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OSMOMETRY WITH MEMBRANES PERMEABLE TO SOLVENT AND SOLUTE

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ANOMALOUS OSMOSIS RESULTING FROM PREFERENTIAL ABSORPTION

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NEGATIVE REFLECTION COEFFICIENTS

Negative Reflection Coefficients

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The reflection coefficient of porous Vycor glass towards aqueous solutions of polyethylene glycol, measured by ultrafiltration, has negative values at lower polymer concentrations. This is in qualitative agreement with the abnormally low and negative values of the apparent osmotic pressure found by Elias for such systems. This work gives an example of anomalous osmosis in a non-electrolyte system.

In a previous paper [1] we reported measurements of the reflection coefficients σ of porous Vycor glass for aqueous sugar solutions. The value of this parameter, approx. 0·2 for all concentrations used, was numerically identical with the ratio
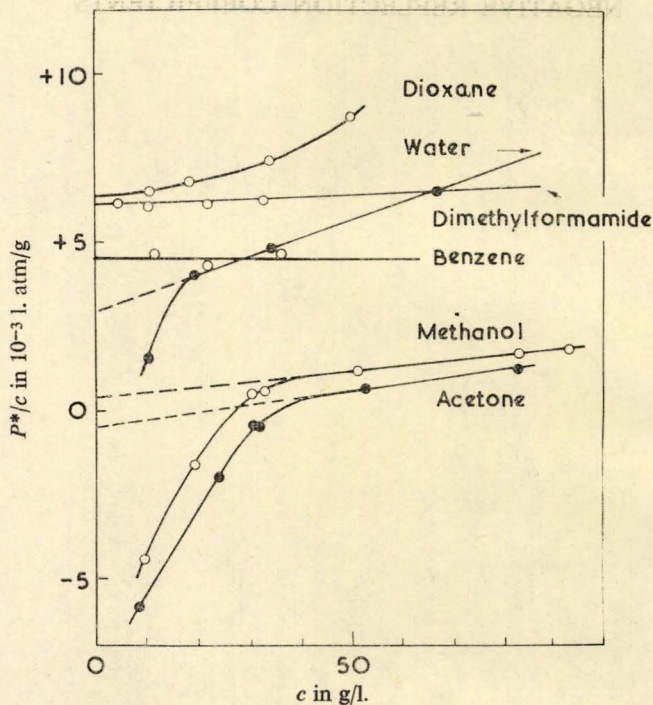

Fig. 1.—Reduced apparent osmotic pressure of PEG 4000 in different solvents according to Elias.[3]

P^*/π between the apparent and the true osmotic pressures of the solutions, as predicted theoretically by Staverman.[2] Although the underlying theory was of a completely general character and the choice of system was quite arbitrary, it may rightly

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be asked whether the results of one experiment are a sufficient basis for generalization. This holds *a fortiori* for the observed independence of concentration of the reflection coefficient, about which the theory does not give any indications.

It is the purpose of this paper to give experimental evidence of systems in which the reflection coefficient varies strongly with concentration ; such variation, however, need not affect the validity of the equation $\sigma = P^*/\pi$.

Recently, Elias [3] made some measurements of the apparent osmotic pressures of polyethylene glycol (PEG) solutions at Vycor membranes. In some cases, dependent on the solvent used, the values of P/c^* below a certain concentration were abnormally low or even negative (fig. 1).

As the osmotic pressure π cannot be negative, the reflection coefficient σ, together with P^*, must change sign in such cases. In order to check this we have measured the reflection coefficients of Vycor towards aqueous solutions of two PEG fractions at various concentrations down to 1 g/l.

EXPERIMENTAL

The type of osmometer and the procedure of measuring σ by ultrafiltration have been described.[1] The PEG fractions used were of average molecular weight 10,000 (Anorgana) and 1,000 (Fluka). For concentration measurements we used a water-interferometer ;
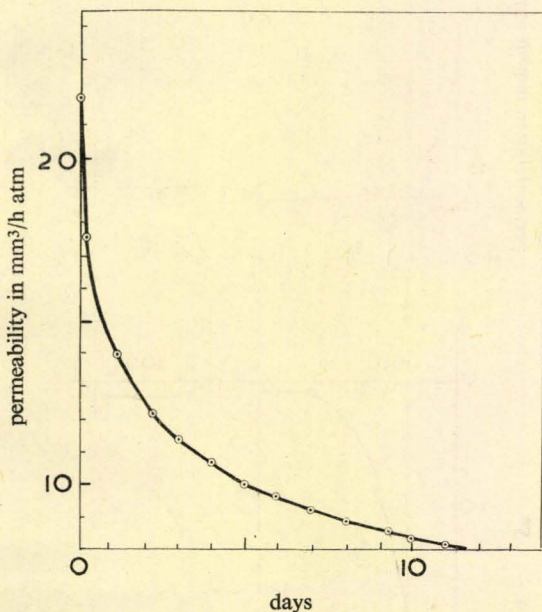

FIG. 2.—Decrease of permeability of Vycor membrane with PEG.

acetone or methanol, though larger effects are expected, could not be used as a solvent. In contrast to our experience with sugar solutions, an experimental complication arose due to the fact that a substantial portion of the polymer was absorbed in the membrane, causing an additional change in the concentration of the solutions to that brought about by ultrafiltration, and thereby giving apparent reflection coefficients S^*. This absorption was accompanied by a considerable decrease in the permeability of the membranes, which made ultrafiltration times of several days necessary in order to get sufficient changes in concentration. As seen from fig. 2 the preceding acclimatization was still more protracted.

Therefore we tried to quicken the absorption of polymer by warming the membranes in solution up to near the boiling point. Although this resulted in a substantially lowered permeability within a few hours, complete saturation could not be reached in this way. In table 1 we quote some preliminary data as to the effect of warming up membrane E in a 4 g/l. aqueous solution of PEG 10,000.

TABLE 1.—DECREASE IN PERMEABILITY OF VYCOR MEMBRANE E AFTER WARMING IN 4 g/l. AQUEOUS SOLUTION OF PEG 10,000

permeability in mm³/h atm for	E
water	23·3
4 g/l. after warming up for 1½ h	10·2
4 g/l. next day	10·3
water after cleaning the membrane	23·8
4 g/l. after warming up for ½ h	14·4
4 g/l. next day	13·4
4 g/l. after 2 days	12·4
4 g/l. after warming up for 3½ h	9·2
4 g/l. next day	9·9
4 g/l. after 2 days	9·9

As seen in table 2 the permeability continues to decrease during subsequent measurements, indicating that the membrane was not yet saturated. The peculiar rise in per-
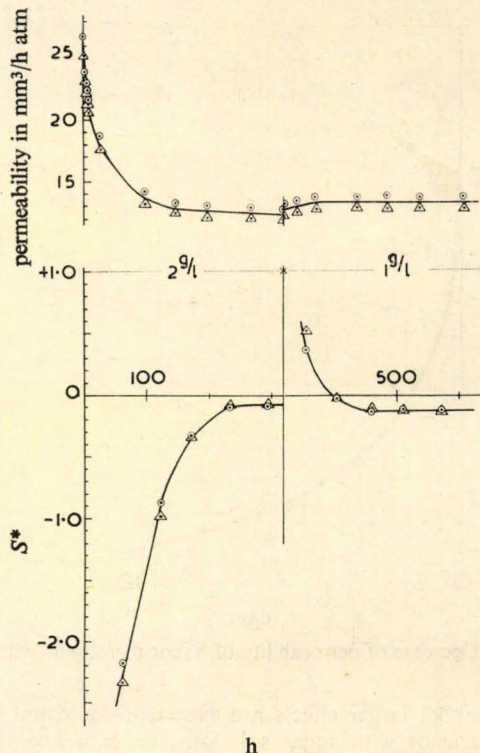

FIG. 3.—Decrease of permeability of Vycor membrane for PEG 1000.

meability during the first days after warming, seen in the last three lines of table 1, seems to be a common phenomenon, which is apparent in table 2 as well. For PEG 10,000 this warming technique resulted at least in an ever decreasing permeability; however, it proved to be less useful in working with aqueous solutions of PEG 1,000. Here the

spontaneous acclimatization at room temperature was faster (resulting in much larger errors if determinations of σ were made too early) whereas the permeability after warming had a value which was relatively high compared with that reached after complete saturation. In PEG 1,000 solutions we preferred therefore acclimatization at room temperature.

Fig. 3 gives an illustration of the necessity of waiting to measure the reflection coefficient until there is no more absorption or desorption of polymer at the membrane.

TABLE 2.—ULTRAFILTRATION OF AQUEOUS SOLUTIONS OF PEG 10,000 THROUGH VYCOR MEMBRANES D AND E

mbr.	conc. in g/l.	permeability (mm³/h atm) before and after ufn.		duration of ufn. (h)	S^*
D	4	8·4	8·2	22·0	−0·03
D	2	7·2	7·3	45·0	−0·38
D	2*	7·3	6·8	65·5	−0·36
D	32	4·9	5·2	47·0	+0·87
D	1	5·4	5·4	89·5	−0·96
D	8	4·5	4·5	45·5	+0·78
E	4	9·9	9·9	22·5	+0·21
E	2	8·3	8·5	45·5	−0·18
E	2*	8·5	7·9	66·0	−0·21
E	32	5·7	6·0	47·5	+0·90
E	1	6·2	6·3	90·0	−0·75
E	8	5·2	5·4	46·0	+0·79

* without preceding warming of membrane in solution.

c in g/l.

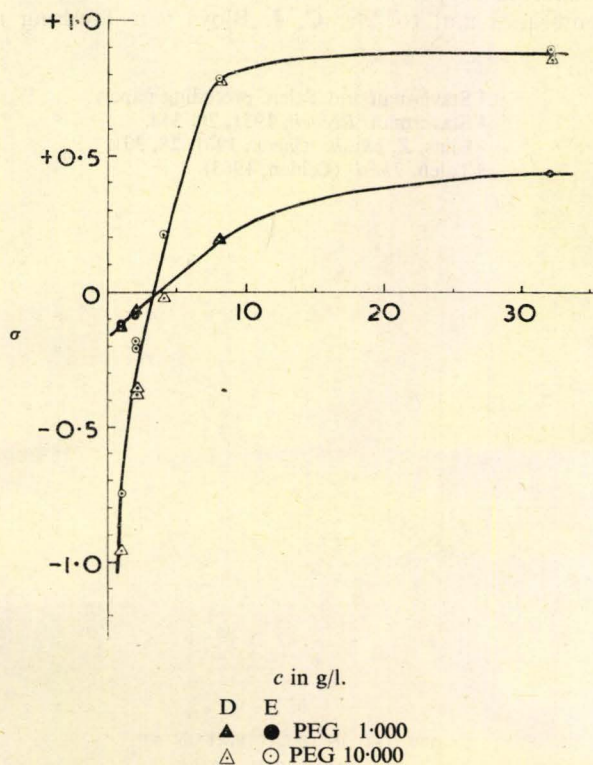| D	E	
▲	●	PEG 1·000
△	☉	PEG 10·000

FIG. 4.—Reflection coefficients as a function of concentration.

RESULTS

In fig. 4 are summarized the values of the reflection coefficients of Vycor for aqueous solutions of PEG 1,000 and 10,000.

Those for PEG 1,000 have been measured under the right experimental conditions of constant permeability of the membrane. Those for PEG 10,000, on the other hand, are taken from table 2 which gives only apparent values S^*, as they are measured before the membrane was saturated with polymer.

Although our identification $S^* = \sigma$ may consequently not be quite correct there is little doubt that the existence of a negative reflection coefficient at low concentration has, at any rate qualitatively, been established for solutions of this polymer. This may be seen, e.g., from the value $S^* = -0.75$ found for membrane E towards 1 g/l. solution in spite of the fact that the permeability has even increased. Moreover, if we compare the two pairs of measurements at 2 g/l., the changes in permeability do not appear to have a significant influence on the values of S^*.

We therefore conclude (i) that, although there exist systems in which the reflection coefficient is not dependent on concentration, this is by no means a general rule, and (ii) that comparison with the results of Elias gives qualitative evidence for the equality $\sigma = P^*/\pi$ to hold also for negative reflection coefficients. Thus, we expect that anomalous osmosis does not invalidate the molecular weight determination described in the foregoing paper.

[1] Staverman and Talen, preceding paper.
[2] Staverman, *Recueil*, 1951, **70**, 344.
[3] Elias, *Z. physik. Chem.*, 1961, **28**, 301.
[4] Talen, *Thesis* (Leiden, 1963).