

THE PREPARATION AND CHARACTERIZATION OF ALUMINA MEMBRANES WITH ULTRA-FINE PORES

PART 4. ULTRAFILTRATION AND HYPERFILTRATION EXPERIMENTS

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Summary

The rejection characteristics of three types of alumina membranes for polyethylene glycol (PEG) polymers and dextrans soluted in water have been investigated. If the temperature at which the membranes are treated is increased, the pore size increases and as a result the cut-off value also increases. The Al_2O_3 -400 membrane (i.e., the membrane treated at 400°C) exhibits a cut-off value of 2,000 for PEG while that of an Al_2O_3 -800 membrane is about 20,000. Both Al_2O_3 -500 and Al_2O_3 -800 membranes show rejections higher than 80% for the dextrans investigated. The rejection behaviour is compared with literature data on Nuclepore membranes. The performance of the alumina membranes is compared with that of other inorganic membranes. Low molecular weight solutes show only small rejection values so far, although high values are reported in the literature for Vycor glass membranes with pores of similar size.

1. Introduction

In this paper some separation characteristics of a new class of alumina membranes, developed at our laboratory [1–3], are presented. Solutions of polyethylene glycol (PEG) polymers and dextrans were chosen for the ultra-filtration experiments, because series of these polymers with a wide range of molecular weights are readily available. Moreover, these solutes are often used for the characterization of polymer membranes and therefore the performance of alumina and polymer membranes can be compared. A comparison of alumina membranes with other inorganic membranes, which are reported in literature, is also made.

The results of some hyperfiltration experiments are given in section 3.3. The direction in which further research should be directed to obtain higher separation factors is indicated.

2. Materials and methods

The synthesis and characterization of alumina membranes have been reported elsewhere [1-3] and therefore only a brief description is given here. A boehmite (γ -AlOOH) sol with 0.07 mol HNO_3 per mol boehmite and support materials as reported before [3] were used to prepare the Al_2O_3 membranes. Three types of membranes were used here. These were obtained by preparing a number of identical membranes at 400°C , some of which were then treated at 500°C and 800°C , respectively. These membranes are coded Al_2O_3 -400, Al_2O_3 -500 and Al_2O_3 -800 respectively. Their characteristics are given in Table 1 and Fig. 1.

TABLE 1

Some properties of the alumina membranes used

Membrane type	BET surface area ($\text{m}^2\text{-g}^{-1}$)	Modal slit width (nm)	Porosity (%)
Al_2O_3 -400	334	2.7	56
Al_2O_3 -500	284	2.9	56
Al_2O_3 -800	183	4.0	55

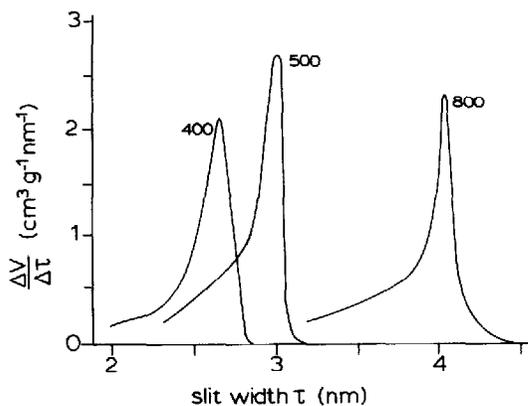


Fig. 1. Pore size distribution curves of the alumina membranes used in this study.

The polyethylene glycol polymers used have weight-average molecular weights of 400, 1000 (purchased from Serva), 3000, 6000, 20,000 (Fluka) and 100,000 (Polysciences), respectively. All dextrans were purchased from Pharmacia. The weight-average molecular weights given in the text are those according to the firm's specification.

The filtration experiments were performed in a stirred dead-end pressure cell (see Ref. [2]). Because the aim of the ultrafiltration experiments is to determine the intrinsic membrane properties, strong fouling of the mem-

brane should be prevented. This was achieved by keeping the polymer concentration and the applied pressure drops low, i.e., $1 \text{ g}\cdot\text{L}^{-1}$ and 1 bar for Al_2O_3 -800 and 3 bar for Al_2O_3 -400 and Al_2O_3 -500, respectively. The retention values for a series of homologous polymers were determined with one membrane, immediately after the flux for pure water was determined and starting with the solute with the lowest molecular weight. To obtain steady-state retention values, the first permeate obtained was discarded. When the total amount of permeate was 3 times the dead volume of the system (i.e., the porosity of the support plus the volume of the outlet of the cell), samples were taken from the permeate. When sufficient permeate was obtained the feed solution was replaced by a solution with a polymer having a higher molecular weight, etc. The solute concentrations in feed and permeate were determined with a Beckman 915 A Total Organic Carbon analyzer.

3. Results and discussion

3.1. Ultrafiltration experiments

The results of the ultrafiltration experiments are presented in Tables 2 and 3 and Fig. 2. Membrane fouling exerted only a minor influence on the ultrafiltration results. This can be concluded when the pure water fluxes are compared with the corresponding product fluxes. The solute retention, SR , is defined as usual as $SR = 1 - C_p/C_f$, where C_p and C_f are the solute concentration in the permeate and feed, respectively. It appears that the cut-off value (the molecular weight of a solute for which a retention of 90% is reached) is 2,000 for Al_2O_3 -400 and about 20,000 for Al_2O_3 -800 (see Fig. 2).

TABLE 2

Solute retention (SR) and flux data for polyethylene glycol (PEG) polymers filtered with 2 types of Al_2O_3 membranes (applied pressure drops: 3 bar for Al_2O_3 -400 and 1 bar for Al_2O_3 -800)

Molecular weight polyethylene glycol (dalton)	Al_2O_3 -400		Al_2O_3 -800	
	SR (%)	Flux ($\text{cm}\cdot\text{bar}^{-1}\cdot\text{hr}^{-1}$)	SR (%)	Flux ($\text{cm}\cdot\text{bar}^{-1}\cdot\text{hr}^{-1}$)
pure water ^a	—	0.14	—	1.1
400	39	0.14	1	1.1
1,000	78	0.14	24	1.1
3,000	94	0.13	34	1.1
6,000	97	0.12	87	1.1
20,000			90	1.0
100,000			95	1.0

^a Permeability for pure water.

TABLE 3

Solute retention (*SR*) and flux data for dextrans filtered with 2 types of Al_2O_3 membranes (applied pressure drops: 3 bar for Al_2O_3 -500 and 1 bar for Al_2O_3 -800)

Molecular weight dextran (dalton)	Al_2O_3 -500		Al_2O_3 -800	
	<i>SR</i> (%)	Flux ($\text{cm}\cdot\text{bar}^{-1}\cdot\text{hr}^{-1}$)	<i>SR</i> (%)	Flux ($\text{cm}\cdot\text{bar}^{-1}\cdot\text{hr}^{-1}$)
Pure water ^a	—	0.15	—	0.73
10,500	94	0.12	84	0.61
70,400			96	0.68
465,000	97	0.12	97	0.69

^a Permeability for pure water.

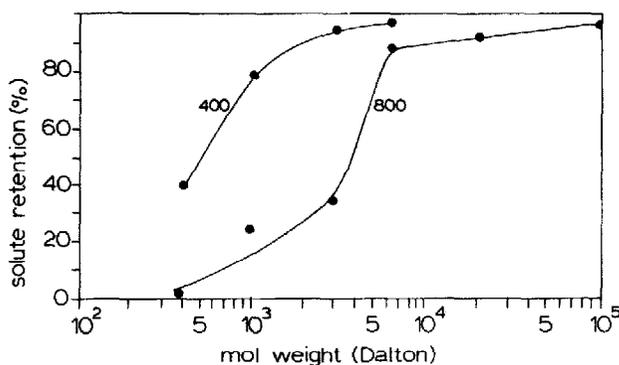


Fig. 2. Solute retention as a function of the molecular weight for polyethylene glycol polymers. The left curve is obtained with Al_2O_3 -400 membranes, the right curve with Al_2O_3 -800 membranes.

In those cases where the reported rejections exceed 90% some increase in the value of *SR* with time is found. For example, the retention of dextran-10,500 for an Al_2O_3 -500 membrane increased from 94% (see Table 3) to 98% after 15 hr of continuous ultrafiltration. These values are 97% and 99.5%, respectively, for dextran-465,000 filtered with an Al_2O_3 -800 membrane.

It is interesting to consider whether the retention data can be related to the structural data of the alumina membranes. Several investigators in the field of membrane science have tried to find relations between the pore size of membranes and the solute size on one hand and the retention of these solutes on the other hand (e.g., Refs. [4–6]). Zeman and Wales [4] have examined these relations for PEG and dextran solutions using Nuclepore membranes with a well-defined pore size. They found that the “pore entrance sieving” relation derived by Ferry [7] fits their results rather well for

SR values smaller than about 80%. This equation relates the solute retention (*SR*) to the ratio of the solute radius and the pore radius (λ).

An accurate comparison of our data with those of Zeman and Wales [4] is complicated by the following matters:

- (1) The retention values are known to be strongly dependent on pressure drop, flux and stirring conditions [4,8].
- (2) The pores of alumina membranes are slit-shaped instead of the cylindrically shaped pores of the Nuclepore membranes.

According to Sarbolouki [6], theory predicts that slit- and cylindrical-shaped pores show about the same retention under similar circumstances, if the slit width equals the diameter of a cylindrical pore and high retention values are considered ($\geq 80\%$). These requirements can be comprehended by noting that when λ approaches the value of 1, the shape of the pore becomes unimportant. To take into account most of the complications given above, a retention value close to 80% was taken as a basis for comparing our results with those of Zeman and Wales (see Table 4). The solute radii were calculated along the same lines as described by Zeman and Wales [4]. For dextran the Stokes radius was used [4] and for PEG polymers the radii of gyration were calculated with the Flory-Fox equation also used by Zeman and Wales [4]. Our experimental result for the filtration of dextran with Al_2O_3 -800 (given in Table 4, 3rd row, 3rd column) is in good agreement with that of Zeman and Wales (3rd row, 7th column). Zeman and Wales only present results for PEG polymers up to retentions of 63%. Their results for PEG and dextran solutions fall on the same curve when *SR* is plotted as a function of λ . If it is assumed that this will hold up to retentions of 80%, our retention data for PEG polymers can be compared with the data for dextrans obtained by Zeman and Wales. This comparison is made in the first and second row of Table 4.

TABLE 4

Comparison of the retention behaviour of the Al_2O_3 membranes with that found by Zeman and Wales [4]. SR_{exp} : solute retention found experimentally with Al_2O_3 membranes when the molecular weight is M_w (from Fig. 2 and Table 3). $SR_{\text{Zeman+Wales}}$: solute retention found experimentally by Zeman and Wales [4] with the same values for λ . Applied pressure drops: Zeman and Wales: 3.3 bar, Al_2O_3 -400: 3 bar and Al_2O_3 -800: 1 bar

Membrane type	Solute type	SR_{exp} (%)	M_w (dalton)	Solute radius (nm)	λ (—)	$SR_{\text{Zeman+Wales}}$ (%)
Al_2O_3 -400	PEG	80	1,000	1.31	0.92	86
Al_2O_3 -800	PEG	80	5,000	2.73	1.4	> 89 ^a
Al_2O_3 -800	dextran	84	10,500	2.38	0.85	83

^a Value for $\lambda = 1.05$.

It appears that the agreement between our data (3rd column) and those of Zeman and Wales (7th column) is somewhat poor. This might be due to a difference in the orientation of the PEG molecules in the pores of the membranes. The alumina membranes have slit shaped pores and the orientation of the linear flexible PEG molecules is restricted only by the slit width ("one-dimensional restriction"), while the PEG molecules inside the nuclepore membranes are "two-dimensionally restricted" in their orientation (cylindrical pores). The PEG molecules might therefore pass the pores of the alumina membranes more easily, resulting in a lower retention value. The good agreement found for dextran (see above) can be explained by taking into account that dextran is slightly branched. Therefore, orientation of the molecules inside the pores of the membranes will play a less important role.

In the reasoning above, specific interactions between the polymeric solute and the membrane have been disregarded. This can be justified as follows. It is known, that the ratio of the "pure water flux" and the product flux during ultrafiltration is a very sensitive measure for fouling and specific interactions. As is shown in Table 2, the product flux for PEG equals the pure water-flux for *SR* values of 80% (this value is used in Table 4). Zeman and Wales also find no indications of specific interactions for PEG on the basis of flux values. As shown in Table 3 for dextran the product flux at a solute retention of 84% is 16% lower than the pure water flux. Zeman and Wales find a decrease of 10% for dextran. Both values are small, indicating a minor influence of fouling on specific interactions. Moreover, both values are close to one another, indicating that specific effects (if present) are comparable.

It should be stressed, that the results presented above serve illustrative purposes only. As has been shown before [1], membranes with larger pores can be prepared by heat-treatment at temperatures above 800°C. Membranes with somewhat smaller pores than used here can be prepared as well, by increasing the amount of acid in the precursor sol, as has been found for HClO₄ [1]. Furthermore, a five-fold increase in product flux can be obtained when the membrane thickness is reduced from 5 μm, as used here, to about 1 μm. Such an increase in flux would bring the alumina membranes and the polymer membranes [8,9] in the same range of flux values at a given value for the retention and for a given polymer solution.

3.2. A comparison of the ultrafiltration properties of alumina with other inorganic membranes

Only a few types of inorganic membranes which are suitable for large-scale separation purposes are presented in the literature. These are: Vycor-type glass membranes, dynamically formed membranes and the Union Carbide/SFEC membranes. A brief description of these membranes will now be given.

No data on the separation of polymers from solvents are available for glass membranes with very small pores. Based on a modal pore size of about 4 nm, a somewhat larger cut-off value than that for Al₂O₃-400 is to be expected. A major drawback of the old generation glass membranes is their instability.

Their matrix dissolves slowly in an aqueous environment [10]. More recently, claims have been made by Schnabel that these problems can be solved by applying organic coatings to the glass surface [11,12]. If these claims prove to be true, these glass membranes should have a membrane performance comparable with the Al_2O_3 membranes.

Dynamic membranes are formed by filtering a colloidal solution through a relatively coarse porous support under cross-flow filtration conditions. After a certain period, a filter-cake is formed, which can be applied as a membrane. Inorganic dynamic membranes which show the best performance so far are the ZrO_2 /PAA (polyacrylic acid) membranes. Here first a ZrO_2 filter-cake is formed. Then PAA is added and the PAA molecules become located in the pores of the ZrO_2 layer [13]. The performance of this type of membrane is described in Ref. [14] and is comparable with that of the Al_2O_3 membranes. Some disadvantages of this type of membrane are its chemical instability, and the fact that it has to be reformed frequently and cannot be obtained in dry form.

The membranes manufactured by Union Carbide/SFEC are composed of zirconia on a carbon support. A lowest cut-off value of 20,000 is reported [15,16], probably for proteins. Because it is known [8] that for a given membrane higher cut-off values can be obtained with flexible polymers than with proteins, the cut-off value for this type of membrane determined with PEG solutions will probably yield a value larger than 20,000. The pores of this type of membrane will then be larger than those of Al_2O_3 -800, which has a cut-off value of 20,000 for PEG solutions.

When the properties of our Al_2O_3 membranes are compared with the inorganic membranes described above, the following conclusions can be drawn:

- (1) The pore size of the Al_2O_3 -400 membrane is smaller than that of the Union Carbide/SFEC-membranes and about the same as the pore size of glass and dynamic membranes.
- (2) Contrary to the new generation glass membranes and the dynamic membranes, the Al_2O_3 membranes do not contain organic groups. Therefore less limitations with respect to temperature and chemical environment are to be expected for Al_2O_3 membranes. Furthermore, the Union Carbide/SFEC membranes have a limited temperature range where they can be applied ($< 120^\circ\text{C}$).

Further research on the stability in more aggressive environments and on the long-term behaviour of the Al_2O_3 membranes is necessary to obtain a complete overview of the areas where Al_2O_3 membranes should be applied preferably.

3.3. *Hyperfiltration experiments*

It has been reported in the literature that neutral low molecular weight solutes can be separated from their solvents with fair retention values using Vycor-type glass membranes [17,18]. ZrO_2 and ZrO_2 /PAA dynamic mem-

TABLE 5

Solute retentions (*SR*) and fluxes for Al_2O_3 -400 membranes during hyperfiltration at pressure drops of 40 bar. Literature data for Vycor-type glass membranes [18,22] and dynamic membranes are also given [14,19]

Membrane type	Solute		Ethanol		s-Butanol		Raffinose	
	<i>SR</i> (%)	Flux ($\text{cm}\cdot\text{bar}^{-1}\cdot\text{hr}^{-1}$)	<i>SR</i> (%)	Flux ($\text{cm}\cdot\text{bar}^{-1}\cdot\text{hr}^{-1}$)	<i>SR</i> (%)	Flux ($\text{cm}\cdot\text{bar}^{-1}\cdot\text{hr}^{-1}$)	<i>SR</i> (%)	Flux ($\text{cm}\cdot\text{bar}^{-1}\cdot\text{hr}^{-1}$)
Al_2O_3 -400	8	0.096	12	0.091	16	0.086	28	0.082
Glass membranes	70	?					26	?
Dynamic membranes (ZrO_2/PAA)	45	0.28			43 ^a	0.24 ^a	60	0.2

^a n-Butanol has been used here.

branes have also been used for this type of separation [19,14]. The results of some preliminary experiments are given in Table 5, together with data from the literature. It appears that the Al_2O_3 -400 membrane shows only low retention values. The conclusion is therefore that pore size is but one of the parameters determining the membrane separation efficiency. The interaction forces between solute, solvent and membrane material play an important role as well. The membrane transport processes can be described with the preferential sorption/capillary flow model, developed by Sourirajan et al. (e.g., Refs. [20,21]), which takes these interaction forces into account. To obtain high separation factors for low molecular weight solutes with our sol/gel type membranes further research should be directed to the following points:

- (1) Changing the nature of the membrane surface by surface modification, in such a way that one component of a mixture is adsorbed preferentially, while the mobility of the adsorbed component should remain large.
- (2) A further development of new types of membrane materials, using similar sol/gel techniques. A further decrease of the pore size of the membranes should be one of the points of attention.

Both directions are under investigation in the current program.

4. Conclusions

- (1) The cut-off values for Al_2O_3 -400 and Al_2O_3 -800 membranes (determined with polyethylene glycol polymers) are 2,000 and 20,000, respectively. Both higher and lower cut-off values can be realized by applying different membrane formation procedures.
- (2) Our retention results agree reasonably well with literature data on polyethylene glycol polymers and dextrans separated with Nuclepore membranes.
- (3) The cut-off value of alumina membranes is lower than that of the Union Carbide/SFEC membrane and falls in the same range as that of dynamic and glass membranes. A superior membrane performance is expected for alumina membranes in chemically aggressive environments and/or at high temperatures.
- (4) The retention values obtained with Al_2O_3 -400 membranes were low for low molecular weight solutes, compared with Vycor glass membranes, which have about the same pore size. This is due to different surface conditions.

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