Effect of Water Sorption Hysteresis on Gas Transport in a Regenerated Cellulose

It is well known that the sorption of water into cellulose exhibits hysteresis over the whole humidity range. But the relation between the water sorption hysteresis and the gas transport characteristics of water-swollen cellulose has not been investigated.

In the present study, the permeation, diffusion, and solubility of hydrogen in the regenerated cellulose which was approximately at equilibrium on both the sorption isotherm and the desorption isotherm were examined.

The apparatus, procedures, and materials used, except for the regenerated cellulose, were the same as those for the previous investigation.[1] The regenerated cellulose film tested in this study was one made by the viscous process by Tokyo Cellophane Co., Ltd., in which neither plasticizer nor anchoring agent was used. The transport characteristics of the water-swollen regenerated cellulose were determined by measuring the steady-state and transient permeation rates of hydrogen through the laminate composed of the cellulose and polyethylene films through which water vapor was steadily permeating from the cellulose to the polyethylene sides. The experiment was based on the fact that the presence of water vapor did not affect the gas permeability of polyethylene but did effect regenerated cellulose. The pressure boundary conditions of this experiment and the analysis of permeation data were previously discussed in detail.[1]

As shown in Figure 1, a typical hysteresis curve was followed by the sorption and desorption of water into and from the regenerated cellulose. The isotherms correspond to the maximum range of relative humidity over which hysteresis occurs.

The effects of varying water content on the permeability and diffusivity of regenerated cellulose film to hydrogen are shown in Figure 2. The ordinate represents the relative permeability P_1/P_1^* and the relative diffusivity D_1/D_1^* on a logarithmic scale, where P_1 and D_1 are the permeability and diffusion coefficients at a given water content, and P_1^* and D_1^* are the corresponding coefficients at water content of 0 g/g given in Table I. It is apparent that the permeability and diffusivity on the desorption side are appreciably larger than those on the sorption side. And it is interesting to note that the permeability on the sorption side first decreased abruptly and then, passing through a minimum, increased with further increase in water content.
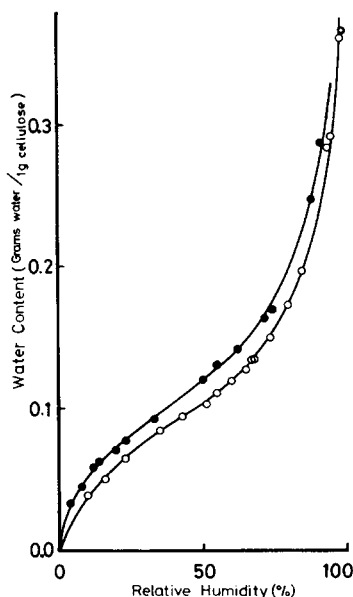

Fig. 1. Sorption and desorption isotherms of water vapor on regenerated cellulose at 25.0°C: (○) sorption, (●) desorption.
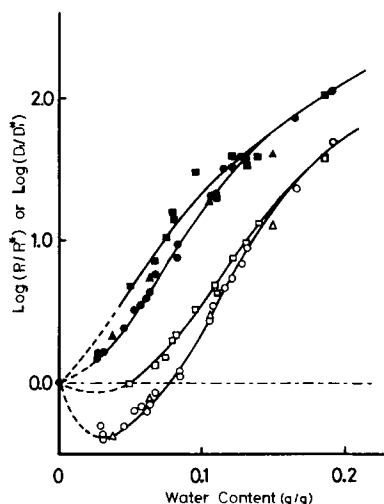
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Fig. 2. Relative permeability and diffusivity of regenerated cellulose to H_2 vs. water content at 25.0°C. Sorption side: $(\bigcirc, \triangle)$ P_1/P_1^*; $(\bullet, \blacktriangle)$ D_1/D_1^*. Desorption side: $(\square)$ P_1/P_1^*; $(\blacksquare)$ D_1/D_1^*. P_1^* = $(\bigcirc)$ 2.43×10^{-13} and $(\triangle, \square)$ 4.03×10^{-13} cm^3 (S.T.P) cm/cm^2 sec cm Hg.

The effect of sorption hysteresis on the relative solubility S_1/S_1^* is shown in Figure 3. The solubility coefficients were calculated from the relation $S_1 = P_1/D_1$. Apparently, the solubility on the sorption side is a little less than that on the desorption side in the region of water content below 0.11 g/g.

The water-swollen cellulose between the sorption and desorption isotherms showed intermediate transport characteristics. That is, values of the permeability, diffusion, and solubility coefficients of the cellulose on traversing the hysteresis loop were between two limiting values of the corresponding coefficients shown in the figures.

Except for the effect of sorption hysteresis on the gas transport characteristics, the results described above may be interpreted in the same way as discussed previously.[1] That is, the relatively small increase in diffusivity at a small amount of sorbed water results from the weak stimulation of the segmental motion caused by the sorbed water. And the reduction of solubility is due to the penetration of water into microvoids or matrixes of the amorphous region. At a large amount of sorbed water, the swelling spreading out the interchain distance serves to increase greatly the segmental motion, and hence the diffusivity is greatly enhanced. The moderate increase in solubility may be caused by the expansion of the cellulose matrixes due to the swelling.

It is generally accepted that the hysteresis of water sorption is due to the irreversibility in the sorption characteristic of cellulose. According to Newns,[2] it follows that during sorption, water first penetrates and clusters into the more accessible regions of the amorphous cellulose, and that this is succeeded by a dissolution of interchain hydrogen bonds. During desorption, the re-formation of the dissolved bonds is hindered by the presence of sorbed water and the rigidity of the structure. This hindered re-formation process will be irreversible and cause the sorption hysteresis.

TABLE I
Transport Parameters of Dry Regenerated Cellulose Film (20 μm thick) to H_2 at 25.0°C

Permeability coefficient, $\dfrac{\text{cm}^3 \text{ (S.T.P.) cm}}{\text{cm}^2 \text{ sec cm Hg}} \times 10^{13}$	Diffusion coefficient, $\dfrac{\text{cm}^2}{\text{sec}} \times 10^{10}$	Solubility coefficient, $\dfrac{\text{cm}^3 \text{ (S.T.P.)}}{\text{cm}^3 \text{ cm Hg}} \times 10^4$
2.43[a]	6.5	3.7[a]
4.03[b]		6.2[b]

[a] Values measured first after mounting the film onto permeation cell.

[b] Reproducible values measured after a series of the time-lag measurements at varying relative humidities up to 100% R.H.
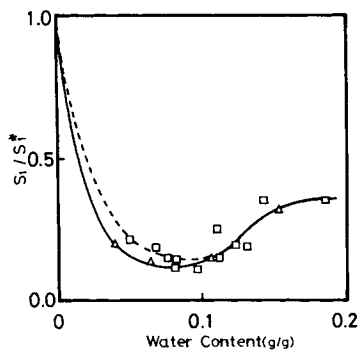
Fig. 3. Relative solubility of regenerated cellulose to H_2 vs. water content at 25.0°C: (△) sorption side; (□) desorption side. $S_1^* = 6.2 \times 10^{-4}$ cm^3 (S.T.P)/cm^3 cm Hg.

It may be understood from these considerations that the sorbed water hindering the re-formation of interchain hydrogen bonds accelerates the segmental motion of cellulose more than the sorbed water which is bound to free hydroxyl groups of cellulose at the early stages of sorption process. The pronounced effect of sorption hysteresis on the gas diffusivity of regenerated cellulose in the region of water content below 0.15 g/g, therefore, may be caused by a difference in sorbing condition of water molecules between sorption and desorption.

It is well known that the volume of water-swollen cellulose on the desorption side is greater than that on the sorption side and that the difference in volume becomes very small at a higher water content.[3,4] The volume hysteresis caused by the rigidity of the structure seems to be reasonably consistent with the effect of sorption hysteresis on the solubility observed in this study. Thus, it can be suggested that the whole volume of microvoids in which the void-filling sorption process of penetrant gas will occur is greater on the desorption side than on the sorption side at any water content below about 0.11 g/g.

References

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