Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Characterization of Ultrafiltration Membranes by Polymer Transport Measurements

Anthony R. Cooper[a]; Dena S. Van Derveer[a]
[a] PROCESS DEVELOPMENT DEPARTMENT DYNAPOL, PALO ALTO, CALIFORNIA

To cite this Article Cooper, Anthony R. and Van Derveer, Dena S.(1979) 'Characterization of Ultrafiltration Membranes by Polymer Transport Measurements', Separation Science and Technology, 14: 6, 551 — 556
To link to this Article: DOI: 10.1080/01496397908068475
URL: http://dx.doi.org/10.1080/01496397908068475

SEPARATION SCIENCE AND TECHNOLOGY, 14(6), pp. 551–556, 1979

NOTE

Characterization of Ultrafiltration Membranes by Polymer Transport Measurements

ANTHONY R. COOPER and DENA S. VAN DERVEER

PROCESS DEVELOPMENT DEPARTMENT
DYNAPOL
PALO ALTO, CALIFORNIA 94304

Abstract

A method has been developed for characterizing the transport properties of ultrafiltration membranes. A solution of a polydisperse polymer is employed, and a steady-state sample of the retentate and ultrafiltrate is taken. Analysis of the amount of polymer in each stream and determination of its molecular weight distribution by gel permeation chromatography allow a complete characterization of the ultrafiltration membrane.

INTRODUCTION

Ultrafiltration membranes have been known for over a century. About a decade ago an improved, asymmetric membrane was developed (*1*), and since then considerable progress has been made in producing uniform membranes with respect to their pore size and high fluxes. This has led to their acceptance in many areas of laboratory research and industrial processing (*2*). However, the detailed transport characteristics of these membranes as a function of molecular weight have not been fully investigated. Normally, the manufacturers designate an upper molecular weight limit of transport, above which less than $\sim 10\%$ transport occurs. This is normally reported for purified proteins because these molecular weight probes are monodisperse. However, the purified proteins are expensive to use if large ultrafiltration modules are to be tested, and are also subject to denaturation in the presence of salts, detergents, or organic solvents. We therefore chose to investigate the molecular weight transport

profiles of ultrafiltration membranes using a synthetic polymer with a distribution of molecular weights. Dextran (Pharmacia Fine Chemicals, Sweden) was chosen as a suitable polymer since it is readily available in a variety of molecular weights in a pure state. The ultrafiltration membranes tested were hollow fiber modules, designated PM10, PM5, and AM2 by the manufacturer, Romicon Inc. (Woburn, Massachusetts).

EXPERIMENTAL

Ultrafiltration

Prior to determining the molecular weight transport profile, the integrity of the ultrafiltration module was checked at normal operating temperature and pressures by recycling a 1000-ppm solution of a polymeric yellow dye. At this concentration, manufacturing defects, pinhole leaks, etc. may be readily seen when the ultrafiltration experiment is performed. The polymeric dye used had been purified by extensive ultrafiltration with a Romicon PM10 membrane. Since all the membranes used in this study were PM10 or more retentive membranes than PM10, no polymeric dye transport was observed for modules free of manufacturing defects.

Experiments showed that using a dextran concentration of 1.0 or 3.8 g/dl had no effect on the results obtained. The retentate and ultrafiltrate dextran solutions were recycled through the modules for 30 min and then the retentate, R_0, and ultrafiltrate, U_0, streams were sampled. These solutions were freeze-dried to determine stream concentrations of the dextran, and molecular weight distributions of R_0 and U_0 were determined by gel permeation chromatography (GPC).

Gel Permeation Chromatography

The gel permeation chromatograph consisted of four columns (61 × 0.53 cm i.d.); two were packed with Glycophase CPG 75 Å and two were packed with Glycophase CPG 500 Å. The solvent flow rate was 1.0 ml/min using 0.27 *M* phosphate buffer pH 7, and the injection concentration was 1 mg/ml. Polymer was detected with a differential refractometer.

RESULTS AND DISCUSSION

The results for the transport data of the various membranes with 10,000 molecular weight dextran are summarized in Table 1. The ratio $[U_0]/[R_0]$

TABLE 1

Retention Characteristics of Hollow Fiber Membranes Using Dextran 10,000 Molecular Weight Polymer at 3.8 g/dl

Membrane type	Nominal molecular weight cut-off	Hollow fiber i.d. (cm)	Operating conditions			Transport results, $[U_0]/[R_0] \times 100$
			Inlet gauge pressure (kPa)	Outlet gauge pressure (kPa)	Temperature (°C)	
PM10	10,000	0.109	172	69	40	22
PM5 (narrow)	5,000	0.051	172	69	40	14
PM5 (wide)	5,000	0.114	172	69	40	12
AM2	2,000	0.109	172	69	40	13

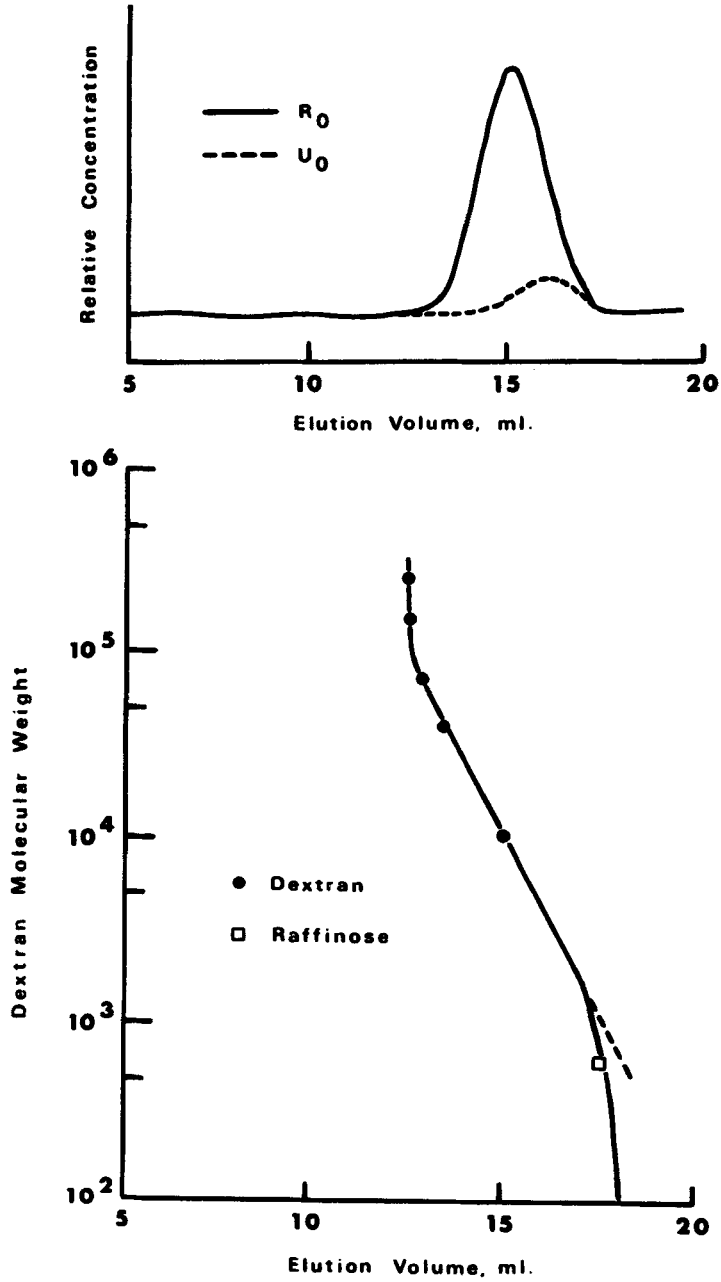

FIG. 1. Top: Gel permeation chromatograms of retentate and ultrafiltrate polymer solution for the 10,000 molecular weight dextran experiment with the PM5 (Narrow) ultrafiltration membrane. Bottom: Gel permeation chromatographic calibration curve for dextran with glycophase CPG columns.

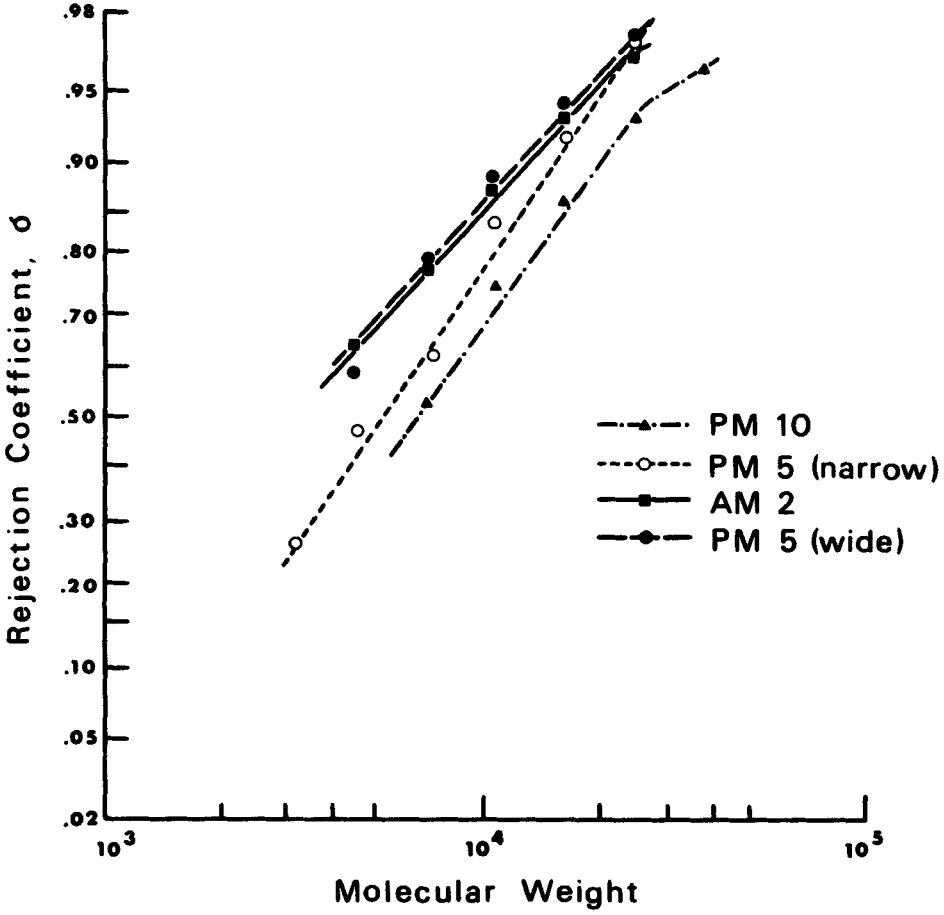

FIG. 2. Rejection coefficient–molecular weight relationships plotted on log-probability paper for PM10, PM5, and AM2 membranes determined using a 10,000 molecular weight dextran.

is a characteristic of each membrane type and may be applied as a quality control test.

A more rigorous approach is to determine the complete rejection coefficient ($\sigma = 1 - ([U_0]/[R_0])$) versus molecular weight relationship for the membrane. This is accomplished using GPC to determine the molecular weight distribution of the dextran in the retentate and ultrafiltrate at initial steady-state conditions.

The GPC calibration curve and the chromatograms of the initial steady-state retentate and ultrafiltrate for the PM5 experiment with 10,000 molecular weight dextran are shown in Fig. 1. At a given molecular weight, the concentration, C, of polymer is calculated from

$$C = \frac{R_H(C_2)}{(2.303)(M)} \times C_T$$

where R_H is the normalized chromatogram height at molecular weight M, C_2 is a constant from the GPC calibration curve

$$V_e = C_1 - C_2 \log M$$

where V_e is the elution volume, and C_T is the total polymer concentration in the stream.

The σ value may be calculated for any number of different molecular weights in this manner. The calculations were performed on a Tektronix TEK 31 programmable calculator. The σ–MW relationships for PM10, PM5, and AM2 membranes calculated from the 10,000 molecular weight dextran experiments are shown in Fig. 2. The results show good linear relationships when plotted on log-probability paper, and suggest the use of the mean μ ($\ln M$ at $P = 0.5$) and the standard deviation s [$2s = \ln M$ (at $P = 0.84$) $- \ln M$ (at $P = 0.16$)] as parameters which uniquely characterize any ultrafiltration membrane. This relationship is valid for the particular molecular weight distribution of the probe polymer employed. The method can be applied as a quality control method for membrane production. It is also a suitable method for monitoring membrane performance and lifetime in various processes.

REFERENCES

1. A. S. Michaels, in *Progress in Separation and Purification*, Vol. 1 (E. S. Perry, ed.), Wiley-Interscience, New York, 1968, pp. 297–334.
2. M. C. Porter and L. Nelson, in *Recent Developments in Separation Science*, Vol. 2 (N. N. Li, ed.), CRC Press, Cleveland, 1976, pp. 227–267.

Received by editor October 31, 1978