Studies on syntheses and permeabilities of special polymer membranes: 38. Formation mechanism of finger-like cavities in membranes from cellulose nitrate and single solvent

Tadashi Uragami, Yoshiaki Ohsumi, and Mizuho Sugihara
Department of Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564, *Japan*

(*Received* 5 *May* 1981; *revised* 1 *September* 1981)

The relationship between the permeation characteristics of an aqueous polymer solution and the asymmetric structure of cellulose nitrate membranes was investigated under various conditions. The conditions and mechanism of the formation of finger-like cavities in cellulose nitrate membranes are discussed in some detail.

Keywords Cellulose nitrate; asymmetric membrane; finger-like cavity; formation condition; formation mechanism; permeation characteristics

INTRODUCTION

Loeb and Sourirajan[1] have prepared an asymmetric cellulose acetate membrane for desalination in reverse osmosis. The fine structure of this asymmetric membrane was observed by electron microscopy[2]. The mechanism of formation of asymmetric membranes has been discussed by many workers. Kesting *et al.*[3-5] have explained, by the phase-inversion of the solid-gel transition of a polymer solution, the formation process of the asymmetric porous membranes. Strathmann *et al.*[6-8] have revealed, using the ternary phase diagram of the three components (i.e. polymer solvent, and precipitant), the formation of asymmetric membranes.

Mazt[9] has found that a finger-like cavity existed in the sponge layer of the asymmetric cellulose acetate membrane. The finger-like cavities were observed in the membranes from cellulose acetate[9], aromatic polyamide[10-12], polysulphone[13], polyurethane[14], poly(vinyl chloride[15]. The mechanism of formation of the finger-like cavities has been discussed by many workers[6-9,14].

This paper deals with physicochemical behaviour of the casting mixture consisting of cellulose nitrate and a single solvent, the permeation characteristics of the aqueous polymer solution and the structure of the resulting membranes. Also the conditions and mechanism of the formation of finger-like cavities in the membranes are discussed.

EXPERIMENTAL

Materials

Daicel best grade cellulose nitrate (CN) which was dried under reduced pressure, having a degree of nitration of 11.5%, a number average molecular weight of 1.20×10^5, and a weight average molecular weight of 3.83×10^5, was employed as the membrane substrate. Pure commercial solvents summarized in *Table 1* were used for the casting solutions. Pure poly(ethylene glycol) (PEG) 1000 used as the feed solute was a commercial source. Distilled water was used as the gelation medium.

Preparation of membranes

The casting solutions were prepared from mixtures of cellulose nitrate and a solvent and kept overnight at the casting temperature (6°–7°C). The membranes were made by pouring the casting solutions onto an applicator for thin layer chromatography, drawing the blade across a glass plate, the solvent was then allowed to evaporate off for a desired period at 6°–7°C and at the desired humidity, the glass plate together with the membrane was immersed into a gelation medium (6°–7°C). After standing for 24 h in the gelation medium, the membranes were removed from the glass plate.

Apparatus and measurements

The apparatus, the experimental procedure, and the analysis of feed and membrane-permeated liquid have been previously reported[16]. The effective membrane area set in the cell was 12.7 cm^2. All experiments were of the short run type. The rejection (R) is defined as

$$R(\%) = (1 - C_t/C_f) \times 100 \qquad (1)$$

where C_f is the starting feed concentration and C_t is the concentration of permeated solution after t h.

A change in the weight of casting mixture per unit area on the glass plate during membrane formation process is given by the following equation.

$$W = (W_t - W_0)/A \qquad (2)$$

where W (g cm^{-2}) is the change in the amount of the casting mixture per unit area, W_0 (g cm^{-2}) is the total

0032-3861/82/070999-06$03.00

Table 1 Effect of casting solvent on permeation characteristics

Number	Casting solvent		Rate of pure water permeability[a] (ml $cm^{-2} \cdot s^{-1}$) x 10^5	Permeation rate[b] (g $cm^{-2} \cdot s^{-1}$) x 10^5	Rejection[c] (%)
1	Formamide	FA	300	290	26.0
2	Methyl alcohol	MeOH	290	240	16.5
3	Triethylene glycol	TEG	140	260	14.0
4	*N,N*-dimethyl formamide	DMF	18	28	14.0
5	*N,N*-dimethyl acetoamide	DMA	48	26	19.0
6	*N*-methyl 2-pyrrolidone	NMP	56	62	24.5
7	Methyl cellosolve	MeCell	5.9	4.2	36.0
8	Ethyl cellosolve	EtCell	0.38	0.82	43.2
9	Methyl carbitol	MeCar	270	410	12.0
10	Ethyl carbitol	EtCar	1400	6600	6.0
11	Butyl carbitol	BuCar	0.13	Impermeable	–
12	Triethyl phosphate	TEP	0.038	Impermeable	–
13	Acetic anhydride	AAn	0.093	Impermeable	–
14	Ethyl lactate	EL	0.072	Impermeable	–
15	Pyridine	Pyr	0.085	Impermeable	–

[a] At 40°C, 2 kg cm^{-2}
[b] For 1% aqueous solution of PEG 1000 at 40°C, 2 kg cm^{-2}
[c] For PEG 1000

weight of starting casting mixture and the glass plate, W_t (g cm^{-2}) is the total weight of the casting mixture and the glass plate after t h, and A (cm^2) is the effective surface area of the glass plate.

The lyophilized membranes were coated with a layer of evaporated gold and then observed by scanning electron microscopy (Japan Electron Optics). Electron micrographs presented in *Figures 2* and *3* were all taken at the same magnification (x 300) and those in *Figures 4* and *5* were at a different magnification.

RESULTS AND DISCUSSION

The effect of the evaporation period on the permeation characteristics is shown in *Figure 1*, where *N,N*-dimethyl formamide was used as casting solvent, water was employed as the gelation medium. The permeation rate of the aqueous solution of PEG 1000 increased and rejection of PEG 1000 decreased with an increase in the evaporation period. In order to explain these permeation characteristics, a change in weight of the casting mixture during the membrane formation process was determined. As is shown in *Figure 1*, the weight of casting mixture increased with increase in the evaporation period. Since the casting solvent, *N,N*-dimethyl formamide, is very highly hygroscopic and the preparation conditions of the membranes were: relatively low temperature and high humidity (7°C, 90%), this increase in weight is mainly caused by the absorption of water molecules into the casting mixture from the atmosphere. *N,N*-dimethyl formamide was a good solvent but water was a strong non-solvent for cellulose nitrate. Therefore, as soon as the water molecules were absorbed into the surface of the casting mixture, coacervated droplets occluded the water molecules as they were formed. Subsequently, phase separation occurred between the coacervated droplets and the casting matrix solution. When the absorption of water molecules further increased during a longer evaporation period, the coacervated droplets became gradually larger and its number increased until finally these droplets contacted each other. Consequently, the precipitated gels, which had a polyhedron structure[3-5], were formed in the surface layer of casting mixture. Therefore, the pore sizes in the surface layer of the membrane obtained became larger as the absorption of water molecules increased. The increase in the permeation rate and the decrease in the rejection with the evaporation period are attributable to the above factors.

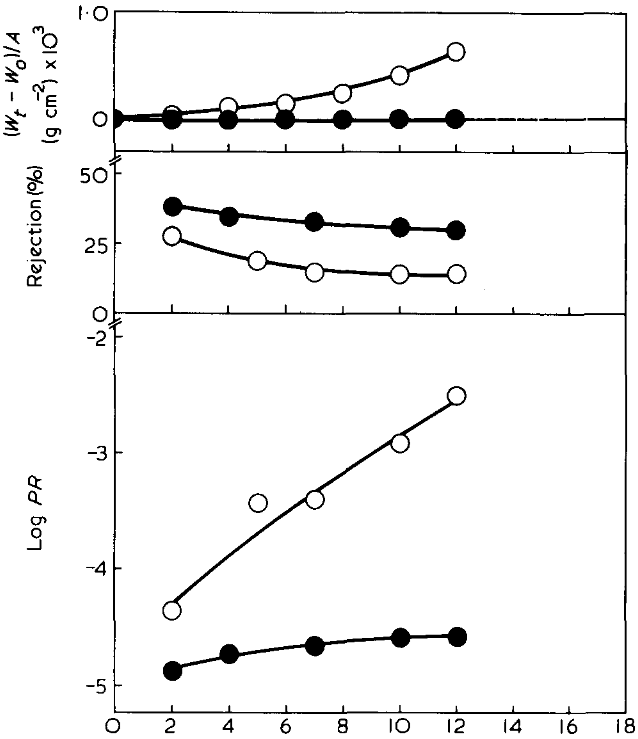


Figure 1 Effect of evaporation period on permeation characteristics. Composition of casting solution, CN/DMF = 13/87 (wt %); relative humidity during preparation of membranes, (○) 90%, (●) 38%; feed, 1% aqueous solution of PEG 1000; operating conditions, 40°C, 5 kg cm^{-2}; PR is permeation rate (g $cm^{-2} \cdot s^{-1}$)

The photographs of the cross section of cellulose nitrate membranes with the change of evaporation period observed under a scanning electron microscope are shown in *Figure 2*, where the preparation conditions of the membranes were the same as in *Figure 1*. A finger-cavity in the sponge layer of the asymmetric membrane was very small at an evaporation period of 1 minute but grew larger over 2 minutes. When the asymmetric

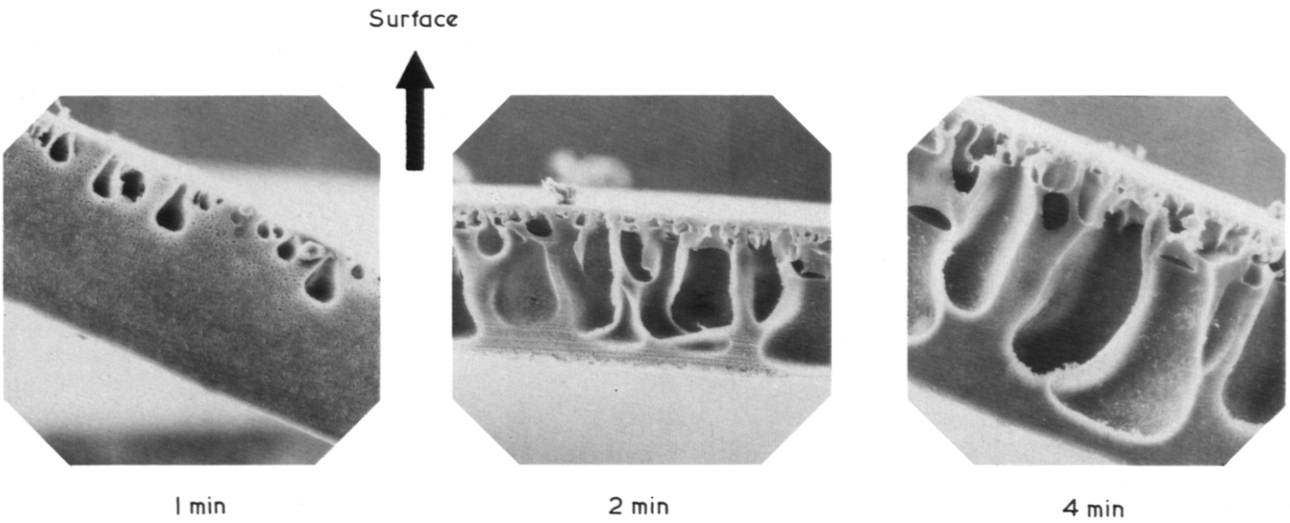


Figure 2 Photographs of cross section of cellulose nitrate membranes with change of evaporation period under 90% humidity. Casting solvent, DMF

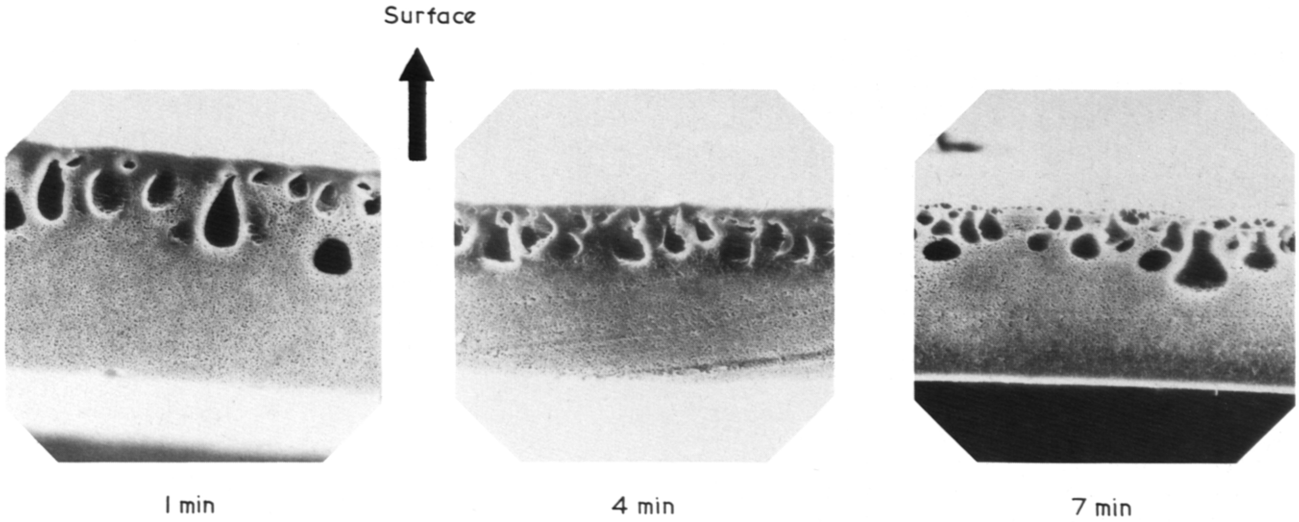
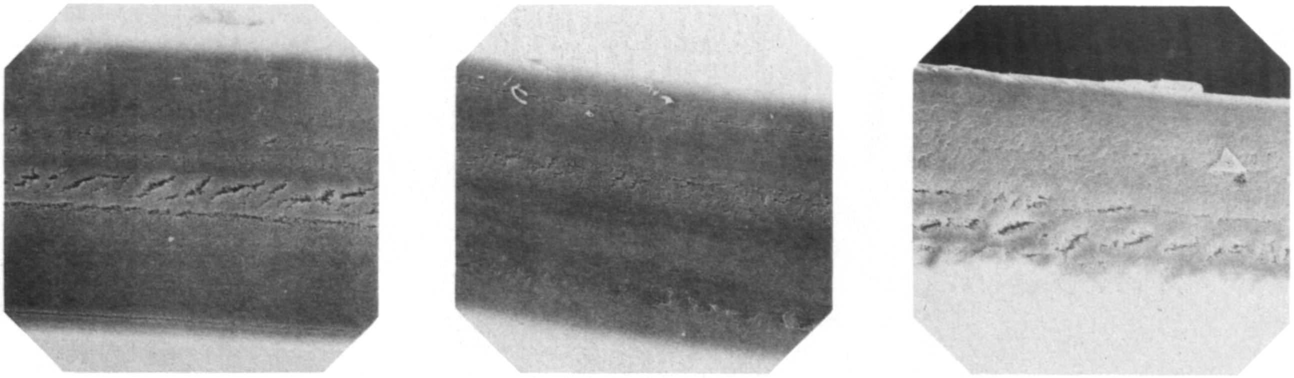


Figure 3 Photographs of cross section of cellulose nitrate membranes prepared at 38% humidity. Casting solvent, DMF

membrane was gelled in water, the aggragation of cellulose nitrate molecules in the surface layer containing the coacerveted droplets was different from that in the matrix casting solution. Therefore, the permeability of the gelation medium into the sponge layer was different as it was governed by the structure of the surface layer of the asymmetric membranes. Consequently, the finger-like cavity in the sponge layer was formed under large pores in the surface, where the permeation rate of the gelation medium into the sponge layer was greater.

It was implied in the above discussion that the permeation characteristics and the formation of finger-like cavity were greatly affected by the structure of surface layer, which was governed by the preparation conditions of the membranes, in particular the humidity, during the membrane formation process. The permeation characteristics were studied by the changing of the humidity during the preparation of the membranes. The results obtained also are shown in *Figure 1*. The increases in permeation rate and weight of the casting mixture with an increase in evaporation period at 38% humidity were very small compared with those at 90% humidity. *Figure 3* shows the cross-sections of the membranes prepared at 38% humidity. The size of the finger-like cavity and the degree of its growth with the evaporation period were considerably smaller compared with those at 90% humidity. Consequently, it is suggested that the amount of water molecules absorbed into the casting mixture from the atmosphere during the membrane formation process affected the degree of aggregation of cellulose nitrate molecules in the surface layer of the casting mixture. In other words it influenced the permeation characteristics of the resulting membranes and the formation of the finger-like cavity.

It was important to investigate whether the formation of the finger-like cavity was dependent on only the absorption of water molecules into the casting mixture during the membrane formation process. Methyl alcohol and ethyl alcohol were selected as casting solvent for the system, which brought the decrease in weight of the casting mixture caused by the evaporation loss of solvent with an increase in the evaporation period. The finger-like cavities were not observed in the membranes prepared from these casting solvents as shown in *Figure 4*. However, when formamide and triethyl phosphate were used as the casting solvent, in spite of the fact that the weight of casting mixture was increased by the absorption of water molecules with the evaporation period, as well as the system of *N*,*N*-dimethyl formamide (*Figure 1*), the formation of the finger-like cavity was not recognized, as

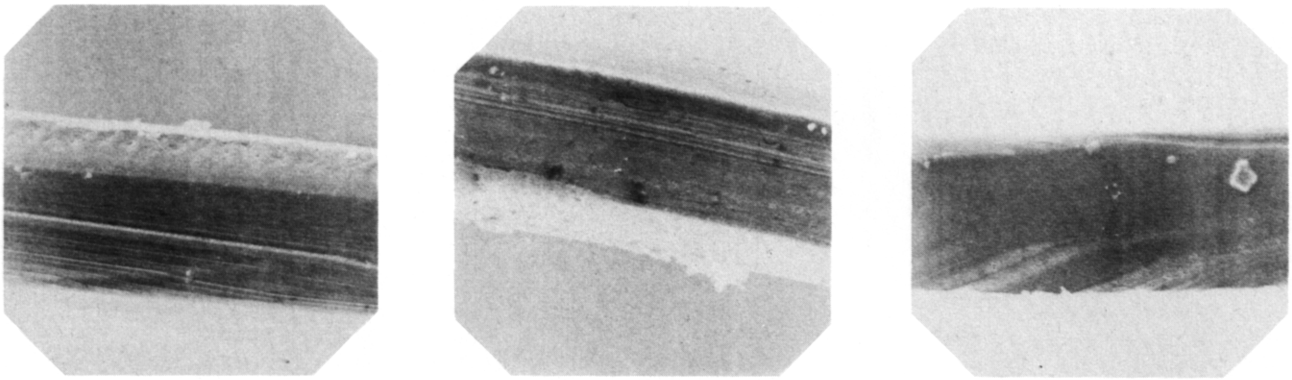


2 min

7 min

12 min

MeOH



2 min

7 min

12 min

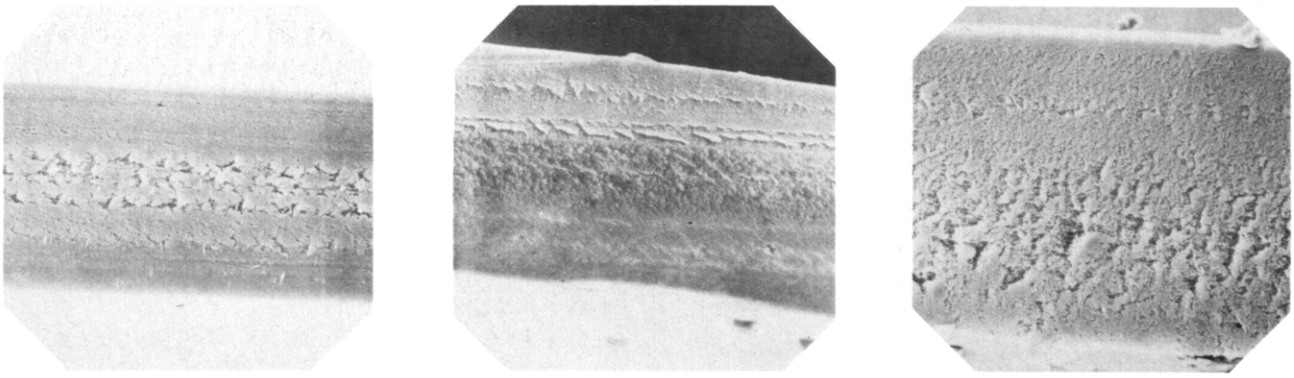
EtOH

Figure 4 **Photographs of cross section of membranes from cellulose nitrate and MeOH or EtOH under 90% humidity**

shown in *Figure 5*. From these results, it was found that the formation of the finger-like cavity was not attributed only to the water absorption into the casting mixture.

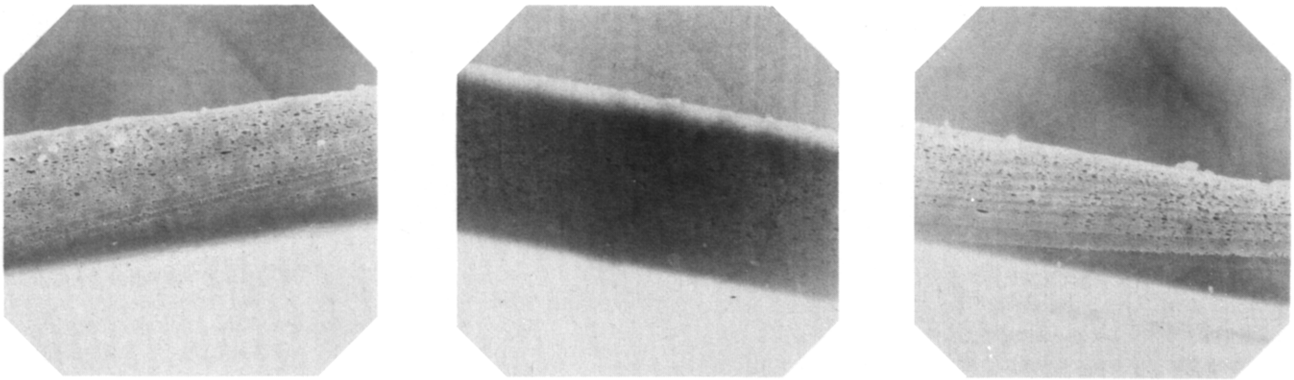
The permeation characteristics of the membranes prepared from various casting solvents are summarized in *Table 1*. In the membranes 1–3 obtained from the solvents the permeation rate was relatively large, the permeation characteristics did not change remarkably with the evaporation period, and the finger-like cavity did not form. In the membranes 4–11, the permeation rate increased with increased evaporation period and the finger-like cavity formed as well as in the *N,N*-dimethyl formamide system. The difference between the permeation rates for the membranes prepared from these solvents is due to the difference in the degree of heterogeneous aggregation of the cellulose nitrate molecules which occur during the gelation process. The membrane having the larger finger-like cavity in the membrane cross section tended to have a greater permeation rate, i.e. larger pore sizes in the surface layer of the resulting membranes. This is supported by the rejections for PEG 1000 of these membranes. In membranes 12–15, the finger-like cavity was not observed. The permeability was extremely small.

As can be seen from *Table 1*, there were similar membrane characteristics in certain solvent groups. Therefore, the relationship between δ_p, the polar force component, and δ_h, the component due to hydrogen bonding, in the solubility parameter of the casting solvent is shown in *Figure 6*. The inside of the broken line represents the soluble region of cellulose nitrate molecules. The solvents which had a greater permeation rate and did not form the localized finger-like cavity are represented in region I. This region was the boundary vicinity in the soluble range for cellulose nitrate molecules. Therefore, the solvents in this region did not act satisfactorily as a good solvent. In other words, the solvation between the solvent molecules and the cellulose nitrate molecules was insufficient, and the interactions between the cellulose nitrate molecules were relatively strong. Since the interaction between the solvent molecules and the water molecules was relatively weak, cellulose nitrate molecules were not aggregated heterogeneously by the absorption of water molecules into the casting mixture and the permeation of the gelation medium into the inside of the casting mixture occurred almost homogeneously. The fact that the membranes which did not have the finger-like cavity and had the greater permeation rates were formed, agrees well with the above discussion.



2 min 7 min 12 min

FA



2 min 7 min 12 min

TEP

Figure 5 Photographs of cross section of membranes from cellulose nitrate and FA or TEP under 90% humidity

The solvents localized in regions II and III gave the membranes having the finger-like cavity. The permeation rates for these membranes changed greatly with the evaporation period. Region II contained non-protonic polar solvents as represented by *N*,*N*-dimethyl formamide. When the solvents in region II were used as the casting solvents for the casting solutions, the gelation of the cellulose nitrate molecules in the gelation step proceeded rapidly. The solvents in region II were good solvents for the cellulose nitrate molecules. Therefore, in order to obtain precipitation of cellulose nitrate as a gel from the casting solutions prepared from these solvents, it was required that a relatively large amount of the gelation medium permeates into the casting mixture. The rapid gelation of the cellulose nitrate molecules is due to these solvents being dissociative and solvated strongly with water molecules which were in the gelation medium, and consequently desolvation (solvent removal) into the gelation medium from the casting mixture was very rapid.

In region III glycol ethers, which formed the finger-like cavity, existed. These solvents were water soluble and solvated strongly with water molecules because of the strong donation by oxygen atoms in glycol ethers. The moment the gelation medium and the casting mixture came in contact, the solvent in the casting mixture desolvated rapidly into the gelation medium because of the polar interaction between the water molecules and the solvent molecules. Consequently, the cellulose nitrate molecules on the interface between the gelation medium and the casting mixture aggregated heterogeneously. At this stage, the structural changes of the cellulose nitrate molecules due to the absorption of water molecules into the casting mixture from the atmosphere during the solvent evaporation process, enlarged the heterogeneous aggregation of the cellulose nitrate molecules during the gelation process. The skin layer in an asymmetric membrane was formed by the aggregation of cellulose nitrate molecules at the moment of gelation. The phenomena after the formation of the skin layer are explained by imagining the existence of a very thin membrane between the gelation medium and the casting mixture. The state of gelation of the cellulose nitrate in the interior of the casting mixture was governed mainly by the structure of the skin layer. That is, if there was a marked heterogeneous aggregation of cellulose nitrate molecules in the skin layer, then the permeation of the gelation medium into the interior of the casting mixture, from a portion of rough packing of cellulose nitrate molecules, was greater than permeation of the dense packing of the cellulose nitrate molecules. Since the interior of the

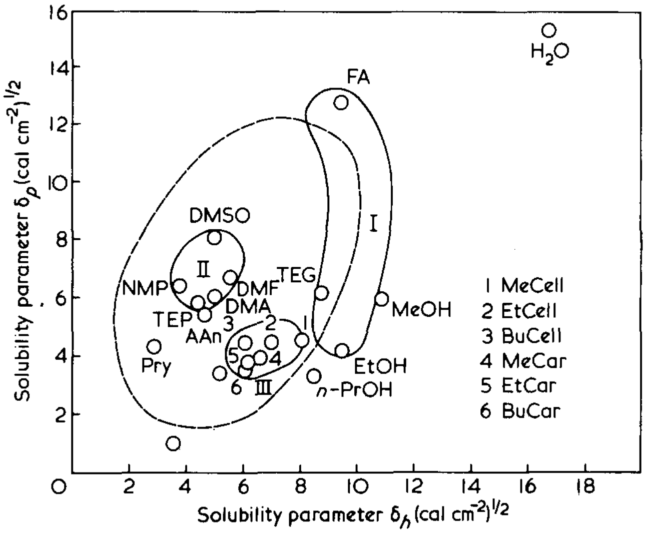


Figure 6 Solubility parameter of casting solvents for preparation of cellulose nitrate membranes

casting mixture was the solution state in an earlier stage of the gelation process, this solution of casting mixture was pushed aside with the gelation medium and at the same time the cellulose nitrate molecules aggregated, and consequently the finger-like cavity formed.

CONCLUSION

The permeation characteristics for the aqueous polymer solution and the structure of the cellulose nitrate membranes which were prepared using a particular single solvent as the casting solvent, were governed significantly by the nature of the casting solvent, i.e., the solvation power for the cellulose nitrate molecules, the hygroscopicity, the affinity with the gelation medium, etc. In particular, it was required that the casting solvent for the formation of finger-like cavity was a very good solvent for cellulose nitrate molecules, that is hygroscopic, and polar.

REFERENCES

1 Loeb, S. and Sourirajan, S. *Adv. Chem. Ser.* 1962, **38**, 117
2 Riley, R. L., Gardner, J. D. and Merten, U. *Science* 1964, **143**, 801
3 Kesting, R. E., Barsh, M. K. and Vincent, A. L. *J. Appl. Polym. Sci.* 1965, **9**, 1873
4 Kesting, R. E. and Menefee, A. *Kolloid-Z. Z. Polym.* 1969, **230**, 341
5 Kesting, R. E. 'Synthetic Polymeric Membranes', McGraw-Hill, New York, 1971, p. 116–157
6 Strathmann, H., Scheible, P. and Baker, R. W. *J. Appl. Polym. Sci.* 1971, **15**, 811
7 Strathmann, H., Kock, K., Amar, P. and Baker, R. W. *Desalination* 1975, 16, 179
8 Strathmann, H. and Kock, K. *Desalination* 1977, **21**, 241
9 Matz, R. *Desalination* 1972, **10**, 1
10 Strathmann, H., Saier, H. D. and Baker, R. W. *Proc. Fourth Int. Symp. on Fresh Water from the Sea* 1973, **4**, 381
11 Strathmann, H., Saier, H. D. and Baker, R. W. 1975, **16**, 179; *ibid* 1977, **21**, 241
12 Tirell, D. and Vogel, O. *J. Polym. Sci., Polym. Chem. Edn.* 1977, **15**, 1889
13 Cahasso, I., Klein, E. and Smith, J. K. *J. Appl. Polym. Sci.* 1977, **21**, 165
14 Koenhen, D. M., Mulder, M. H. and Smolders, C. A. *J. Appl. Polym. Sci.* 1977, **21**, 199
15 Hirose, S. and Shimidzu, A. *J. Polym. Sci.* 1979, **23**, 3193
16 Uragami, T., Fujino, K. and Sugihara, M. *Makromol. Chem.* 1976, **55**, 29