

HYSTERESIS IN SORPTION

XIII. Mode of Preparation of Silica Gel and Its Influence on Hysteresis

BY T. KRISHNAPPA,* K. SUBBA RAO,† AND B. SANJIVA RAO,§ F.A.Sc.
(Department of Chemistry, Central College, Bangalore, S. India)

Received January 6, 1947

INTRODUCTION

A SURVEY of the literature on sorption indicates that the sorptive capacity of an adsorbent is greatly influenced by the method of its preparation. Silica gel whose sorptive capacity has been extensively studied can be prepared in several ways. Glassy silica gel³ is prepared by allowing to set to a jelly, a silicic acid sol obtained by the interaction of sodium silicate and hydrochloric acid. Chalky silica gel has been obtained by Holmes, Sullivan and Metcalf¹ by precipitating the gel from a solution of sodium silicate by ferric chloride solution. "Wet heat treatment"² has been found to lessen the shrinkage of the gel on drying and has yielded a product of greater porosity. Bartell and Fu² have obtained a sample of chalky gel by adding a saturated solution of nickel nitrate to a mixture of sodium silicate and hydrochloric acid before the latter sets to a jelly.

In a study of the hysteresis effect in sorption, Rao, K. S. has found that gels obtained by precipitation (titania,⁴ alumina,⁵ and ferric oxide⁶) gave hysteresis loops markedly different from that of glassy silica gel⁷ prepared from silicic acid jelly. The mode of preparation of an adsorbent therefore, seems to influence the hysteresis by its effect on the size and shape of cavities. To confirm this view, hysteresis was studied with silica gels prepared by different methods.

EXPERIMENTAL

Preparation of silica gel by precipitation

Silica gel A (transparent variety).—0.3 litre of 0.5 N sodium silicate solution was slowly dropped into 3 litres of 0.5 N ammonium chloride solution, the latter being mechanically stirred vigorously. A gelatinous precipitate was slowly formed. The precipitate was filtered over a cloth filter and washed free of chloride. The precipitate was next dried in an

* Mysore Government Scholar, University of Sheffield, Sheffield.

† Senior Research Fellow of the National Institute of Sciences of India,

§ Principal and Professor of Chemistry, Central College.

electric oven at 120° C. for about 24 hours. The resulting product was hard, transparent and glassy.

Silica gel B (opaque variety).—Ten volumes of 0·8 N ammonium chloride were mixed with one volume of 0·8 N sodium silicate in the way already indicated. A gelatinous precipitate was quickly formed. This was filtered, washed and dried as above. The dried gel was hard and opaque.

Activation of gels

The gels were activated by heating to 450° C., in a current of dry air for 4 hours in an electric furnace.

Residual water in gels

The residual water in the activated gel was determined by igniting to constant weight over a Fisher burner, a known weight of the gel in a platinum crucible. Gel A contained 5·2% residual water and gel B contained 5·57%.

Sorption and desorption

A series of sorptions and desorptions of water vapour at 30° C. on the gels was conducted. The time required for completing three cycles of sorptions and desorptions with silica gel A was 3 months and for 4 cycles with gel B was 4 months. At the end of the first desorption, the amounts of water held irreversibly in gels A and B were 1·9% and 3·5% respectively. At saturation pressure, gel A took 85·8 gm. of water per 100 gm. of activated gel, whereas gel B took 131·4 gm. The results obtained are graphically represented in Figs. 1 and 2. The hysteresis loops of the two samples of

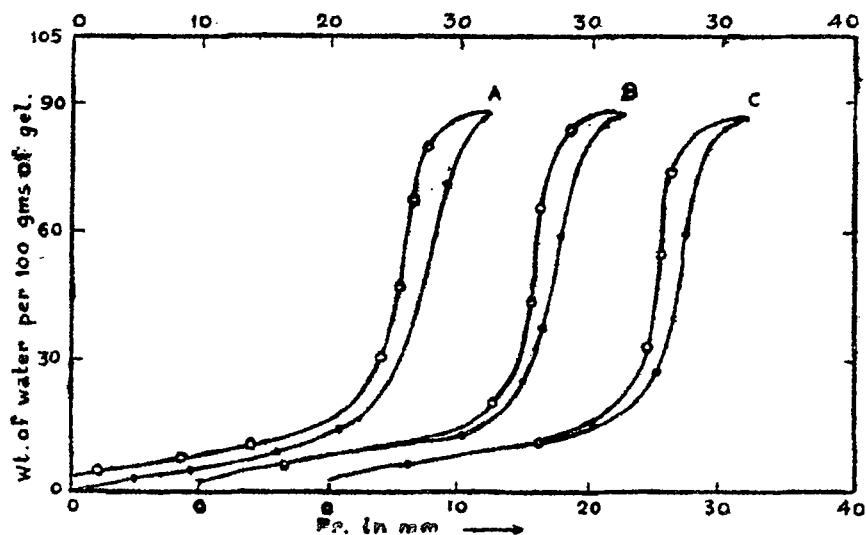


FIG. 1. Precipitated silica gel (Glassy)—water (A 1st cycle, B 2nd cycle, C 3rd cycle)

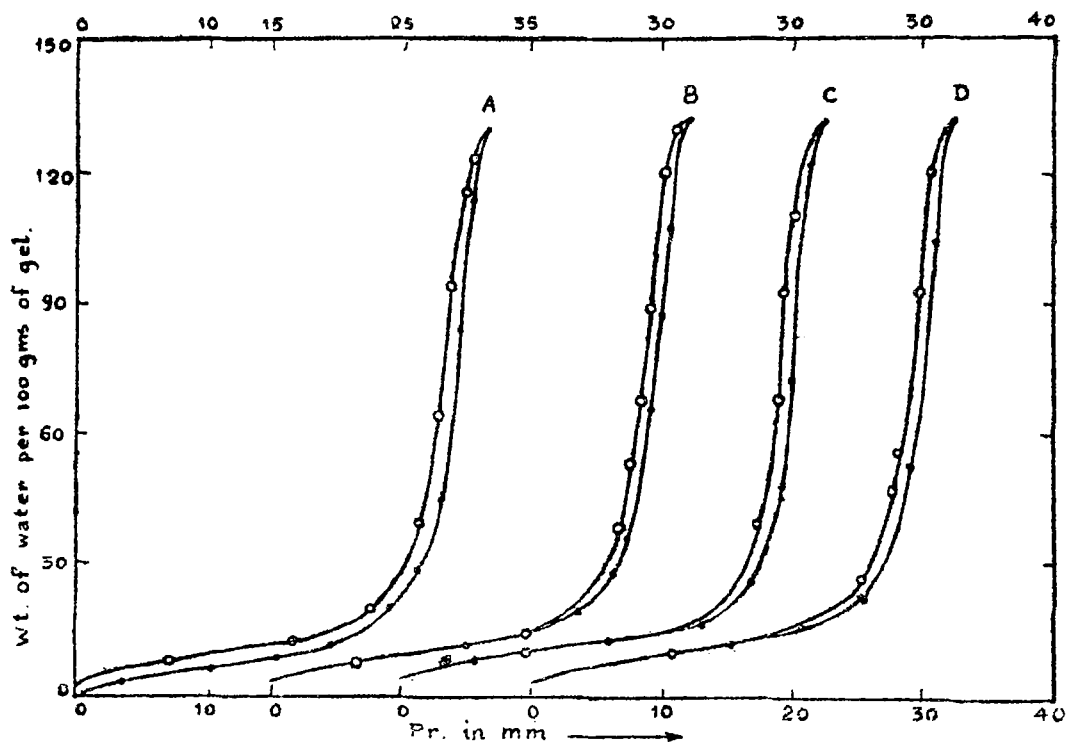


FIG. 2. Precipitated silica gel (Opaque)—water (A 1st cycle, B 2nd cycle, C 4th cycle, D 5th cycle)

precipitated gels A and B together with the hysteresis loop (reproduced from Rao, K. S., *J. Phys. Chem.*, 1941, **45**, 513) of glassy silica gel obtained from silica jelly are shown in Fig. 3.

DISCUSSION

The two samples of precipitated silica gel have shown a permanent and reproducible hysteresis effect for water vapour. At low relative humidities, the two gels take up water to about the same extent. At saturation pressure, however, there is a marked difference in the sorptive capacities of the two gels. Gel A takes 85.8 gm. of water per 100 gm., whereas gel B takes 131.4 gm. In both cases, for high values of humidity the sorption and desorption curves rise steeply and are almost perpendicular to the pressure axis. This indicates that the major part of the capillary volume in both the gels is concentrated in a narrow region of capillary radius.

A study of Fig. 3 reveals that in gel B the cavities and their necks are wider than those in gel A. The loops of the two samples of precipitated

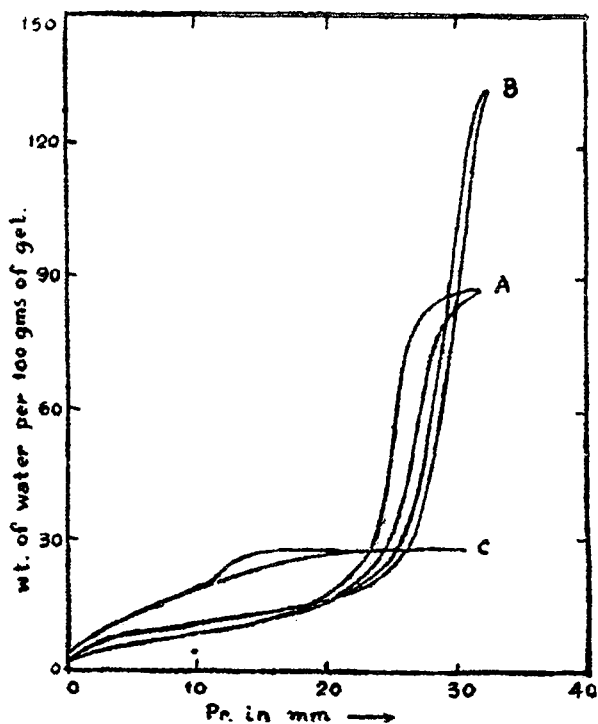


FIG. 3. A Precipitated silica gel (Glassy)
 B " " (Opaque)
 C Set silica gel glassy (Reproduced from Rao, K. S. *Jour. Phys. Chem.*, 513, 45, 1941)

silica gels A and B are similar in shape to those of gels of titania, alumina and ferric oxide (*loc. cit.*) which were obtained by precipitation.

The hysteresis loop of silica gel C obtained from silicic acid jelly presented in a previous paper⁷ is reproduced in Fig. 3 for comparison. Up to 60% humidity this gel retains more water than the precipitated gels. But beyond this value, its capacity for water remains practically the same, while the precipitated gels show a marked increase in sorptive capacity at higher pressures. At the saturation pressure, the adsorbent C got from the jelly retains only 28% water, whereas the precipitated gel B retains 131.4% water. The shapes of the hysteresis loops given by the two gels are quite different. At about 60% humidity, the hysteresis loop of gel C terminates, while those of the precipitated gels just commence. The relative positions of the loops indicate that in gel C the cavities and their necks are very much smaller than those in the precipitated gels. The foregoing results indicate prominently how the mode of preparation of the adsorbent has a profound influence

on the nature of the capillaries as revealed by the form of the hysteresis loop.

SUMMARY

By employing the quartz fibre spring technique, the hysteresis in sorption has been studied, of water vapour at 30° C. on precipitated silicic acid gel. A comparative study has been made with regard to the shape and size of the hysteresis loops of precipitated silica gel with that of the adsorbent obtained from silicic jelly.

The mode of preparation of the gel was found to greatly influence the shape and size of the hysteresis loop.

REFERENCES

1. Holmes, Sullivan and Metcalf .. *Ind. Eng. Chem.*, 1925, 17, 280.
2. Bartell and Fu .. *Colloid Symposium Annual*. Edited by H. B. Weiser, John Wiley and Sons, 1930, 7, 135.
3. McGavack and Patrick .. *J. Amer. Chem. Soc.*, 1920, 42, 946.
4. Rao, K. S. .. *J. Phys. Chem.*, 1941, 45, 500.
5. ————— .. *Current Science*, 1940, 9, 68.
6. ————— .. *J. Phys. Chem.*, 1941, 45, 522.
7. ————— .. *Ibid.*, 1941, 45, 513.