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# Whisker growth by means of porous glass

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Porous glass serves as a habit modifier for the growth of whiskers of organic materials as well as inorganic salts. The role of the surface structure of this hydrophilic membrane was shown.

## 1. Introduction

We have recently studied the growth of whiskers of various inorganic salts from aqueous solutions by means of cellulose acetate (CA) membranes [1, 2]. A model describing the growth process was suggested, showing the porous CA membrane to serve as a habit modifier [2]. Although whiskers of quite a long list of materials could be grown via CA membranes, the method was limited to inorganic salts or small ionic organic molecules (e.g. oxalic acid, glycine) which do not react with the CA polymer and precipitate out of aqueous solution. In that respect, these results are similar to those obtained with other porous cellulose-based membranes, such as cellophane [3–5].

In the present work, whiskers of inorganic salts as well as organic materials, soluble in water, were grown by means of porous glass membranes [6]. Both CA and glass membranes are known for their affinity to water. However, while the cellulose-based membranes exhibit both hydrophobic (backbone) and hydrophilic (functional groups) character, the glass has only a hydrophilic character. Hence the glass membrane seems to be promising as a habit modifier for whisker growth of a larger variety of materials.

## 2. Experimental details

The porous glass used (Vycor 7930) was purchased from Corning Glass Works, USA. The glass, prepared by the leaching of borosilicate glass, constitutes a porous open structure, the average pore diameter being $4 \pm 0.3$ nm. Cleaning of the glass was carried out according to the instructions of the manufacturer [6, 7].

Discs of porous glass, 1.5 mm thick, were sawn from a rod of diameter 15 mm. No surface polishing was carried out. The cleaned discs were half-submerged in the growth solutions, the whiskers growing on top of the exposed surface. The growth solutions were prepared from analytical grade reagents and deionized water. The concentration of the solutions varied between 0.5 and 3 M. Whiskers were grown at room temperature.

The composition and morphology of the whiskers were determined by powder X-ray diffraction, optical and scanning electron microscopy.

## 3. Results

Whiskers of various inorganic and organic materials, all soluble in water, grew by means of porous glass membranes (Table I). The list includes some of the materials which also grow whiskers via CA membranes, organic materials of different families which do not grow whiskers via CA membranes, and $KMnO_4$ which reacts with the CA polymer but grows whiskers via the glass membrane. Typical SEM micrographs of whiskers are shown in Fig. 1. All whiskers studied were single crystals, not hollow, with the growth proceeding from the bottom as in the case of whiskers grown via CA membranes [1, 2]. In general, the whiskers were quite fragile and could be separated from the glass very easily, probably because of their small dimensions (Fig. 1). The geometry of the experimental set-up yielded whiskers $\approx 1$ cm long within several days. In the case of KCl only, $\approx 10$ cm long whiskers could be obtained.

TABLE I Materials from which whiskers were obtained via porous glass and CA membrane

| Solute | Porous glass | CA membrane |
|---|---|---|
| KCl | + | + |
| NaCl | + | + |
| $NH_4Cl$ | + | + |
| $NaNO_2$ | + | + |
| $NaNO_3$ | + | + |
| $KNO_3$ | + | + |
| $Pb(NO_3)_2$ | + | + |
| $FeSO_4 \cdot 7H_2O$ | + | + |
| $CuSO_4 \cdot 5H_2O$ | + | + |
| $KMnO_4$ | + | − |
| $K_2Cr_2O_7$ | + | + |
| Glycine | + | + |
| L-phenylalanine | + | − |
| Oxalic acid | + | + |
| Malonic acid | + | − |
| Thiourea | + | − |
| $K_2CrO_4$ | − | + |
| $K_2SO_4$ | − | + |

*Research carried out while on sabbatical leave at the Hebrew University of Jerusalem.

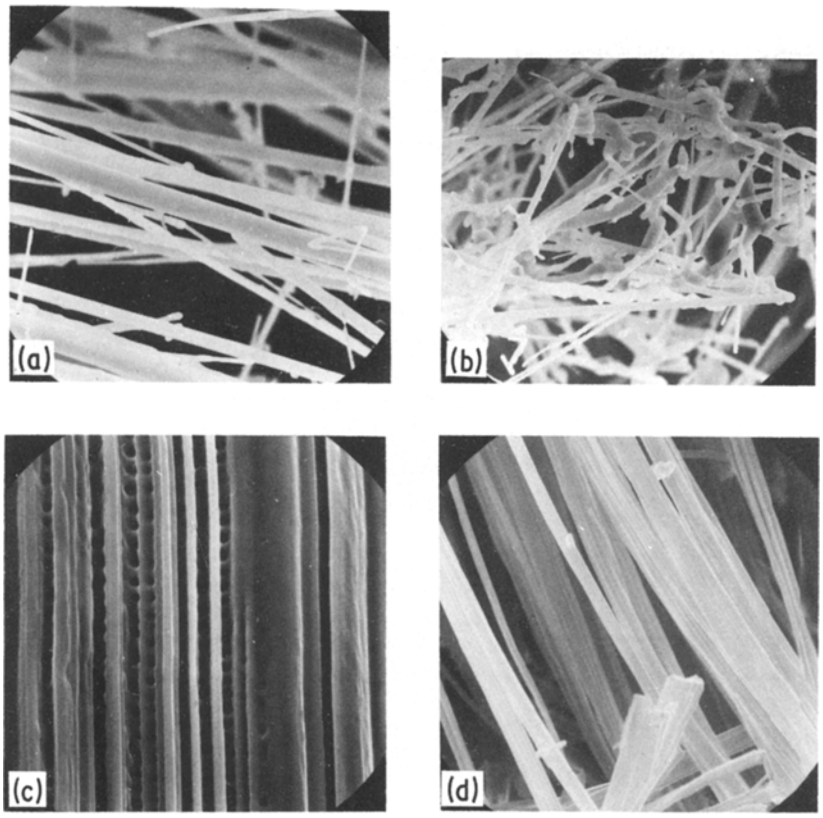

*Figure 1* SEM micrographs of whiskers: (a) KCl, × 1000; (b) $KNO_3$, × 550; (c) $Pb(NO_3)_2$, × 2000; (d) L-phenylalanine, × 1000.

Careful examination of the whiskers and glass membrane by optical microscopy and SEM was carried out. Examples of whisker root, cross-section and tips are shown in Fig. 2. In all cases studied the tips of the whiskers were rounded, with the cross-section exhibiting an arbitrary shape, not reminiscent of any crystallographic structure. The roots were observed to emerge from the glass surface, not penetrating the porous bulk membrane. The linear dimensions of the cross-section of the whiskers ($\leqslant 0.5\,\mu$m) are much larger than the average pore diameter as reported by the manufacturer. However, the sawing damages the glass surface, leaving it rough and with "craters" of various dimensions much larger than the average pore diameter (Fig. 3).

## 4. Discussion

The partially submerged glass in the solution loses water from its exposed surface by evaporation. Since the porous glass is known to be "thirsty" [6, 7] the lost water is replaced by solution transported within the membrane. The continuous evaporation of water leads to saturation of the solution on the exposed surface of the membrane, resulting eventually in the growth of whiskers, with the glass membrane serving as a habit modifier. The behaviour of this system can be explained by the model suggested earlier for the growth of whiskers by means of CA membranes [1, 2]. This model explains the habit modification of materials that are largely divergent in structure and properties (e.g. NaCl and $CS(NH_2)_2$) by the porous membranes.

The present work shows that the habit modification is a result of the surface structure of the exposed membrane. This is based on the following observations: (a) in no case was a whisker observed to penetrate the glass membrane, as was also observed in the case of CA membranes; (b) the whiskers exhibit a

*Figure 2* SEM micrographs of (a) root of $Pb(NO_3)_2$ whisker, × 5400; (b) cross-section of $KNO_3$ whisker, × 10 000; (c) tips of $Pb(NO_3)_2$ whisker, × 2000.

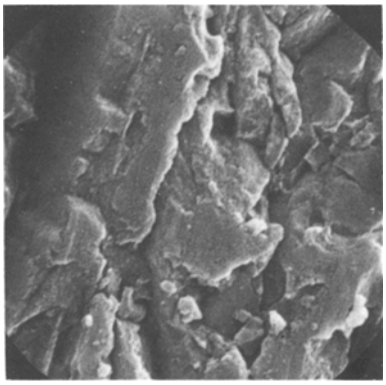

*Figure 3* SEM micrograph of the surface of the porous glass disc, × 1000.

morphology stemming from the rough "crater" structure of the surface rather than from the internal pore structure. The large difference in structure between bulk and surface of the non-polished porous glass membranes supported the second observation. The open porous internal structure of the glass serves only as channels for transporting the solution from the solution reservoir to the exposed surface at an appropriate rate. The physical dimensions of the craters or pores in the bulk and/or on the surface of a membrane determine, among other parameters, the whisker growth. Preliminary results indicate that pores having relatively large dimensions do not serve as habit modifiers, while those with dimensions too small do not let the solute pass through. This observation is under further study.

In the three-component system membrane–water–solute, each component interacts with the other two. In the case where the interaction membrane–water is stronger than that of water–solute or membrane–solute, and if water is scarce, the solute will precipitate out of the system. However, when the interaction membrane–solute is the strongest, the solute remains within the membrane and no whiskers are obtained. Hence, in the case of organic materials (not including zwitter ions like glycine) no whiskers were obtained when using CA membranes because of the hydrophobic character of the latter. However, using a membrane which is hydrophilic allows whisker growth of organic solutes.

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