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Studies on Ultrafiltration

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A high pressure cell for the study of ultrafiltration through membranes was built and ultrafiltration experiments were carried out with solutions of some oligosaccharides and sodium bromide. With the oligosaccharides comparative osmotic measurements were also carried out. The experimental data were interpreted on the basis of a previously presented theory of ultrafiltration and good agreement between theory and experiments was found. The validity of Onsager reciprocal relations was proved within the limits of experimental error.

The present article is concerned with an experimental study of ultrafiltration through membranes. It is an extension of the theoretical work presented in a preceding article,[1] in which the theory of the ultrafiltration process was derived, the treatment being based on irreversible thermodynamics. The object of the present work has been to provide a general experimental background of the problem and make comparison between experiments and theory possible.

EXPERIMENTAL

Ultrafiltration cell. The cell was built of nonmagnetic stainless steel and was capable of withstanding high pressure. It was constructed according to the requirements specified in the preceding article.[1] Thus, the solution compartment on the high-pressure side was large and provided with a magnetic stirrer. By this means the concentration in this compartment was kept uniform and nearly constant during the experiment. On the other hand, the compartment on the low-pressure side was very small. The membrane was supported by a fine-mesh stainless steel wire gauze, which was placed directly on the plane surface of a stainless steel block. The latter was provided with a few shallow drainage-grooves. Thus, this compartment was composed essentially of the void space in the mesh. In order to tighten the gauze radially, its brim was provided with a PVC packing, which filled the void space in the mesh, and was applied to the gauze in the form of a solution of PVC in cyclohexanone. The two cell blocks were held together by two powerful yokes. For temperature control the cell was enclosed in a close-fitting box, the walls of which were covered with coils of copper tubing through which thermostated water was circulated.

The solution volume to be filtered was supplied from a cylindrical container on top of the cell. Pressure was applied from a nitrogen bomb, which was connected *via* stainless steel capillary tubing. The cell had the following dimensions:

membrane area $S = 78.6$ cm^2
volume of the compartment on the high pressure side $V = 136$ cm^3
volume of the compartment on the low pressure side $= 2$ cm^3
volume of the supply cylinder $= 30$ cm^3.

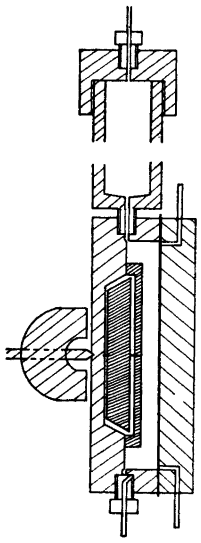

Fig. 1. Cross-section of ultrafiltration cell.

A cross-section of the cell is shown in Fig. 1.

For an accurate measurement of the filtration pressure a pressure gauge was connected to the high-pressure gas system. This was a closed mercury column manometer. It had the form of a U-tube, its closed end being filled with nitrogen. It allowed accurate measurements to be made up to a pressure of about 15 atm.

Membrane. The membrane was a partially acetylated cellophane membrane, of the type described in Ref. 2. In the present case the acetylation was carried out in a 1:1 mixture of acetic anhydride in pyridine, at 55°C for 16 h.

Osmotic measurements. As a supplement to ultrafiltration, osmotic measurements were also carried out. The instrument used in these measurements was a symmetric block-type osmometer provided with organic liquid manometers, of a type described in earlier articles.[3,4] The treatment of data also followed the lines of earlier articles.[5] Thus, the time dependence of the measured pressure difference is represented by the formula

$$p(t) = A(\mathrm{e}^{-mt} - \mathrm{e}^{-nt}) + p_0\,\mathrm{e}^{-nt} \tag{1}$$

where p_0 is the pressure difference at zero time and the parameters A, m, and n have the following expressions

$$A = \frac{\sigma}{1 - (m/n)} \frac{RT}{M_2} \Delta c_0 \tag{2}$$

$$m = \frac{2S'L_{22}v_1\gamma(1 - \bar{c}_3)}{V'd} \frac{RT}{M_2} \tag{3}$$

$$n = \frac{aS'L_{11}v^2{}_1(1 - \bar{c}_3)}{d} \tag{4}$$

Here S' is the membrane area and V' the volume of the osmometer half-cell. The parameter a in (4) is an apparatus constant. With the rather stiff membranes used in the present experiments the balloon effect was negligible, hence

$$a = \frac{2\varrho}{\pi r^2\ 1033}\ \text{atm cm}^{-3} \tag{5}$$

where ϱ is the density of the manometer liquid in the osmometer and r is the radius of the manometer capillaries. For the osmometer used the following data apply

ϱ = 0.655 (hexane, 25°C)
r = 0.0249 cm
S' = 38.0 cm² (membrane area)
V' = 4.56 cm³ (volume of half-cell)

The membrane used in the osmotic measurements was identical with the one used in ultrafiltration. It was removed from the ultrafiltration cell and mounted in the osmometer after the ultrafiltration experiments were completed. The osmotic experiments were carried out differentially, the mean concentrations $\bar{c}$ having values in the vicinity of those encountered in the corresponding ultrafiltration experiments. All osmotic measurements were carried out at 25°C.

Chemicals. The measurements were carried out with aqueous solutions of the following substances:

Glucose. Anhydrous D-glucose from Fisher's Scientific Company, U.S.A. The sample was dried in vacuum at 85°C.

Sucrose. The sample was a "Baker's Analyzed" reagent and was dried in vacuum at 85°C.

Raffinose. Raffinose hydrate from British Drug House Ltd. The anhydrous product was prepared by drying to constant weight in vacuum at 85°C.

Sodium bromide. The sample was a "Baker's Analyzed" reagent and was dried at 300°C.

Performance of the ultrafiltration experiments. The experiments were started by filling the cell and the cylindrical container with a solution of known concentration. This was done *via* the inlet in the bottom of the cell, thus avoiding trapped air. Pressure was then applied and filtration started. The first few ml of filtrate were discarded, after which the filtrate was collected in a weighing-bottle, and the amount collected during a measured time interval was determined by weighing. The filtrate was then analyzed for its solute content. During the experiment occasional readings of the filtration-pressure were made. All the experiments were carried out at 25°C.

Concentration determination. The concentration determination in the filtrate involved some novel features. It was pointed out in a previous article [2] that osmometry with tight membranes provides a sensitive method for concentration determination. Here the method was tried in the experiments with oligosaccharides. The solution to be analyzed was matched in the osmometer against a solution of known concentration and from the rate of change of the level difference in the capillaries the concentration of the unknown solution was deduced. In general two runs were made, with reference solutions having concentrations on either side of the unknown concentration. In the present case the membrane was of the same type as used in the ultrafiltration experiments and the osmometers were of the type mentioned above. With this experimental arrangement a concentration difference of 10^{-4} M could be determined with an accuracy of about 10 %. This means that in the case the unknown concentration is in the vicinity of 0.01 M, the error is of the order of 0.1 %.

In the case of NaBr the analysis was carried out by titration with $AgNO_3$, using eosin as indicator.

RESULTS AND DISCUSSION

The treatment of the experimental data was carried out according to the general lines specified in the preceding theoretical article.[1] The primary experimental quantities to be determined were the total mass flow, J, and the solute concentration in the filtrate, c'. From the concentration of the filtrate and the known concentration of the solution in the ultrafiltration cell, c, the concentration difference $\Delta c = c' - c$ and the separation efficiency $\delta = -\Delta c/c$ could be calculated. It should be observed in this connection that with the present experimental arrangement the process is quasi-stationary rather than

Table 1. Primary experimental data from ultrafiltration experiments.

Initial solution	P atm.	J g/min	$\bar{c}'$ g/l	δ
Glucose $c = 0.8419$ g/l	3.704	0.0455	0.4759	0.445
	5.010	0.0630	0.4384	0.494
	7.092	0.0916	0.3863	0.553
	9.662	0.1273	0.3525	0.594
	12.05	0.1608	0.3260	0.626
Sucrose $c = 0.4409$ g/l	3.445	0.0480	0.1019	0.776
	6.411	0.0910	0.0777	0.832
	9.680	0.1382	0.0693	0.851
	12.82	0.1842	0.0620	0.868
Sucrose $c = 4.409$ g/l	2.602	0.0314	1.003	0.779
	3.319	0.0404	0.873	0.810
	4.034	0.0507	0.768	0.834
	4.528	0.0566	0.763	0.835
	7.404	0.0962	0.6274	0.867
	9.730	0.1286	0.5323	0.888
	12.09	0.1639	0.5141	0.892
	13.25	0.1824	0.5203	0.891
Sucrose $c = 14.917$ g/l	3.221	0.0277	3.154	0.797
	4.314	0.0411	2.637	0.832
	5.368	0.0533	2.229	0.859
	11.63	0.1321	1.766	0.890
Raffinose $c = 1.8767$ g/l	1.020	0.01235	0.2285	0.884
	1.039	0.01260	0.2220	0.888
	1.564	0.01931	0.1988	0.901
	1.585	0.01987	0.1564	0.922
	3.766	0.0474	0.1054	0.947
	6.950	0.0927	0.0817	0.959
	9.297	0.1246	0.0938	0.953
	10.67	0.1450	0.0999	0.950
	13.42	0.1869	0.0837	0.958
NaBr $c = 10.294$ g/l	2.143	0.0283	9.745	0.0543
	2.692	0.0361	9.648	0.0640
	3.368	0.0457	9.467	0.0820
	5.116	0.0687	9.140	0.1146
	6.625	0.0900	8.933	0.1352
	7.985	0.1077	8.791	0.1493
	9.021	0.1230	8.654	0.1630
	11.23	0.1568	8.365	0.1918
H_2O	1.210	0.01710		
	2.280	0.03102		
	3.267	0.04454		
	5.951	0.08380		
	8.722	0.1257		
	12.53	0.1842		
	13.41	0.1984		

stationary, as during the filtration process solute is enriched in the solution on the high pressure side and accordingly its concentration gradually rises. This was taken into account in the calculations (see Appendix) and all δ-values listed below have been properly corrected. The primary data from ultrafiltration experiments are listed in Table 1.

It follows from the treatment in Ref. 1 that the relation between the separation efficiency and the filtration pressure may be written in linearized form as follows

$$1/\delta = 1 + k_1(1/P) \tag{6}$$

with

$$1 = (1 + \sigma)/2\sigma \tag{7}$$

$$k_1 = \frac{L_{22}\,\gamma\,RT}{\sigma\,L_{11}v_1M_2} \tag{8}$$

The experimental data are found to fit eqn. (6) well, which is illustrated in the case of the oligosaccharides in Fig. 2. The coefficients in (6) were also determined by the method of least squares and the results are listed in Table 2.

From the total mass flow, J, and solute concentration in the filtrate, c', the individual mass flows, J_1 and J_2, may be determined. Considering the solvent flow, J_1, we find that with the dilute solutions used in the present investigation we have for all practical purposes $J_1 = J$. According to eqn. (18) of Ref. 1 we then have the following approximate formula

$$J = k_2\left(P + \sigma\frac{RT}{M_2}\,\Delta c\right) \tag{9}$$

with

$$k_2 = \frac{L_{11}Sv_1(1 - \bar{c}_3)}{d} \tag{10}$$

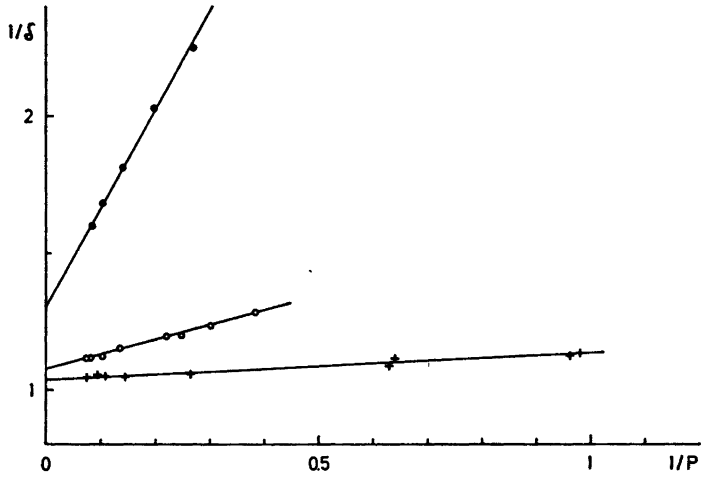

Fig. 2. Plots of ultrafiltration data according to eqn. (6) for solutions of glucose ●, sucrose ○, and raffinose +.

Table 2. Results of ultrafiltration experiments.

Solute g/l	l	Std.dev. of l	k_1 atm.	Std.dev. of k_1	k_2 g/min atm.	σ	Std.dev. of σ
Glucose c = 0.8419	1.327	0.038	3.362	0.081	0.0136	0.605	0.028
Sucrose c = 0.4409	1.106	0.012	0.627	0.024	0.0142	0.825	0.016
c = 4.409	1.078	0.008	0.524	0.019	0.0137	0.865	0.012
c = 14.92	1.065	0.035	0.594	0.064	0.0124	0.885	0.055
Raffinose c = 1.877	1.037	0.004	0.095	0.008	0.0131	0.932	0.009
NaBr c = 10.29	2.12	0.32	35.2	0.76	0.0138	0.309	0.061
H_2O					0.0137		

In Fig. 3 plots according to eqn. (9) of the experimental data for pure water and a sucrose solution are shown. The curves are found to bend upward at high pressure, indicating a deviation from the linear law. The slopes in eqn. (9) for the different solutions were determined graphically, using the straight part of the curves, and the results are listed in Table 2.

With sucrose measurements were carried out at different concentrations and the data in Tables 1 and 2 reveal a marked concentration dependence in the ultrafiltration process, the efficiency δ increasing and the total mass flow J decreasing with increasing concentration. This indicates a strong interaction between solute molecules and may be interpreted as being due to clogging of the membrane by the solute.

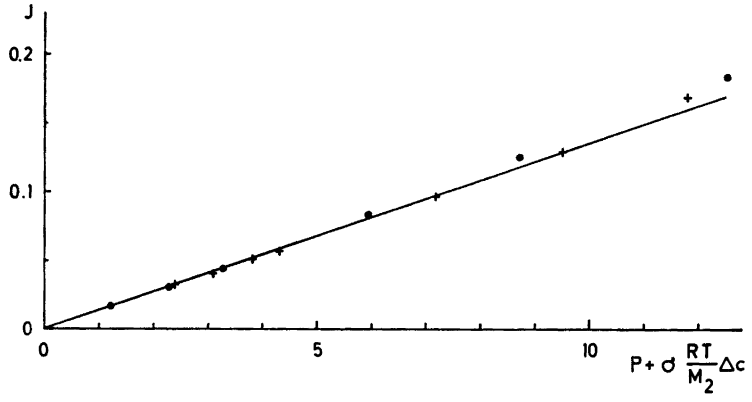

Fig. 3. Plots of ultrafiltration data according to eqn. (9) for a sucrose solution (c = 4.409 g/l) +, and pure water ●.

In the osmotic experiments the parameters A, m, and n were determined. The results for the different oligosaccharides are listed in Table 3. In the case of NaBr the solute permeation was too fast to allow reliable osmotic data to be obtained.

Table 3. Results of osmotic experiments.

Solute	$\bar{c}$ g/l	Δc g/l	$A \times 10^3$ atm.	$m \times 10^3$ min^{-1}	$n \times 10^3$ min^{-1}	σ	$\Delta\sigma$
Glucose	0.5796	0.0940	−28.61	6.0	4.7	0.62	± 0.02
Sucrose	0.4680	0.1040	7.41	0.88	4.7	0.81	± 0.015
Raffinose	1.925	0.2026	9.30	0.18	4.7	0.91	± 0.015

We are now in the position to compare the results from ultrafiltration with those of osmosis. Considering the reflexion coefficient σ we recall from Ref. 1 that in ultrafiltration and osmosis different cross-coefficients in the phenomenological equations are dominant. Hence, a comparison of σ-values determined by these two methods provides an experimental basis for the verification of Onsager reciprocal relations. It is seen from Tables 2 and 3 that in all cases investigated the two σ-values lay within experimental error from each other. Thus, within the limits of experimental accuracy, this proves the validity of the reciprocal relations. We shall next consider in more detail the limitations imposed on this proof by the experimental error. We observe that the phenomenological coefficients L_{12}, L_{21} are roughly proportional to $1 - \sigma$. This follows from the definition of σ and the relative magnitudes of the phenomenological coefficients. This means that the relative errors of the phenomenological coefficients become magnified in comparison to those of σ, and the situation becomes increasingly unfavourable as σ approaches unity. Thus, in the case of ultrafiltration we find the errors in L_{21} to be about 7, 9, and 13 % for glucose, sucrose, and raffinose, respectively, and in the case of osmosis the errors in L_{12} are of the same order of magnitude. Considering the uncertainty in the reciprocal relations we find from the observed differences between the two σ-values and their respective errors that the differences between L_{12} and L_{21} for glucose, sucrose and raffinose may not surpass 16, 25, and 58 % of the mean values of the respective coefficients. We thus find that from experimental standpoint considerable uncertainty remains about the validity of the reciprocal relations and that, owing to the unfavourable influence of experimental error, an accurate verification of these relations is extremely difficult.

We may also compare some other results from the ultrafiltration and osmotic experiments. We observe that

$$\frac{k_1 k_2 \sigma}{S} = \frac{mV'}{2v_1 S'} = \frac{L_{22}\gamma(1 - \bar{c}_3)}{d} \frac{RT}{M_2} \tag{11}$$

and

$$\frac{k_2}{S} = \frac{n}{av_1 S'} = \frac{L_{11} v_1 (1 - \bar{c}_3)}{d} \tag{12}$$

A comparison of these quantities is made in Table 4. Although in some instances large deviations occur the agreement may be considered satisfactory, in view of the great differences in experimental conditions between the two sets of measurements and the experimental errors involved.

Table 4. Comparison of ultrafiltration and osmotic data.

Solute	$\frac{k_1 k_2 \sigma}{S} \times 10^3$	$\frac{m\ V'}{2v_1 S'} \times 10^3$	$\frac{k_2}{S} \times 10^4$	$\frac{n}{av_1 S'} \times 10^4$
Glucose	0.35	0.36	1.73	1.90
Sucrose $c = 4.409$ g/l	0.079	0.053	1.74	1.90
Raffinose	0.0148	0.0108	1.67	1.90

APPENDIX

To estimate the effect of solute enrichment on the high pressure side of the membrane, we consider the following mass balance equation for solute:

$$V\ \mathrm{d}c = (c_0 - c')\ \mathrm{d}v \tag{13}$$

where

v = volume of filtrate
V = volume of ultrafiltration cell
c_0 = concentration of initial solution
c' = concentration of filtrate
c = concentration of solution in ultrafiltration cell.

By definition

$$\delta = -\frac{\Delta c}{c} = \frac{c - c'}{c} \tag{14}$$

Hence, from (13) and (14) we get

$$V\ \mathrm{d}c = [c_0 - (1 - \delta)c]\ \mathrm{d}v \tag{15}$$

Observing that δ is a constant at constant filtration pressure, eqn. (15) may be integrated and we get

$$\frac{\ln\,[1 - (1 - \delta)\,(c/c_0)]}{1 - \delta} = -\frac{v}{V} + C$$

With the initial conditions $c = c_0$ for $v = 0$, we get

$$C = \frac{\ln\,\delta}{1 - \delta} \tag{16}$$

Hence

$$\frac{c}{c_0} = \frac{1 - \delta\,\exp[-v(1 - \delta)/V]}{1 - \delta} \tag{17}$$

The mass balance equation may also be stated in its integrated form as follows:

$$V(c - c_0) = (c_0 - \bar{c}')\, v \tag{18}$$

where $\bar{c}'$ is the mean concentration of the filtrate. As $\bar{c}'$ is the experimentally determinable filtrate concentration we define the following experimentally accessible quantity

$$\delta' = \frac{c_0 - \bar{c}'}{c_0} \tag{19}$$

According to (18)

$$\delta' = \frac{V}{v}\left(\frac{c}{c_0} - 1\right) \tag{20}$$

The right member of (20) may be evaluated with the help of eqn. (17). Expanding the exponential into Taylor series, breaking off after the second order term and substituting into (20), we get

$$\delta' = \delta\,[1 - (v/2V)(1 - \delta)] \tag{21}$$

For small corrections this may be expressed in the form

$$\delta = \delta'\,[1 + (v/2V)(1 - \delta')] \tag{22}$$

In the present experiments the filtration volume v was usually of the order of 10 — 20 ml. Thus, with $V = 136$ ml the correction was in general of the order of a few per cent.

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