

## Freezing and Nonfreezing Water in Cellulose Acetate Membranes\*

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### Synopsis

The relative amounts of freezing and nonfreezing water in various cellulose acetate (CA) membranes were determined by differential scanning calorimetry. It was found that: (1) A significant fraction (17–40%) of the water (1.0–3.1 g H<sub>2</sub>O per gram dry CA) in any membrane does not freeze at temperatures as low as –60°C. (2) The amount of nonfreezing bound water (0.4–0.7 g nonfreezing water per gram dry CA) depends upon the nature of the membrane and is significantly higher than the total amount of water (all of which is nonfreezing) absorbed from liquid water by a *dense* film of the same polymer (~0.18 g water per gram dry CA). The structures of the membranes were studied by scanning electron microscopy. The results suggest that the amounts of nonfreezing water in cellulose acetate membranes decrease with the increase in the packing density (compactness) of the polymer within the membrane. In dense films, the extent of polymer–polymer interactions within the polymeric matrix is high, and therefore the macromolecular chains are less accessible to bind water.

### INTRODUCTION

The application of membrane techniques for filtration concentration and separation purposes is continuously increasing. An outstanding example is desalination by reverse osmosis. It is now generally agreed that the selectivity characteristics of membranes are very significantly determined by the relative solubilities and diffusivities of the solvent (most commonly water) and the solute in these membranes.<sup>1–3</sup>

An understanding of the properties of water in the widely used cellulose acetate membranes seems therefore to be highly important. However, although several studies of the interaction of water with cellulose acetate membranes have been carried out during the last ten years, different views have been expressed concerning the extent of water binding and the existence of structured water in these membranes.<sup>4–7</sup> The purpose of this study was to help clarify the extent and the nature of water–polymer interactions in various cellulose acetate membranes. The techniques employed were differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and nuclear magnetic resonance (NMR).

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## EXPERIMENTAL

### Materials

The cellulose acetate (CA) used in this study was Eastman's type E-398-10. Acetone and dimethyl sulfoxide (which were used as film-casting solvents) were of analytical-grade purity, whereas formamide and triethyl phosphate were practical grade. Binary polymer solutions contained 20% CA. (All percentages and ratios given below refer to weight per cent and weight ratios.) The ternary solution consisted of 25:30:45 CA:formamide:acetone. This formulation, which is the Manjikian-modified Loeb-Sourirajan solution (see ref. 3, pp. 58-63 and 112-116 for explanation of this name), will be abbreviated in this paper as the modified Loeb formulation.

### Membrane and Dense Film Preparation

A thin (~0.3 mm) film of CA solution was cast at ambient temperature on a glass plate and precipitated in an ice-water bath. Films of binary solutions were immersed in water immediately after their casting, whereas the ternary (modified Loeb) solution was allowed to evaporate at ambient atmosphere for a predetermined period prior to its precipitation in the water bath. All membranes were annealed in a water bath at 80°C or at 95°C for 30 min. All membranes were stored in distilled water until use.

The dense CA film was cast from 20% CA in acetone and evaporated to dryness at ambient conditions (~24 hr). This dense film was then soaked with water for at least 48 hr prior to its testing.

The detailed preparation procedures of the membranes used in this study are described in Table I and in the coding of the membranes. Membranes are coded according to their preparation procedure. The first letters stand for the type of polymer used (CA = cellulose acetate). The next two figures represent the concentration, expressed in weight per cent, of the polymer in the casting solution. The next letter identifies the casting solvent: triethyl phosphate (T), dimethyl sulfoxide (S), or a 2:3 formamide:acetone mixture (L). The air exposure period between casting and immersion in water is described in the next two letters, IL standing for immedi-

TABLE I  
Preparation Procedures of the Various CA Membranes used in this Study

Membrane no.	Type of membrane	CA in casting solution, %	Casting solvent	Air exposure period	Temp. of annealing bath, °C
1	CA-20-T-IL-80	20	triethyl phosphate	none	80
2	CA-20-T-IL-95	20	triethyl phosphate	none	95
3	CA-20-S-IL-80	20	dimethyl sulfoxide	none	80
4	CA-25-L-IL-80	25	2:3	none	80
5	CA-25-L-5M-80	25	formamide:acetone	5 min	80
6	Dense Films	20	acetone	~24 hr	~23

ately leached, and 5M for 5 minutes air exposure period. The last two figures in the code describe the temperature ( $^{\circ}\text{C}$ ) of the water bath in which membranes were annealed for 30 min.

### Differential Scanning Calorimetry of Wet Membranes

The membranes studied by DSC were wiped with filter paper to remove extra external water and then sealed in aluminum pans to prevent evaporation during the measurement. Sample size was about 1.5 mg. The total water content of the membranes studied was determined from the weight loss after drying a wiped, wet membrane under vacuum ( $<5$  mm Hg) at  $80^{\circ}\text{C}$  to constant weight. The sealed pans were cooled to  $-25^{\circ}\text{C}$  (well below the appearance of a freezing peak,  $0^{\circ}\text{C}$  to  $-10^{\circ}\text{C}$ ) and then heated to  $+20^{\circ}\text{C}$  at a rate of  $5^{\circ}\text{C}/\text{min}$ . A few samples were cooled to  $-80^{\circ}\text{C}$ , and no difference in results was observed. The area under the melting peak was measured, and the amount of freezing water was computed from a calibration curve obtained by measuring weighed samples of pure water. The justification for assuming the heat of fusion of water in membranes to be practically identical to that of pure water is discussed below. The amount of nonfreezing water was taken as the difference between the total water content in the membrane and the amount of freezing water.

### Scanning Electron Microscopy

Scanning electron micrographs (SEM) were taken of cross sections of membranes which had been allowed to dry at ambient conditions after immersion in a solution of 66:30:4 water:glycerol:Triton X-100 (commercial name for a solution of isooctyl phenoxy polyethoxy ethanol). These membranes were mounted obliquely on the specimen mount (so that the "cross section" would be exposed to the incident electron beam) and coated with gold. Cross sections were obtained from fresh edges prepared by splitting the membranes at liquid nitrogen temperatures. The axis about which the plane of the cross section was tilted relative to the incident electron beam ran horizontal (left to right) in all the micrographs. The scale indicated refers to sample magnification along that direction. The actual vertical distances are larger by 10-30% than indicated by the scale, depending on the tilting.

## RESULTS AND DISCUSSION

### Distribution of Freezing and Nonfreezing Waters in Wet CA Membranes

Typical melting endotherms of water in membranes 1 and 4 (CA-20-T-IL-80 and CA-25-L-IL-80) and of pure water are shown in Figure 1. The temperature values given in this figure were reproducible within  $1^{\circ}$ - $2^{\circ}\text{C}$  but obviously deviate about  $5^{\circ}\text{C}$  from the true values. Such a deviation does not affect, however, any of the arguments and conclusions given below. Comparing the shapes of the melting peaks shown in Figure 1, one notices

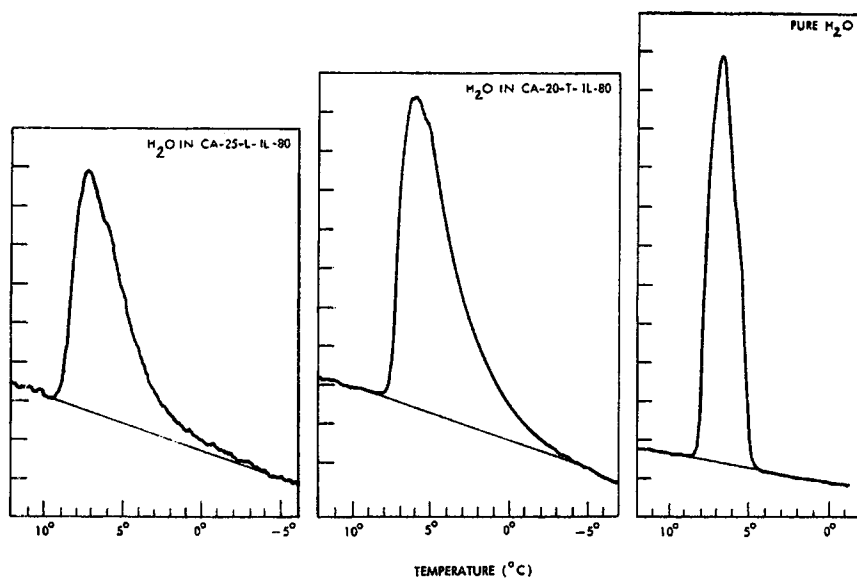


Fig. 1. Typical DSC melting endotherm of water in membranes and of pure water.

that the melting peaks of the wet membranes are "tailed" toward the low temperature region and start 5°–10°C lower than the melting peak of pure water. This could result from a freezing point depression in capillaries.<sup>8</sup> However, since the curvatures of the solid–air and of the ice–water interfaces are not known, the thermodynamic equations relating the lowering of the freezing temperature to the radius of the liquid-containing capillary cannot be used.

As mentioned in the experimental section, we have assumed the heat of fusion for the freezing water in our membranes to be identical to that of pure water. This seems justified by the fact (see Fig. 1) that most, more than 60%, of the melting water in our membranes melts in the same temperature range as pure water, and by the fact that the heat of fusion of the freezing water in similar hydrophilic polymeric substrates has been shown to be practically identical to the heat of fusion of pure ice. Thus it has very recently been shown<sup>9</sup> that the heat of fusion of the freezing water contained in a series of Hydrogel membranes covering a large range of degrees of hydration is in good agreement with the heat of fusion of normal ice.

Independent NMR and DSC determinations of the amount of nonfreezing water in collagen fibers indicated also that the heat of fusion of the freezing water in that system is essentially that of pure water.<sup>10</sup> ("Tailing" of the melting peak toward the low temperature region was observed also in the water–collagen system.<sup>10</sup>)

The water contents and the amounts of freezing and nonfreezing water in various CA membranes and in a dense cellulose acetate film are given in Table II. The results indicate that: (1) A significant fraction (17–40%) of the water in any membrane, and *all* the water absorbed by the dense film,

does not freeze upon cooling down to  $-60^{\circ}\text{C}$ , or at least does not exhibit a sharp freezing point. (2) The amount of nonfreezing bound water (0.4–0.7 g nonfreezing water per gram dry CA) depends upon the nature of the membrane and is significantly higher than the total amount of water (all of which is nonfreezing) absorbed from liquid water by a *dense* film of the same polymer ( $\sim 0.18$  g water per gram dry CA).

TABLE II  
Water Contents and Distribution of Freezing and  
Non-Freezing Waters in Various Wet CA Membranes

Membrane no.	Type of membrane,	H <sub>2</sub> O in wet membrane, %	Weight of water per g dry CA, g	Fraction of nonfreezing H <sub>2</sub> O from total water	Weight of nonfreezing water per g dry CA, g
1	CA-20-T-IL-80	71	2.4	0.28	0.67
2	CA-20-T-IL-95	63	1.7	0.24	0.41
3	CA-20-S-IL-80	76	3.1	0.17	0.53
4	CA-25-L-IL-80	63	1.7	0.29	0.50
5	CA-25-L-5M-80*	51	1.0	0.40	0.41
6	Dense Film	15	0.18	1.00	0.18

\* While the values of the total water contents and the fractions of nonfreezing water out of the total water were reproducible to better than  $\pm 2\%$  from one membrane sample to another, the deviations of these values in CA-25-L-5M-80 membranes were about  $\pm 15\%$ . This probably occurred because the evaporation of the acetone was performed under uncontrolled temperature, relative humidity, and gas-stirring conditions.

### Dependence of Nonfreezing Water Content on Membrane Structure

To help understand the reasons for the differences in the amounts of nonfreezing water in our membranes, we have studied the structure of these membranes by means of scanning electron microscopy. The low-magnification cross sections in the scanning electron micrographs shown in Figure 2 indicate that, of the five membranes in this study, only membrane 3 (CA-20-S-IL-80, shown in Fig. 2e) is highly nonuniform and contains large cavities. We can, therefore, estimate an average volume concentration of the polymer in the other four membranes from their water contents given in Table II.

What can the water contents and the scanning electron micrographs of the various membranes teach us about the differences in the amount of nonfreezing water in these membranes? Let us consider first the pair of membranes 1 and 2 cast from triethyl phosphate (coded T) and explain why an increase in annealing temperature from  $80^{\circ}\text{C}$  to  $95^{\circ}\text{C}$  is accompanied by a considerable decrease in the amount of bound (nonfreezing) water (0.67 to 0.41 g nonfreezing water per gram dry CA). (The term "bound water" used in this article should not be confused with "structured" or "ice-like" water. This is clearly indicated by the NMR data given below.) The average polymer density in the  $95^{\circ}\text{C}$ -annealed membrane is higher than that in the  $80^{\circ}\text{C}$ -annealed ones, as indicated by its lower total water con-

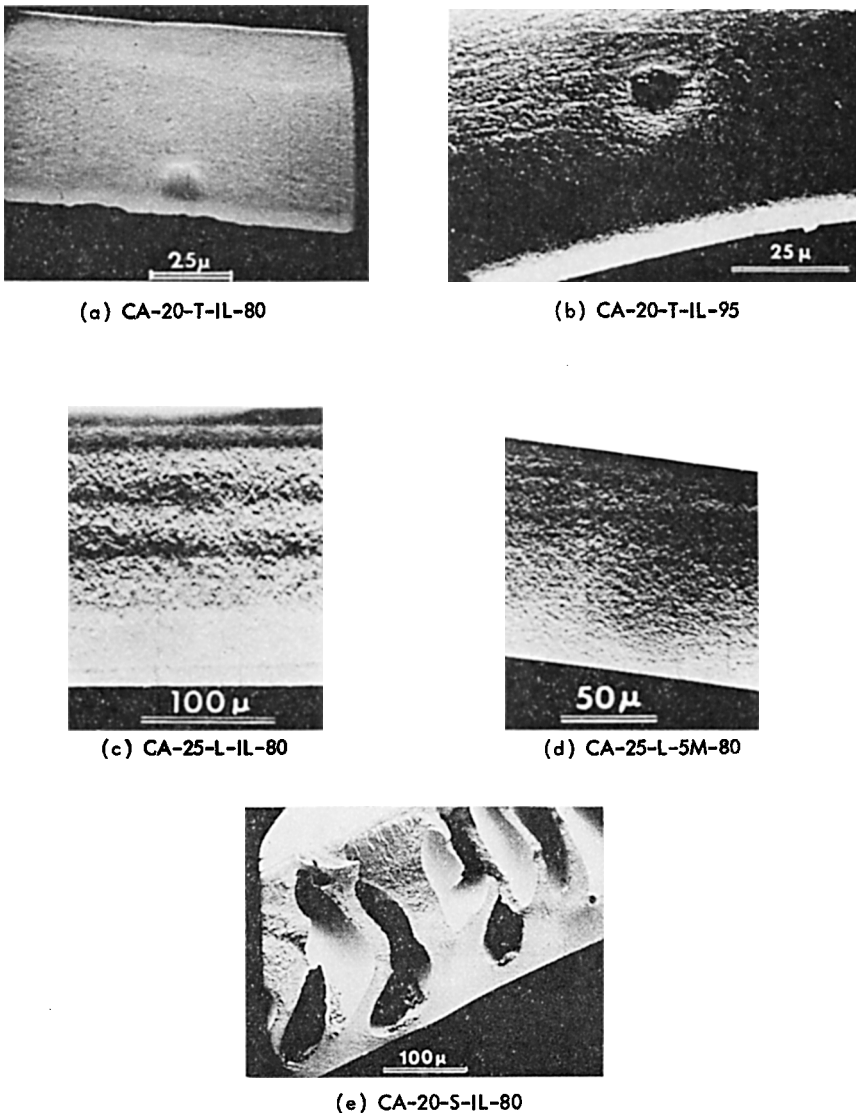


Fig. 2. Scanning electron micrograph of cross sections of the CA membranes used in this study. The upper surface of the cross sections corresponds to air-solution interface of the cast solution.

tent. Furthermore, higher-magnification scanning electron micrographs suggest that, while the volume distribution of the polymer in membrane 1 (CA-20-T-IL-80) is uniform and the average pore size is probably lower than  $500 \text{ \AA}$ , the CA-20-T-IL-95 membrane (no. 2) is more heterogenous, containing pores  $500\text{--}1000 \text{ \AA}$  in diameter which are bounded by relatively dense and thick polymeric walls. This is also indicated by the fact that the  $80^\circ\text{C}$ -annealed membrane is transparent, whereas the  $95^\circ\text{C}$ -annealed one is

slightly turbid. Therefore, the true packing density (compactness) of the polymer in the polymeric phase of the 95°C-annealed membrane is even higher than that estimated from the water content. However, an increase in the compactness of the polymer means that the extent of polymer-polymer interactions is larger and the accessibility of the polymeric chains to interact with water is lower.

The observation that both the total water content of cellulose acetate membranes cast from triethyl phosphate solution and the amount of bound water in these membranes decrease with an increase in the annealing temperature is in agreement with similar observations on CA membranes cast from different solvent systems. Thus, it has been found by Vincent et al.<sup>5</sup> that the amount of bound water in Loeb-Sourirajan membranes (varying between 0.10 and 0.44 g H<sub>2</sub>O per gram dry CA) decreased by 10–40% when the annealing temperature was increased from 25°C to 84°C. It should be noted that, while the amount of water bound to the CA-20-T-IL-80 membrane (0.67 g H<sub>2</sub>O/g CA) is higher than that bound to the CA-20-T-IL-95 membrane (0.41 g H<sub>2</sub>O/g CA), the former does not reject any salt<sup>11</sup> while the 95°C-annealed membrane rejects 94% NaCl from a 5000-ppm solution at 40 atm pressure differential.<sup>12</sup> A study of the relations between the amounts of nonfreezing water in various uniformly swelled CA membranes containing only bound (nonfreezing) water and their permeability to electrolytes is in progress.

The larger amounts of water bound to membrane 4 (0.50 g H<sub>2</sub>O/g CA) as compared to that bound to membrane 5 (0.41 g H<sub>2</sub>O/g CA) can be explained by reasoning similar to that used in the membranes cast from triethyl phosphate (nos. 1 and 2). The significantly lower total water content of the CA-25-L-5M-80 membrane (no. 5) indicates that the density of the polymeric phase in the 5-min dried membrane is much higher than that of the immediately leached one (no. 4). Consequently, the number of sites on a cellulosic chain which are not bound to another polymeric chain, and are free to interact with water, is smaller. The weight of nonfreezing water per gram dry CA-25-L-5M-80 membrane is, therefore, only 0.41 g, as compared to the 0.50 g H<sub>2</sub>O/g CA in the CA-25-L-IL-80 membrane.

In view of the explanations mentioned above, it may appear surprising that the amount of nonfreezing bound water in membrane 3 (CA-20-S-IL-80) is low (only 0.53 g H<sub>2</sub>O per gram dry CA), although its total water content is the highest (3.1 g H<sub>2</sub>O per gram dry CA). This can, however, be explained in view of its structure shown in Figure 2e. It is obvious from this figure that the density of the cellulose acetate phase in this membrane is larger than that which would be deduced from its total water content; and, consequently, the extent of its hydration is relatively low.

It should be emphasized here that while an increase in the total water content of membranes cast from the *same* solution is indicative of greater accessibility to binding water, this variable cannot be used for determining the water binding capability of membranes cast from *different* solutions. Thus, although the water contents of membrane 2 (CA-20-T-IL-95) and

membrane 4 (CA-25-L-IL-80) are similar ( $\sim 63\%$ ), the amount of non-freezing water in the latter membrane (0.50 g H<sub>2</sub>O/g dry CA) is larger than that in the triethyl phosphate-cast membrane (0.40 g H<sub>2</sub>O/g dry CA). This indicates that the total water content (*average* density of the polymeric phase) and uniformity of low-magnification SEM cross section are only rough measures of the *true* compactness of the polymeric phase. The composition of the casting solution determines the fine details of the nature and the extent of polymer-polymer interactions within the membrane, e.g., per cent crystallinity, nature of functional group interacting, etc., and, consequently, the nature and the extent of its interactions with water.

The amounts of nonfreezing water in the membranes studied in this investigation (0.4–0.7 g water per gram CA) are significantly higher than the total amounts of water (0.12–0.18 g water per gram dry polymers) adsorbed by powder or by a *dense* film of cellulose acetate equilibrated with water-saturated vapors<sup>6,13–15</sup> or swelled in water. As shown in Table II, all the water molecules contained in such *dense* polymeric matrices are bound and do not freeze. It seems, therefore, that the water-binding capability of cellulose acetate (and possibly also of other hydrophilic polymer) films or membranes may be determined much more by the compactness of the polymeric phase within the film than by its chemical nature. The conclusion that the water binding capability of CA membranes may be much more dependent on membrane structure than on its chemical composition is in accordance with the observations of Vincent et al.<sup>5</sup> on the 4.5-fold variation (0.10 to 0.44 g bound water per gram dry CA) in the bound-water content of Loeb-Sourirajan-type desalination membranes.

The observation that water-binding capability of hydrophilic polymeric membranes depends on their morphology implies that the determination of pore-size distribution in these membranes from adsorption isotherms may not be correct. More specifically, the extra amounts of water adsorbed (from the vapor phase) by membrane as compared to the amounts adsorbed by a *dense* film are not necessarily due to capillary condensation. It may be mentioned that this method of attributing the larger amounts of water adsorbed by CA membranes to capillary condensation (and a resultant calculation of the pore-size distribution in these membranes) has been applied to Loeb-type membranes<sup>6</sup> which were studied by us and shown to contain amounts of nonfreezing water 3 to 4 times larger than the amount of water adsorbed by a dense film of cellulose acetate.

### Nature of Bound Nonfreezing Water

The NMR spectrum of the water in a CA-20-T-IL-95 membrane (no. 2) was monitored by a wide-line spectrometer as the temperature was slowly lowered from 20° to –50°. The sharp room-temperature NMR line was greatly reduced in intensity and somewhat broadened as part of the water froze between 0° and –10°C. However, little change was observed in the line between –10° and –50°C. The width of the observed water line in the “frozen” membrane was less than 2 kHz, compared to the observed proton NMR line width of polycrystalline ice, which is about 67 kHz.<sup>16</sup>



The 2-kHz NMR line belongs to water whose rotational diffusion is restricted, but which is still *highly mobile compared with ice*. The superimposed ice and CA spectra comprise a very broad background NMR line which was not detected in this experiment. An extensive NMR study of the properties of water in cellulose acetate membranes is now being conducted.

## CONCLUSIONS

The experimental observations presented above suggest that:

1. A significant fraction of the water in various wet cellulose acetate membranes does not freeze, probably because of strong interaction with the polymer.
2. The amount of nonfreezing bound water depends on membrane morphology, increasing with decrease in the packing density (compactness) of the polymer within the membrane.
3. All the water contained in dense polymeric films is bound to the polymer and does not freeze.
4. The nonfreezing bound water is highly mobile compared with ice.

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The commercial names are given for identification purposes only and do not imply an endorsement by the National Bureau of Standards.

## References

1. U. Merten, Ed., *Desalination by Reverse Osmosis*, MIT Press, Massachusetts, 1966.
2. K. S. Spiegler, Ed., *Principles of Desalination*, Academic Press, New York, 1966.
3. S. Sourirajan, *Reverse Osmosis*, Logos Press, London, 1970.
4. R. D. Schultz and S. K. Asunmaa, Paper No. WD 1112, Astropower Laboratory, McDonnell Douglas Corporation, Newport Beach, California, July 1969.
5. A. L. Vincent, M. K. Barsh, and R. E. Kesting, *J. Appl. Polym. Sci.*, **9**, 2363 (1965).
6. H. K. Lonsdale, U. Merten, and R. L. Riley, *J. Appl. Polym. Sci.*, **9**, 1341 (1965).
7. H. Yasuda, C. E. Lamaze, and A. Peterlin, *J. Polym. Sci. A-2*, **9**, 1117 (1971).
8. R. Defay, I. Prigogine, A. Bellemans, and D. H. Everett, *Surface Tension and Adsorption*, Longmans, London, 1966.
9. H. Yasuda, H. G. Olf, B. Crist, C. E. Lamaze, and A. Peterlin, Preprint No. 313, Camille Dreyfus Laboratory, P. O. Box 12194, North Carolina 27709, March 1971.
10. R. E. Dehl, *Science*, **170**, 738 (1970).
11. R. Bloch, and Frommer, M. A., *Desalination*, **7**, 259 (1970).
12. Hydronautics, Incorporated, Quarterly Progress Report 813-5 to the Office of Saline Water, March 1969.
13. P. T. Newsome and S. E. Sheppard, *J. Phys. Chem.*, **36**, 930 (1932).
14. A. M. Thomas, *J. Appl. Chem.*, **1**, 141 (1951).
15. J. L. Bert, I. Fatt, and D. N. Saraf, *Appl. Polym. Symposia*, **13**, 105 (1970).
16. K. Kume, *J. Phys. Soc. Japan*, **16**, 290 (1961).

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