HYSTERESIS IN SORPTION

XIV. Influence of the Temperature of Activation of Titania Gel on the Hysteresis Effect

By R. S. Subramanya,* K. Subba Rao‡ and B. Sanjiva Rao,§ F.A.Sc.
(Department of Chemistry, Central College, Bangalore, S. India)

Received January 6, 1947

Introduction

The influence of the temperature of activation of silica gel on the hysteresis effect in the sorption of water has been indicated in a previous paper.[1] With progressive increase in the temperature of activation, the gel exhibited changes in capillary volume over certain ranges of temperature. A similar study of the effect of activation temperature of titania gel on the hysteresis effect exhibited by the gel in regard to sorption of water, is presented in this paper.

Experimental

Preparation of titania gel

The gel was prepared by the method described in an earlier paper.[2]

Activation of titania gel

The gel was activated by heating it in a current of dry air at the following temperatures, 30° C., 97° C., 214° C., 400° C., 600° C., and 1,000° C. For heating the gel at 30° C. and 97° C., a water-bath was used. For activation at higher temperatures an electric furnace was employed. Temperatures above 400° C. were measured with a suitable thermocouple.

Sorption and desorption of water vapour on the activated gel

The quartz fibre spring technique[2] was employed in the investigations. The activated gel was introduced into the glass bucket attached to the spring and was degassed at 10^{-3} mm. pressure for five hours. Sorption and desorption of water vapour on the activated gel were studied at 30° C. The results are shown in Fig. 1. The hysteresis loop obtained in the second cycle of sorption and desorption in each case has been indicated.

---

* Lecturer in Chemistry, intermediate College, Mysore.
‡ Senior Research Fellow of the National Institute of Sciences of India.
§ Principal and Professor of Chemistry, Central College.

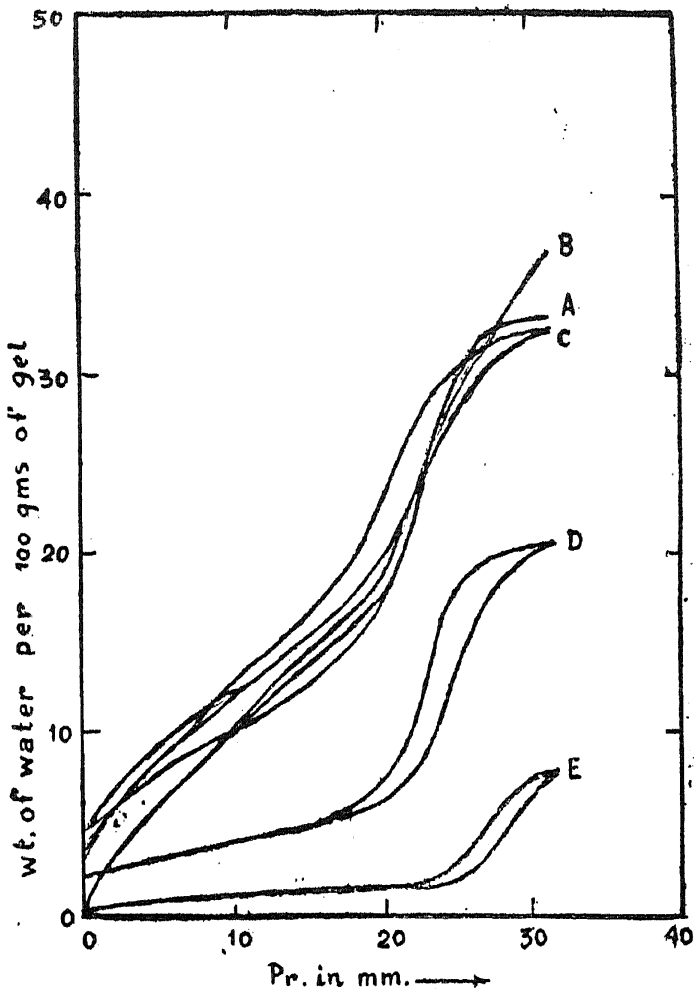

FIG. 1. Sorption of water on titania gel activated at A 30° C., B 97° C., C 214° C., D 400° C, E 600° C.

At the end of the first desorption in each gel, some amount of the water was retained by the gel irreversibly. This bound water has been indicated in Table I. The residual water in the activated gel was determined by igniting to constant weight in a platinum crucible, a known weight of the gel. The residual water thus determined in each activated gel and also the sorptive capacity as determined by the total amount of water taken at saturation pressure have been indicated in Table I.

TABLE I

Activation temperature in °C.	Bound water per 100 gms. of activated gel	Residual water per 100 gms. of activated gel	Sorptive capacity at saturation pressure per 100 gms. of cultivated gel
30	..	15·1	33·16
97	3·6	14·6	36·90
214	3·3	11·6	32·90
400	1·5	7·3	20·50
600	0·5	1·6	8·00
1000	0·0	0·0	0·00

Discussion

The following facts are noteworthy:—

1. *Sorptive capacity*

Examination of Table I and Fig. 1 reveals a small increase in sorptive capacity of gel for water at saturation pressure by an increase in the temperature of activation from 30° C. to 97° C. At higher temperatures there is a progressive decrease in the sorptive capacity which drops to zero at 1000° C.

2. *Area of the hysteresis loop*

With increase in the temperature of activation from 30° C. to 97° C., there is a small increase in the area of the loop. With a further increase in temperature however, the area of the loop becomes smaller.

3. *Position of the tail-end of the hysteresis loop*

With the exception of gel activated at 30° C., the relative vapour pressure corresponding to the tail end of the hysteresis loop progressively increases with the temperature of activation. The position of the tail end indicates the smallest neck radius in the gel. Thus, gels activated at 214° C., 400° C. and 600° C, have in them smallest necks of radii of 4 Å, 14·5 Å and 29·5 Å respectively. In gel activated at 97° C., the loop starts from zero relative vapour pressure and this indicates that the necks of cavities in this gel are extremely small and are of molecular dimension.

4. *Bound water and residual water*

The percentage of bound water and of residual water progressively decreases with an increase in the activation temperature.

The foregoing observations lead to the following conclusions:—

The decrease in sorptive capacity of the gel for water vapour at saturation pressure indicates a decrease in total capillary volume. With an increase in the temperature of activation from 30° C. to 97° C., the total capillary space in the gel slightly increases. Above 97° C., it progressively diminishes and at 1000° C., the capillary space is completely lost.

That the hysteresis effect is due to cavities with constricted ends has already been established.[2] The area of the hysteresis loop being a measure of the total cavity volume, the relative magnitudes of the loops indicate that the total cavity volume is higher in gel activated at 97° C. than in gel activated at 30° C. Above 97° C., the loop progressively diminishes in size indicating a diminution in total cavity volume.

Barring gel activated at 30° C., the smallest neck radius in the different gels increases in the temperature of activation, *i.e.*, as the temperature is increased, the smallest cavity necks are destroyed.

The bound water is attributed to the finest crevices in the activated gel retaining a portion of sorbed water irreversibly. The decrease in bound water with an increase in the temperature of activation (Table I) indicates that fine crevices of molecuclar dimensions are decreasing.

It follows from these observations that an increase in the temperature of activation from 30° C. to 97° C. brings about an increase in total capillary space and in total cavity volume. Above 97° C., the gel suffers structural change. There is progressive decrease in the total capillary space and in the total cavity volume. The smallest cavity necks collapse. At 1000° C., there is entire breakdown of the structure with complete loss of the capillary space.

It is obvious from these results that there is an optimum temperature of activation (presumably between 97° C. and 214° C.) in the case of titania for getting gel of maximum sorptive capacity. Existence of an optimum temperature of activation has been reported for gels of silica, alumina and ferric oxide.[3]

Summary

The effect of variation of activation temperature on the hysteresis effect has been studied for titania gel. Sorption and desorption of water vapour at 30° C. on titania gels activated at 30° C., 97° C., 214° C., 400° C., 600° C. and 1000° C. have been measured.

At different temperatures of activation, permanent and reproducible hysteresis loops have been obtained. There is however, a marked variation in the total sorptive capacity, the area of the hysteresis loops and the relative vapour pressures corresponding to the tail end of the hysteresis loops.

The results indicate that with an increase in the temperature of activation from 30° C. to 97° C., there is a small increase in the total capillary space and in the total cavity volume. Above 97° C., the gel suffers a structural change with a diminution in capillary space and in cavity volume. There is also a collapse of the smaller cavity necks. At 1000° C., there is a breakdown of the gel structure and a complete collapse of the capillary space.

References

1. Krishnappa, T., Rao, K. S., and Rao, B. S. .. "Hysteresis in Sorption—XII," *Proc. Ind. Acad. Sci.*, 1947, **25**, 174.
2. Rao, K. S. .. *J. Phys. Chem.*, 1941, **45**, 500.
3. ——— and Rao, B. S. .. *Proc. Ind. Acad. Sci.*, 1936, **4**, 562.