Pore Size Distribution and Sorption–Desorption Hysteresis with Water

The presence of permanent and reproducible hysteresis loops for the sorption–desorption of water vapor on gelatin (Difco) has been considered in the light of the cavity concept by Rao and Das (1). They have attempted to explain quantitatively on the basis of the shape and size of the hysteresis loops, that both the necks and cavities suffer contraction, the latter suffering more than the former. According to this theory, the pore size distribution of the system should also change with reference to the number of cycles. Therefore, abrupt changes should occur even at the 7th cycle, where the equilibration has been carried out to a longer time so that the system had the facility to swell to a greater extent. In this communication, pore size distribution analyses of Difco gelatin by the method of Barrett *et al.* (2) for the meso pores and through the method of Mikhail *et al.* (3) for the micropores are presented. The basic experimental data in the form of volume of water adsorbed as a function of relative pressure for these systems reported by Rao and Das (1) were utilized for the computation of pore size distributions. The applicability of these methods of analysis for pore structure analysis in such a system has been already established by us (4). The pore size distribution curves at 1st and 12th cycles are shown in Fig. 1 and those at the 3rd and 7th cycles are shown in Fig. 2. It is seen that there is no contraction of pore size distribution in the 1st, 3rd, and 7th cycles while the curve corresponding to the 12th cycle shows the disappearance of higher radius (~200 Å) as well as lowest radius (~45 Å) pores simultaneously. It was found that the system does not contain any appreciable number of micropores to a measurable extent. The situation found at the 12th cycle can be due to:

(a) Pores of radius ~178 Å contracting and pores of radius ~48 Å swelling to ~116-Å-radius pores after 12 cycles.
(b) Pores of radius ~178 Å contracting to ~116-Å-radius pores simultaneously with the collapse of 48-Å-radius pores.

The result obtained for other gelatin systems and the decrease in the sorptive capacity with increasing cycles seem to suggest that (b) is more likely to occur.

It is to be noted that the contraction of the pores due to repeated cycling can take place only at the

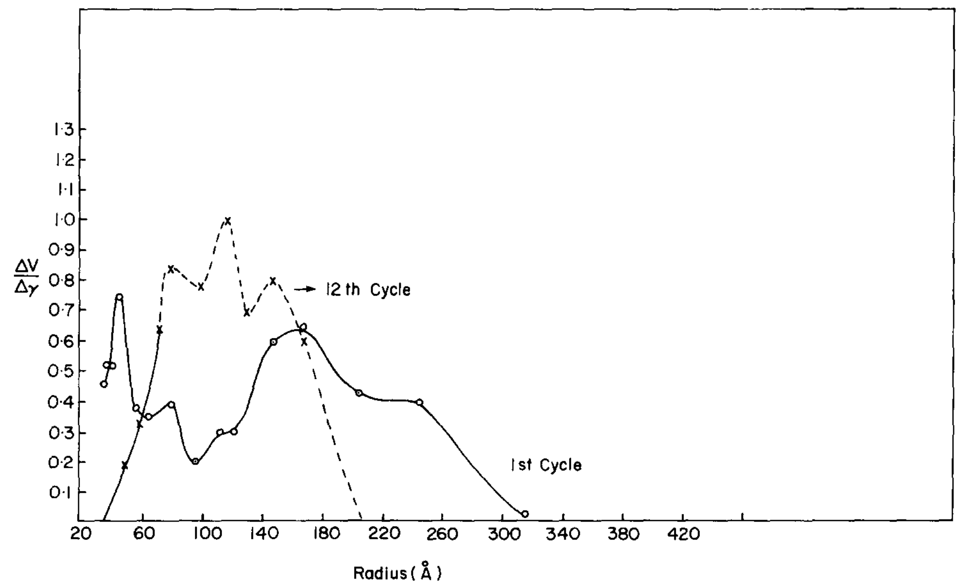

FIG. 1. Pore size distribution plots for gelation (Difco) after 1st and 12th cycles of water sorption–desorption.

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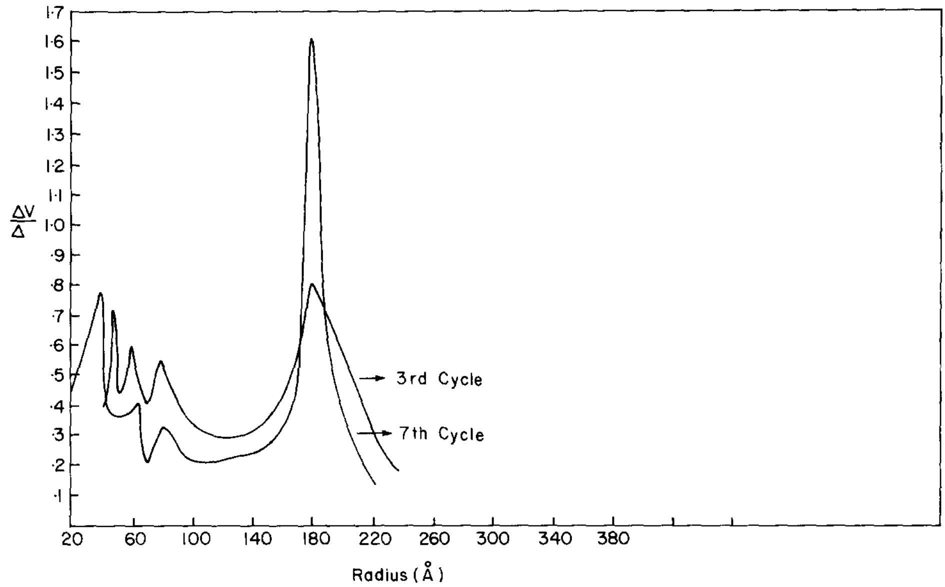

FIG. 2. Pore size distribution plots for gelation (Difco) after 3rd and 7th cycles of water sorption–desorption.

time of desorption. The hysteresis effects are interpreted as due to the entrapping of water by the neck of the cavity at the time of desorption, which is sudden and abrupt. It is important to note that the contraction of the entire pore structure which is accompanied by the desorption process will also entrap water. This entrapment will play a definite role in giving rise to more pronounced hysteresis.

It may, therefore, be concluded that the analysis of hysteresis loops should take into account the pore structure distribution of the system.

REFERENCES

1. Rao, K. S., and Das, B., *J. Phys. Chem.* **72**, 1223 (1968).
2. Barrett, E. P., Joyner, L. G., and Halenda, P. P., *J. Amer. Chem. Soc.* **73**, 373 (1951).
3. Mikhail, R. S. H., Brunauer, S., and Bodor, E. E., *J. Colloid Interface Sci.* **26**, 45 (1973).
4. Sanjeevi, R., Ramanathan, N., and Viswanathan, B., *J. Colloid Interface Sci.* **57**, 207 (1976).

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