Sélégny (Reidel, Dordrecht, The Netherlands, 1974) p. 57.