Observations relating to oxygen permeability measurements on membranes

Michael L. Hitchman*, **Malcolm B. Huglin**, **Susan Melling**† and
Mat B. Zakaria‡
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

(*Received 2 December 1983; revised 11 April 1984*)

A cell for electrochemically measuring dissolved oxygen permeability coefficients (P_d) has been constructed and tested successfully with Teflon® FEP membranes of previously established P_d values. Mixtures of n-butyl acrylate, *N*-vinyl-2-pyrrolidone and a crosslinking agent have been copolymerized to complete conversion via γ-irradiation. Thin discs of the products have been swollen in water to yield new hydrogels with equilibrium water contents (EWC) of 39–73%. The observed exponential increase in P_d with EWC was of a similar form to that reported by other workers for chemically different hydrogels. At a fixed EWC, there was an increase in P_d with thickness of membrane, in accord with the theoretical model for multilayer diffusive transport. However, the results also indicate the effect of the aqueous boundary layer on the measured value of P_d. The need is demonstrated for measurements on highly permeable hydrogels with aqueous environments to be conducted under well-defined transport controlled conditions, if reliable values of P_d are to be obtained.

(Keywords: n-butyl acrylate–*N* vinyl-2-pyrolidone copolymers; Teflon; hydrogel; oxygen electrode; permeability coefficient; diffusion coefficient)

INTRODUCTION

A variety of hydrophilic polymeric materials has been developed in recent years for contact lens manufacture[1]. For this purpose the polymer, especially in its swollen hydrated form, should be free from gross optical heterogeneity[2], which can be manifested by opacity, and one of the most important parameters characterizing its performance is its permeability to oxygen. There are two types of permeability reported[3–7] in the polymer and ophthalmological literature. Gaseous oxygen permeability, P_g, refers to both sides of the membrane bounded by gaseous oxygen. Although also commonly measured *in vitro*, the dissolved oxygen permeability, P_d, (i.e. with both sides of the membrane bounded by aqueous solutions) is a somewhat closer simulation of the *in vivo* situation with respect to soft contact lenses. For this measure of permeability, an oxygen electrode can be employed as a means of affording reliable values[7].

In the present paper we report measurements of dissolved oxygen permeability for synthetic copolymeric hydrogels (i.e. water swollen xerogels) comprising n-butyl acrylate (BA), *N*-vinyl-2-pyrrolidone (VP) and a crosslinking agent, 1,1,1-trimethylolpropane trimethacrylate (TPT). In addition to those just given, the following abbreviations are also adopted: GMA, glyceryl methacrylate; HEMA, 2-hydroxyethyl methacrylate; MMA, methyl methacrylate; PU, polyurethane; PVA, poly(vinyl alcohol); STY, styrene.

EXPERIMENTAL

Materials

The purification of monomers and mode of preparing the copolymers have been described fully elsewhere[2,8,9]. Here only the main features are summarized. Mixtures of BA, VP and TPT were placed in glass ampoules, the internal surface of which had been previously siliconized to facilitate removal of the final rod of xerogel. After outgassing by freeze–thaw cycles the ampoules were sealed under vacuum (10^{-5} mm Hg) and subjected to γ-irradiation from a 9000 Ci ^{60}Co source to a total dose of 1 Mrad at a dose rate of 0.01 Mrad/h. The clear solid rods of resultant xerogel were then oven cured for 24 h at 100°C and then lathe-cut into thin discs[9]. Since polymerization proceeded to 100% conversion, the overall composition of the xerogel is the same as that of the feed mixture. For a specified monomer, this composition is on the basis of the total mass of monomers; for the crosslinking agent, it is on the basis of the mass of all constituents. For example, the designation BA30/VP70/TPT1 means that BA comprises 30 wt% of (BA + VP), VP comprises 70 wt% of (BA + VP) and TPT comprises 1 wt% of (BA + VP + TPT).

The hydrogels were obtained by swelling the xerogel discs in de-ionized water to equilibrium ($\approx$2 weeks) at room temperature. The equilibrium water content (EWC) expressed as a percentage was obtained as

$$\mathrm{EWC} = 100 \times \frac{\text{weight of hydrogel} - \text{weight of xerogel}}{\text{weight of hydrogel}}$$

Specific water content (C_w) is also used by some workers and is referred to later in the text. It is defined simply as $C_w = \mathrm{EWC}/100$.

Present addresses:
* Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK
† 5 Aldridge Close, Worsley, Mesnes, Wigan WN3 5NU, UK
‡ Jabatan Kimia, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia

0032–3861/84/101441–05$03.00

The Teflon FEP membranes used here were commercial (du Pont) samples having nominal thicknesses within the range 25–250 μm.

Measurement of dissolved oxygen permeability

The permeability cell used to measure dissolved oxygen permeability allowed the testing of both thick and thin membranes and also enabled the thickness of the contacting aqueous layer on one side of the membrane under test to be carefully controlled. The assembled cell is shown schematically in *Figure 1*. The oxygen electrode (Orbisphere Laboratories, Geneva) had a gold disc cathode of diameter 2.00 mm and a large annular silver anode, which was insulated from the cathode by epoxy resin. The body of the electrode was also of insulating epoxy resin. The cylindrical (diameter 40 mm) cell was made from Perspex. The electrode fitted into the cell body and its position could be adjusted by means of a precision screw thread; a turn of 30° moved the electrode a distance of 54.2 μm. Electrolyte (1 M KOH|0.01 M KCl)[7] filled the space above and around the electrode. An O-ring on the electrode prevented any seapage of electrolyte out through the annular clearance between the electrode and the cell. After addition of the electrolyte, the membrane sample to be tested (diameter ≈25 mm) was rested on top of the cell body and was secured by the annular top cover fitted with an O-ring. With care even very thin membranes could be mounted so that they were taut and free from wrinkles. Any surplus electrolyte was then removed carefully with distilled water. For the hydrogels, the membranes were covered with a thin layer of water (≈1 mm) to prevent them from drying out. With a membrane thereby positioned, current-voltage curves for oxygen reduction were recorded using a potentiostat and scan unit (Oxford Electrodes) and a chart recorder.

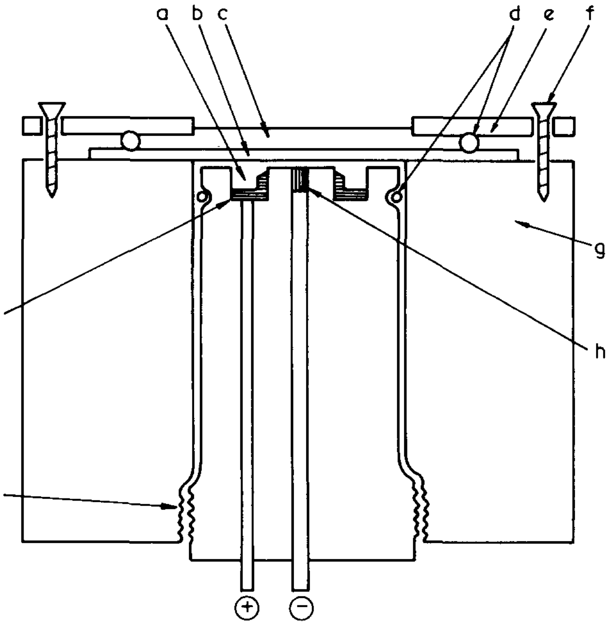

Figure 1 Permeability cell. a–electrolyte (1 M KOH + 0.01 M KCl); b–membrane; c–distilled water; d–O-ring; e–top cover; f–screw; g–cell body (Perspex); h–gold cathode; i–silver anode; j–screw thread for adjusting distance between membrane and electrolyte

Voltammograms, as typically found for oxygen reduction with a membrane covered gold cathode, were always obtained. A wide current plateau corresponding to transport limited conditions was observed, the centre of the plateau occurring at ≈ −0.85 V. This potential value was used for the current measurements required for the calculation of membrane permeabilities. Membrane thicknesses were measured with a surface profile monitor (Sloan Dektak).

All permeability measurements were conducted at an ambient temperature of 20°–1°C except for those used to determine the activation energy for permeation. For these experiments the permeability cell was housed in a double walled glass vessel through which water from an external circulatory thermostat bath was passed. Measurements of the transport limited current were made at 20°, 25°, 30°, 35° and 40°C.

RESULTS AND DISCUSSION

Calculation of oxygen permeability coefficient

Of the several ways of expressing permeability coefficient[10,11] the most commonly used are in the dimensional forms (area·time^{-1}) or [volume(STP)·length]/(area·time·pressure). Here the latter form is adopted, P_d being calculated from equation (1)

$$P_d=\frac{i_L bV}{nFap_{O_2}} \qquad (1)$$

where i_L = steady state reduction current (A)
b = thickness of the membrane (cm)
V = molar volume of gas at STP (22414 cm^3 mol^{-1})
n = number of electrons involved in the reduction of 1 mol of oxygen (4)
F = Faraday's constant (96490 C mol^{-1})
a = area of cathode (0.03 cm^2)
p_{O_2} = partial pressure of oxygen in dry air (15.92 cm Hg)

On subsequent inclusion of the multiplicative factor 10^{-10}, the resultant value of the permeability coefficient appears in Barrer units (BU)[11–13], where

$$1\ \mathrm{BU}=\frac{10^{-10}\cdot\mathrm{cm}^3(\mathrm{STP})\cdot\mathrm{cm}}{\mathrm{cm}^2\cdot\mathrm{s}\cdot\mathrm{cmHg}}$$

The adoption of BU is purely one of convenience, since for gas permeability through most polymeric materials the values of P_d (or P_g) thereby appear as simple numbers without exponential factors[11].

Permeability of Teflon FEP membrane

The measured values of b for the three Teflon FEP membranes were 24, 52 and 250 μm, which are close to the quoted nominal thicknesses.

In order to test the permeability cell and the electrochemical method of determining permeability coefficient, measurements were made on these membranes. The value of P_d for the 24 μm sample was found to be dependent on the thickness of the electrolyte layer (l) in such a way that the apparent value of P_d decreased with increasing l, as evidenced by a decreasing value of i_L. As shown earlier[7], the true value of P_d can be obtained using a plot of $1/i_L$ vs. l and substituting into equation (1) the value of i_L derived after extrapolation to $l=0$. In contrast to the 24 μm membrane, the two thicker samples manifested constancy of i_L over a wide range of electrolyte thickness. This is understandable in terms of the relative resistances to oxygen transport. The theory shows[7] that, for the electrolyte layer to have no effect on transport, it is necessary that

$$lP_m/bD \ll 1 \qquad (2)$$

where P_m is the permeability coefficient and D is the oxygen diffusion coefficient in the electrolyte, both quantities being expressed as (area · time^{-1})[10]. For FEP membranes $P_m \approx 10^{-6}$ cm^2 s^{-1},[14] while a typical value of D is $\approx 10^{-5}$ cm^2 s^{-1}. Thus the condition of equation (2) becomes

$$l/10b \ll 1 \qquad (3)$$

This might be expected to hold for $l/b \leq 1$, as indeed is found. Hence for both the thicker membranes the value of i_L at the minimum thickness of electrolyte (i.e. ≈ 50 μm) could be used for the calculation of P_d.

For all of the FEP membranes, a precision of better than $\pm 5\%$ was found for i_L, when replicate runs were made and the cell was reassembled between the runs. From the values of i_L the values obtained for P_d were 6.85, 4.17 and 5.73 BU for the membranes of thickness 24, 52 and 250 μm respectively. The average value of 5.58 BU at 20°C is in reasonable agreement with the value of 5.9 BU (25°C) obtained by Rogers[15] and the values of 4.5 BU (25°C) quoted by the manufacturer, 4.9 BU (25°C) obtained by Pasternak *et al.*[16] and 3.9 BU (room temp.) reported by Yasuda and Stone[4,5].

For the 52 μm membrane, values of P_d at the five previously quoted temperatures yielded good linearity (correlation coefficient = 0.999) in the Arrhenius plot of $\ln P_d$ vs. (1/temperature). The value of 40.5 kJ mol^{-1} thereby derived for the activation energy of permeation agrees well with the value of 38.9 kJ mol^{-1} obtained previously[17].

Permeability of BA/VP/TPT hydrogels

Provided the EWC is not very low, i.e. for those hydrogels of practical applicability, the literature as well as the present work (*vide infra*) indicate that P_d is generally within the range 15–30 BU (cf. *Table 2*). This is about 3–6 times larger than the value found for FEP membranes and so the condition of equation (3) will become approximately $l/2b \ll 1$. With the hydrogels used here being of thickness ≈ 200 μm, then, the minimum electrolyte layer thickness of ≈ 50 μm will just satisfy the criterion. Accordingly, the values of P_d for the hydrogels were determined directly from the results with this minimum thickness.

Table 1 gives the values of P_d determined for BA/VP/TPT hydrogels of different composition, the samples all being of the same thickness, 226 (± 8) μm. The variation of P_d with equilibrium water content is shown in *Figure 2*, which also includes for comparison data obtained by other workers for related types of material. The plot for the present data is reasonably linear, least squares analysis yielding the relationship

$$\log P_d = 0.350 + 0.0151 \text{ EWC} \qquad (4)$$

Table 1 Dissolved oxygen permeability coefficients (P_d) at 293K for BA/VP/TPT hydrogels of constant thickness but different compositions

Composition BA/VP/TPT	EWC (%)	b (μm)	P_d (BU)
20/80/1	72.9	218	24.0
30/70/1	62.9	220	22.9
44/56/1	55.0	218	14.3
50/50/1	39.2	234	9.04

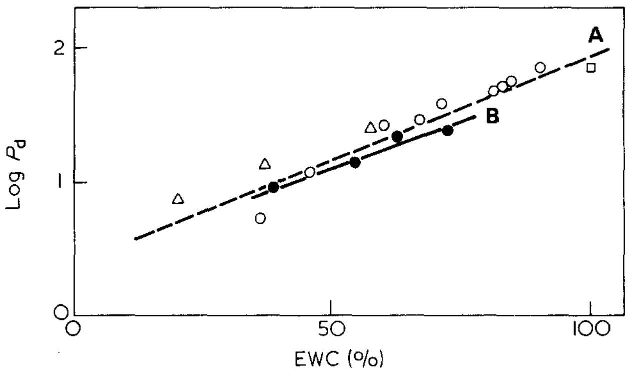

Figure 2 Log P_d *versus* equilibrium water content for hydrogels. (●)–BA/VP/TPT at 293 K (this work); (□)–pure water[18,19] at 293 K; (○)–VP/MMA[20] at 298 K; (△)–GMA/PU/VP[20] at 298 K. Least squares fit of all the data are represented by the broken line (A) and for the present data alone by the full line (B)

The effect of water content of a hydrogel on the permeability of dissolved oxygen is well established. Increasing water content increases P_d, as would be expected for the case of oxygen permeating mainly through the water in the swollen matrix. For hydrogels having EWC in excess of $\approx 35\%$ the interrelationship is reasonably linear on a semi-log plot and, as observed by others, is independent of the nature of the xerogel[21]. Again this is consistent with a model of oxygen permeating through absorbed water. This independence of P_d on chemical nature of the hydrogel can be seen, if the least squares line for BA/VP/TPT (equation (4)) is compared with that for all the data points relating to three chemically different hydrogels (*Figure 2a*), viz.

$$\log P_d = 0.385 + 0.0159 \text{ EWC} \qquad (5)$$

It is interesting to note that Tighe[3] obtained a very similar relationship to equations (4) and (5) for VP/HEMA hydrogels at 34°C, viz.

$$\log P_d = 0.380 + 0.0160 \text{ EWC} \qquad (6)$$

Another way of illustrating the relative independence of P_d on the nature of the membrane at high water content is to compare values of P_d at a fixed EWC. This is done in *Table 2*, where each P_d has been interpolated to EWC = 60% from published plots. The average value of P_d is 27.5 BU with a spread of ± 5.9 BU at the 95% confidence level. The constancy of the results is remarkably good, even though the data encompass a 19°C range of temperature. However, this is again in accord with a model of oxygen permeating through adsorbed water since, as the temperature changes, P_d will be affected by two opposing contributions, namely the solubility and the diffusion coefficient of oxygen in water. When the

Table 2 Coefficients of dissolved oxygen permeability (P_d) in the vicinity of 300Kfor BA/VP/TPT and other hydrogels, all interpolated to conditions of equilium water content (EWC) of 60%.

Xerogel component	Plot	Temp (K)	P_d (BU)	Ref.
BA/VP/TPT	log P_d – EWC (linear)	293	18.0	this work
GMA/MMA	log P_d – $(1/C_W)$ (linear)	296–310	29.3	21
GMA/PU/VP	log P_d – EWC (linear)	298	28.0	20
HEMA	log P_d – $(1/C_W)$ (linear)	296–310	29.3	21
HEMA/MMA	log P_d – EWC (linear)	307	34.2	3,22
HEMA/STY	log P_d – EWC (linear)	307	34.2	3,22
HEMA/VP	log P_d – EWC (linear)	307	34.2	3,22
HEMA/VP	log P_d – $(1/C_W)$ (linear)	296–310	29.3	21
PVA	log P_d – $[(1/C_W) - 1]$ (linear)	307	39.0	23
VP/MMA	log P_d – EWC (curve)	310	34.0	20
VP/MMA	log P_d – EWC (curve)	298	22.0	20
VP/MMA	log P_d – EWC (linear)	310	20.0	24,25
VP/MMA	log P_d – C_W (curve)	310	23.0	26
VP/MMA	log P_d – $(1/C_W)$ (linear)	296–310	29.3	21

temperature falls from 39° to 20°C, there is a resultant increase of about 39% in the oxygen solubility[18], while the diffusion coefficient decreases by about 38%[27]. The overall effect of temperature on P_d is thus relatively small.

It is known that the thickness of the hydrogel can also affect the measured value of P_d[28]. This arises because of the influence on the apparent permeability of boundary layers in the aqueous environments on either side of the membrane. If the thickness of these boundary layers are denoted for δ_1 and δ_2, then by an analysis analogous to that given previously for a two layer model[7], one can show that the net transport controlled flux (j_L) is given by

$$\frac{1}{j_L}=\frac{1}{(D/\delta_1)C_\infty}+\frac{1}{(D/\delta_2)C_\infty}+\frac{1}{(P_m/b)C_\infty} \tag{7}$$

where D is the oxygen diffusion coefficient for both of the aqueous environments; C_∞ is the dissolved oxygen concentration; P_m is the permeability coefficient of the membrane in the absence of any contribution to transport control from the aqueous environments. The transport controlled flux can also be represented by

$$j_L=P_dC_\infty/b \tag{8}$$

where P_d is the apparent, measured permeability coefficient. Combination of equations (7) and (8) and rearrangement yield

$$\frac{1}{P_d}=\left(\frac{\delta_1+\delta_2}{D}\right)\left(\frac{1}{b}\right)+\frac{1}{P_m} \tag{9}$$

which is analogous in form to the expression derived by Hwang *et al.*[6,28–30].

Data for the hydrogel BA30/VP70/TPT1 are plotted according to equation (9) in *Figure 3*, which shows that P_d increases with increasing thickness of membrane. The effect of the boundary layers in the aqueous phases can be estimated by considering the slope of the line in *Figure 3*, which is found by least squares analysis to have a value of 1.39×10^{-3} BU^{-1} cm. This is equal to $(\delta_1+\delta_2)/D$. For a membrane of thickness $b\approx0.02$ cm, then the resistance to transport of the boundary layers as compared with that of the membrane is given by

$$[(\delta_1+\delta_2)/D][1/b]=1.39\times10^{-3}/0.02\approx0.07\ \mathrm{BU}^{-1}$$

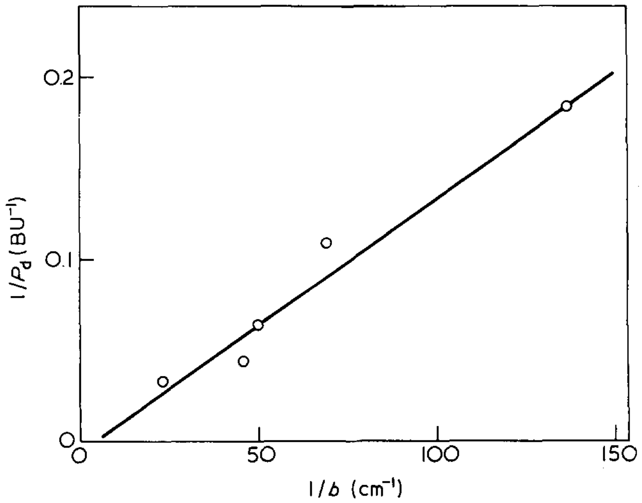

Figure 3 Plot illustrating the effect of membrane thickness on the dissolved oxygen permeability of BA30/VP70/TPT1 hydrogels at 293 K

Unfortunately, since the ordinate intercept in *Figure 3* is negative, no meaningful value of $1/P_m$ can be derived from this plot in order to compare with this value and so make an estimate of the two terms on the right hand side of equation (9). However, if the value of 0.07 BU^{-1} obtained above is compared with the value of $1/P_d$ from *Figure 3* corresponding to a membrane of $b=0.02$ cm, it is seen that this value of $1/P_d$ is also of the order of 0.07 BU^{-1}. Consequently, it is apparent that the effect of the boundary layer is significant.

Other workers have noted similar effects for various hydrogels[20,21,24,31]. Estimates of the thickness of the aqueous boundary layers have been made[18,19,32] by multiplying the slope of a plot such as that in *Figure 3* by the value of P_d for water; boundary layer thicknesses within the range 0.003–1 cm have been obtained[20,21,24,31]. From our data a value of 0.1 cm is found, which is comparable to the thickness of the water layer placed on top of the hydrogels in order to stop them drying out. However, although our cell design afforded control of the aqueous layer thickness on the electrode side of the membrane, it did not provide any means of setting up well controlled convection to establish a diffusion layer thickness of known dimensions at the outer surface of the membrane. This lack of any well defined transport conditions in the aqueous layer on the membrane probably accounts for the greater scatter of data points as compared with results for the Teflon FEP membranes, and also for the negative ordinate intercept in *Figure 3*. In order to obtain more reproducible results and to make more meaningful comparisons among different sets of data, it is absolutely essential to ensure that there is well characterized transport of oxygen up to the hydrogel surface. To do this it is not sufficient to have merely agitation. What is required is a form of stirring which is both well defined and calculable. This could be readily achieved with our cell by, for example, inverting the cell configuration in order to make it into the form of a disc rotating in a large volume of water. This work has just commenced and results will be reported.

ACKNOWLEDGEMENT

One of us (M.B.Z.) thanks Universiti Kebangsaan Malaysia for financial support provided under the aegis of its Staff Training Scheme.

REFERENCES

1 Refojo, M. J. in 'Encyclopedia of Chemical Technology' (Eds. H. F. Mark, D. F. Othmer, C. G. Overberger, G. T. Seaborg) Interscience, New York, 1979, Vol. 6, p. 720

2 Huglin, M. B. and Zakaria, M. B. *Polymer* 1984, **25**, 797

3 Tighe, B. J. *Br. Polym. J.* 1976, **8**, 71

4 Yasuda, H. and Stone, Jr., W. *J. Polym. Sci.* 1966, **4**, 1314

5 Yasuda, H. *J. Polym. Sci. A1* 1967, **5**, 2952

6 Hwang, S.-T., Tang, T. E. S. and Kammermeyer, K. *J. Macromol. Sci. Phys.* 1971, **85**, 1

7 Hale, J. M. and Hitchman, M. L. *J. Electroanal. Chem.* 1980, **107**, 281

8 Huglin, M. B., Zakaria, M. B. and Yahya, I. B. *Polymer* 1982, **23**, 340

9 Huglin, M. B. and Zakaria, M. B. *J. Appl. Polym. Sci.* 1983, **28**, 2451

10 Hitchman, M. L. and Gnaiger, E. in 'Polarographic Oxygen Sensors, (Ed. E. Gnaiger and H. Forstner), Springer Verlag, Berlin/Heidelberg, 1983, Ch. 1.3

11 Huglin, M. B. and Zakaria, M. B. *Angew. Makromol. Chem.* 1983, **117**, 1

12 Leboeuf, A. R. U.K. Pat. 2054614 (1981)

13 Leboruf, A. R. Ger. Pat. 3023096 (1981)

14 Hitchman, M. L. 'Measurement of Dissolved Oxygen', John Wiley & Sons/Orbisphere Corporation, New York, 1978, p. 72

15 Rogers, C. E. in 'Engineering Design for Plastics' (Ed. E. Baer) Rheinhold, New York, 1964, p. 609

16 Pasternak, R. A., Burns, E. L. and Heller, J. *Macromolecules* 1971, **4**, 470

17 Ref. 14, p. 107

18 Ref. 14, p. 195

19 Davidson, J. F. and Cullen, E. J. *Trans. Inst. Chem. Engrs.* 1957, **35**, 51

20 Hosaka, S., Adachi, Y. and Tanzawa, H. *Maku* 1980, **5**, 245 (CA 1980, **93**, 240384e)

21 Refojo, M. F. and Leong, L. F. *J. Membr. Sci.* 1979, **4**, 415

22 Ng, C. O. and Tighe, B. J. *Br. Polym. J.* 1976, **8**, 118

23 Yang, W.-H., Smolen, V. F. and Peppas, N. A. *J. Membr. Sci.* 1981, **9**, 53

24 Hosaka, S., Yamada, A., Tanzawa, H., Momose, T., Magatani, H. and Nakajima, A. *J. Biomed. Mater. Res.* 1980, **14**, 557

25 Hosaka, S., Mori, Y., Kenjo, H., Tanzawa, H., Momose, T., Magatani, H. and Nakajima, A. *Kobunshi Ronbunshu* 1979, **36**, 265 (CA 1979, **91**, 62693r)

26 Hosaka, S., Tanzawa, H., Kenjo, H. and Okado, S. *J. Jpn. Cont. Lens Soc.* 1980, **22**, 367

27 Akgerman, A. and Gainer, J. L. *Ind. Eng. Chem. Fundam.* 1972, **11**, 373

28 Hwang, S.T. and Kammermeyer, K. *Progr. Separ. Purif.* 1971, **4**, 1

29 Hwang, S.-T. and Kammermeyer, K. *ACS Div. Org. Coat. Plast. Pap.* 1974, **34**, 500

30 Hwang, S.-T. and Kammermeyer, K. *Polym. Sci. Technol.* 1974, **6**, 197

31 Lee, C. W. and Chang, H. N. *Hwahak Konghak* 1979, **17**, 117 (CA 1979, **91**, 109464j)

32 Hamelblau, D. M. *Chem. Rev.* 1964, **64**, 527