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PREFACE

Studies of water in all its phases constitute an important part of the laboratory studies of the Division of Building Research. So important is this work that a small group within the Building Materials Section of the Division is devoting all its time to this one subject, the results of this work being applicable to more practical studies of various building materials.

This translation describes some significant work in relation to the depression of the freezing-point of water when adsorbed in various materials. Many studies have been made of this subject with the object of relating the effect of pore structure to the phenomenon. In this work the depression of the melting-point of water adsorbed silicic acid gel, permulite and ion exchange resin IR-45 was investigated with a differential calorimeter.

The significant results obtained are thought to be of interest not only to workers in this Division but to others concerned with this important aspect of the properties of water. The translation is, therefore, published by the Division in its regular series as a further contribution to building science in Canada.

Ottawa
February 1962

R.F. Legget
Director

NATIONAL RESEARCH COUNCIL OF CANADA

Technical Translation 1010

Title: The melting-point depression of water in sorbed state

Author: Y. Iwakami

Reference: J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi), 80 (10): 1094-1097, 1959

Translator: K. Shimizu

THE MELTING-POINT DEPRESSION OF WATER IN SORBED STATE

The author has reported on several occasions⁽¹⁻⁴⁾ that the factors controlling the depression of the melting-point of adsorbed material are the pore size distribution, the nature and the quantity of material adsorbed. The object of the present experiments was to investigate the changes in the melting-point of the adsorbate when the adsorbent was subjected to radioactive rays which cause changes in the conditions of its surface.

As adsorbate, water was used, the adsorbent being silicic acid gel, permutite, and ion exchange resin amberlite IR-45. As the source of radioactive rays cobalt 60 was used. Water was adsorbed by exposed and unexposed material, and the melting-point of water in the adsorbed state was measured by a differential calorimeter. The results differed depending on the adsorbent. However, the experimental values showed good agreement with the theoretical ones, which were obtained using our equation relating the depression of the melting-point of water to the size of the pore and the amount of adsorbed water.

1. Introduction

Silicic acid gel, permutite and ion exchange resin amberlite IR-45 are all good adsorbents; when water is adsorbed the phenomenon of depression of the melting-point of water can be observed. However, the extent of depression depends on the pore size distribution of the adsorbent. Thus, if changes are introduced in the pore size distribution of these capillaries by some means, it seems reasonable to assume that there will be a change in the melting-point of water adsorbed by the adsorbent. The present report is concerned with the melting-point of water in the adsorbed state which was measured by means of a differential calorimeter. Silicic acid gel, permutite and ion exchange resin amberlite IR-45 were exposed to strong gamma rays of cobalt 60. The results from the

exposed material were compared to those from unexposed material.

2. Experiments

Commercially available silicic acid gel, permutite and amberlite IR-45 were dried in an air dryer at 110°, 130° and 90° for approximately 6 hours, respectively. They were then sealed in several glass tubes and used as unexposed material. Some of these tubes were placed near a source of cobalt 60 in sealed glass tubes and were exposed to the gamma rays for 48 hours at 10000 r-unit/min. This was used as exposed material.

For the exposed and unexposed material thus prepared adsorption isotherms at 0°C were obtained using benzene adsorbate. From these isotherms the pore size distribution for each adsorbent was calculated. These are shown in Fig. 1 to 3.

In Fig. 1, the maximum points show good agreement in exposed and unexposed cases; however, there are discrepancies in other parts. In Fig. 2, there is a small discrepancy even at the maximum points. In Fig. 3, one notes a marked influence at the maximum point due to exposure. It appears reasonable to assume that there will be a difference in melting-points if a substance is adsorbed by unexposed and exposed material with different pore size distribution even if the adsorbate is the same and is adsorbed in equal amounts. Thus, approximately an equal amount of water was allowed to be adsorbed by unexposed and exposed adsorbents, and the melting-point of this water was measured by means of a differential calorimeter. The structure of the calorimeter which was used in the present experiments is shown in Fig. 4.

A and B are both vessels made of copper; the upper portions are connected by fused glass capillaries. Equal amounts of adsorbent are introduced into these containers, A and B, through C and D. After inserting thermocouples E and F, as shown in the figure, they are evacuated through G, H and I. Next, silicic acid gel, permutite and amberlite IR-45 were heated to 110°C, 130°C and 90°C, respectively, by means of heater J. The evacuation was carried out for

approximately 6 hours to a high vacuum. After being restored to room temperature, a cooling agent of a mixture of dry ice and methanol was introduced into the Dewar's vessel, K, the calorimeter was cooled from outside, and the temperature inside A and B was lowered to approximately -60°C . The test material inside A and B was heated by means of heater J, maintaining a difference in temperature between A, B and the heater J as close as possible to 3°C . No. 0 in Fig. 5-7 shows the difference between the temperatures of vessels A and B, i.e. the differential temperature corresponding to the temperature of either A or B. Next, a known quantity of water is allowed to be adsorbed by the adsorbent in either A or B. The system is then cooled to approximately -60°C and heated in the same way as before. This gives the differential temperature curve No. 1. The temperature at the maximum of this curve is the melting-point of water in the adsorbed state. Similar procedures were repeated with different amounts of water. The results are curves No. 2 and No. 3.

3. Results and Discussion

Fig. 5 (1) and (2) resemble each other except for curve No. 1. This shows that there is hardly any effect due to exposure. Fig. 6 (1) and (2) show that the maximum point shifts to the left due to exposure. In Fig. 7 (1) and (2) the maximum point shifts to the right due to exposure and the slope of the curves increases. This could indicate possibly a change in the pore size distribution due to exposure keeping in mind that the melting-point of adsorbed water is lowered with the decrease in the radius of the capillaries. However, in the present paper, in order to treat the phenomenon in a quantitative way, the curve relating $r^2 \cdot \Delta a / \Delta r$ and r , i.e. the relation between the amount melted and radius, was obtained as in the previous reports⁽²⁻⁴⁾. These are shown in Fig. 8-10. In the case of silicic acid gel in Fig. 8, the maximum point appears at the same place in exposed and unexposed material; the curves are similar. Thus, it resembles Fig. 5 (1) and (2). In the case of permutite in Fig. 9, the maximum point, which exists in the case of

unexposed material, disappears with exposure. Thus, this means that the maximum point in Fig. 6 (2) continues to shift to the left. In the case of amberlite IR-45 in Fig. 10, the maximum point becomes markedly higher due to exposure and at the same time shifts in the direction in which r decreases. On the basis of this the increase in slope and the shifting of the maximum point to the right in Fig. 7 (2) can be explained. Since there has been a change in the relation between $r^2 \cdot \Delta a / \Delta r$ and r due to exposure, as was shown above, theoretical values of the melting-point based on the equation relating the depression in melting-point (ΔT) to the amount adsorbed (a) were calculated in the same way as shown in previous reports. These were compared with experimental values and shown in Table I. It is observed that there is a good agreement between the experimental values and the theoretical values. The radius, r , shown in the table is the one which has been used in calculating the melting-points and corresponds to the maximum amount of water melted. With different amounts of adsorbed water the melting-point also changes. This is evident in the table. Further, the table shows that, even in the same adsorbent, there is a marked change in melting-point even for the same adsorbed amount depending on whether the adsorbent had been exposed to gamma rays or not. The fact that there is a good agreement between the theoretical values thus obtained and observed values means that it is possible to explain the change in melting-point with respect to each adsorbent by the application of the melting-point depression equation, taking into account the pore size distribution of the adsorbent both in exposed and unexposed cases. It can also be said that the above experimental evidence confirms the melting-point depression equation mentioned in previous reports based on the theory of capillary condensation.

The author wishes to express his appreciation to Dr. Masaichiro Saito for his generous assistance.

(Apr. 1959, Nippon Kagaku-Kai 12th year lecture)

References

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2. Iwakami. Nikka, 72: 707, 1951.
3. Iwakami. Nikka, 77: 1499, 1956.
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350, 1957.

Table I

Unexposed Material					Exposed Material				
	Adsorbed amt. a mg/g	Radius r Å	m.p. obs. °C	m.p. theor. °C		Adsorbed amt. a mg/g	Radius r Å	m.p. obs. °C	m.p. theor. °C
Silicic Acid Gel									
No. 0	0	—	0	0		0	—	0	0
No. 1	358	43.9	-34.5	-33.9		398	42.8	-37.0	-36.1
No. 2	440	47.6	-32.5	-31.6		512	47.4	-32.5	-31.8
No. 3	908	49.0	-31.0	-30.5		920	49.0	-31.0	-30.5
Permutite									
No. 0	0	—	0	0		0	—	0	0
No. 1	151	39.1	-38.5	-40.5		158	45.9	-33.5	-33.2
No. 2	185	49.6	-31.5	-30.0		224	75.0	-19.0	-18.5
No. 3	375	60.0	-22.5	-23.9		396	∞	0.0	0.0
Amberlite IR-45									
No. 0	0	—	0	0		0	—	0	0
No. 1	47	33.8	-48.0	-49.0		55	34.7	-49.5	-47.4
No. 2	75	38.0	-43.5	-42.0		87	35.7	-45.5	-45.8
No. 3	378	41.0	-38.5	-38.1		397	36.0	-45.0	-45.3

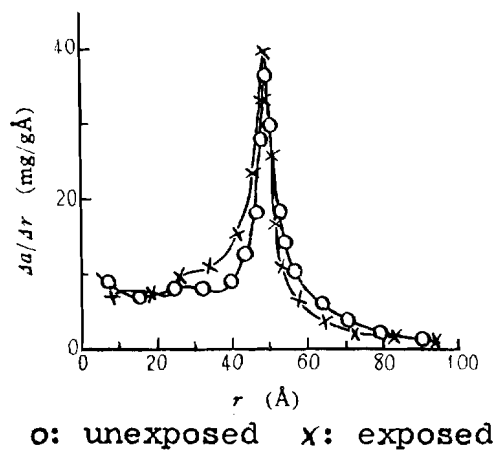


Fig. 1

Silicic acid gel

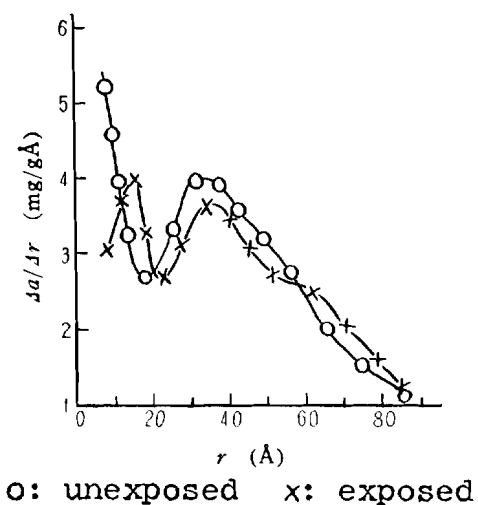


Fig. 2

Permutite

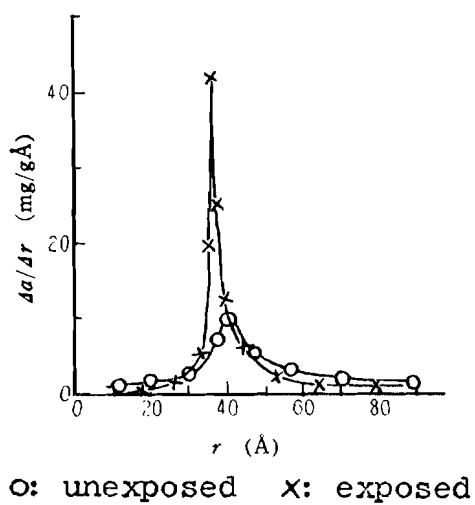


Fig. 3

Amberlite IR-45

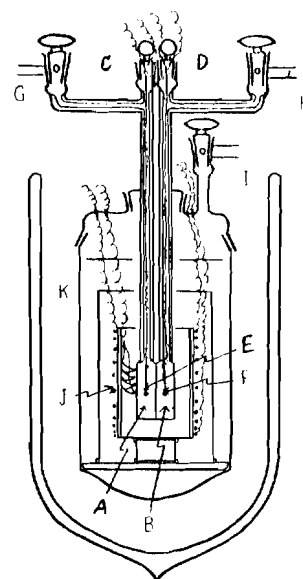


Fig. 4

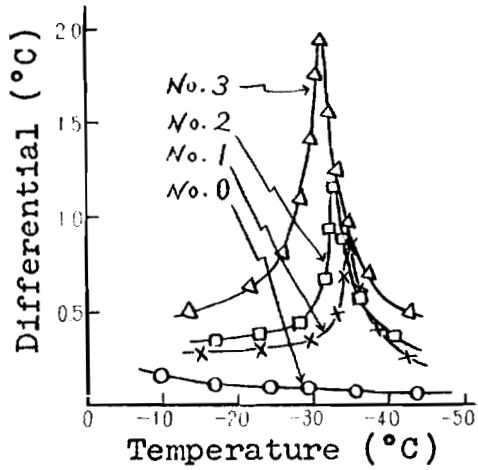


Fig. 5 (1)
Silicic acid gel
(unexposed)

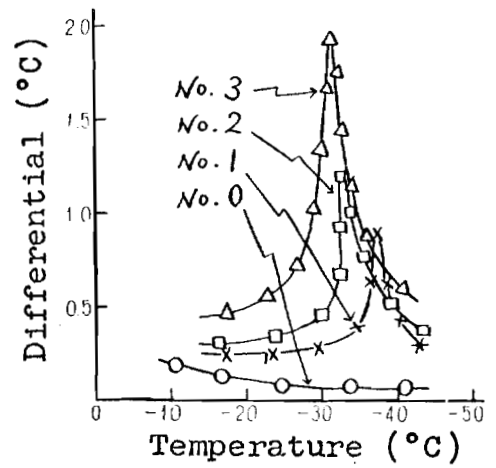


Fig. 5 (2)
Silicic acid gel
(exposed)

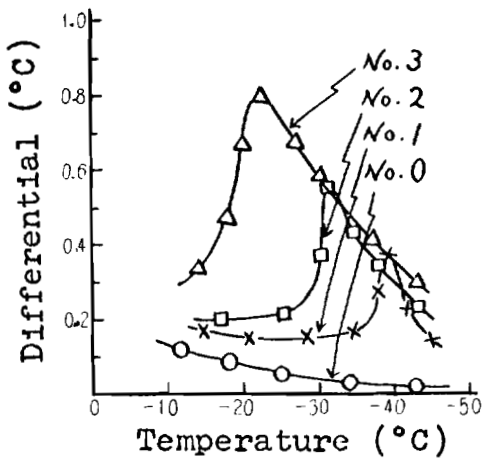


Fig. 6 (1)
Permutite (unexposed)

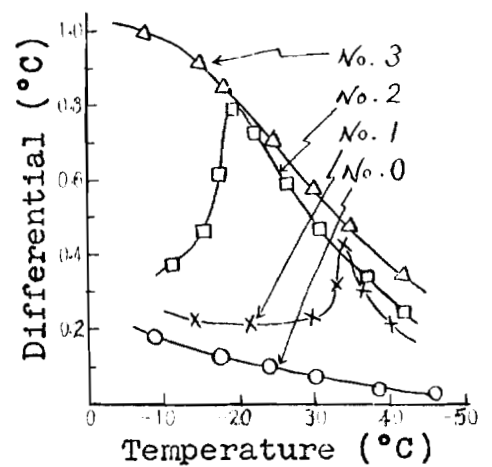


Fig. 6 (2)
Permutite (exposed)

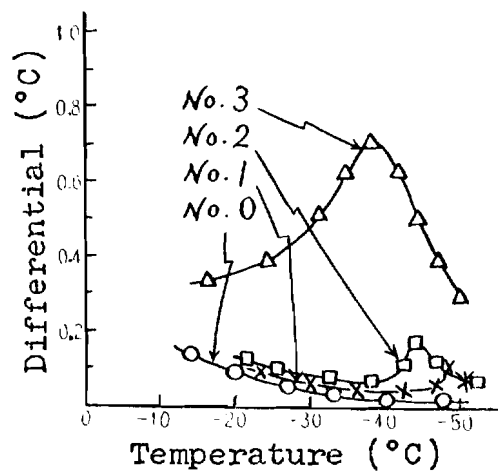


Fig. 7 (1)

Amberlite IR-45
(unexposed)

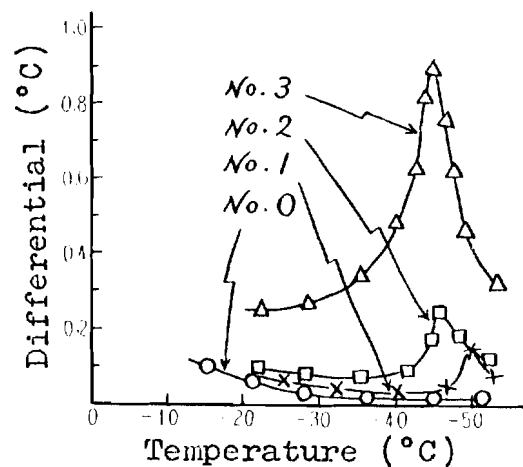
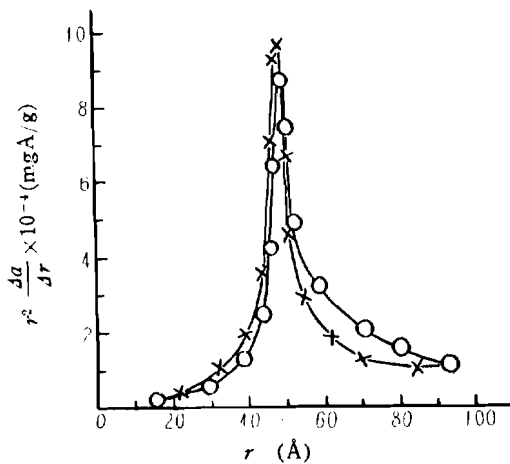


Fig. 7 (2)

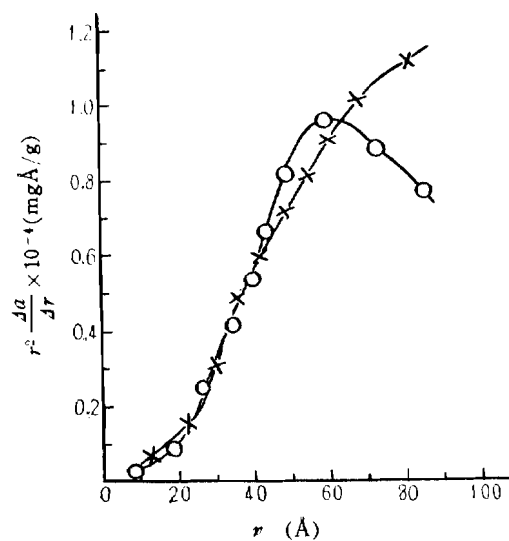
Amberlite IR-45
(exposed)



o: unexposed x: exposed

Fig. 8

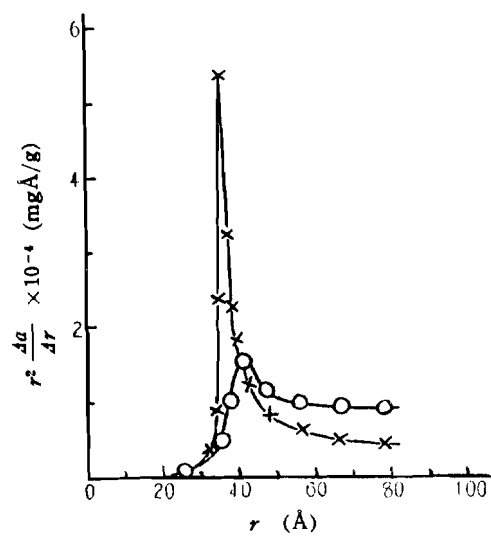
Silicic acid gel



o: unexposed x: exposed

Fig. 9

Permutite



o: unexposed x: exposed

Fig. 10

Amberlite IR-45