Heats of Wetting of Polysaccharides. I. Heats of Wetting of Various Polysaccharides

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Introduction

The interaction between polysaccharides and water has been investigated chiefly by graphing adsorption isotherms or X-ray patterns, and their heats of wetting have been relatively overlooked.

About fifty years ago, Rodewald and Kattein⁽¹⁾ measured heats of wetting of various starches, then in 1917 Katz⁽²⁾ reported his data concerning adsorptions and heats of wetting of many substances including cellulose and inulin. More recently Schrenk *et al*⁽³⁾., Dumanskii and his collaborators⁽⁴⁾, and Wahba⁽⁵⁾ published their results in starch and cellulose.

The present writer also measured heats of wetting of various polysaccharides, such as potato starch, potato amylose, potato amylopectin, inulin, glycogen and konjac mannan, but found no regularity between heat of wetting and molecular constitution.

Apparatus and Procedure

The apparatus used resembles the one constructed by Harkins and his collaborator,⁽⁶⁾ and is illustrated in Fig. 1a.

When the rod A is pushed down, the ampoule S breaks and the content is immersed into water, the temperature in D_1 rises owing to the heat of wetting of the sample and electrical potential difference appears at the ends of the thermocouple. This potential is measured with a potentiometer. Then a known amount of electric current is passed through H, the potential difference produced is measured again. We can estimate the heat of wetting by comparing these two potential differences.

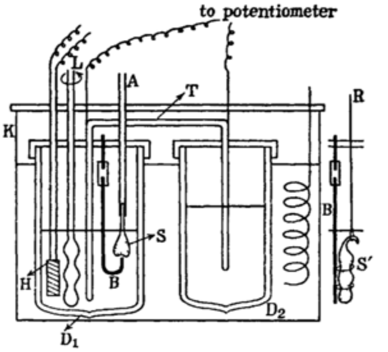

Fig. 1a. 1b.

K	thermostat (constant within 1/100°C.)
D_1, D_2	Dewar's vessels
T	Cu-constantan thermocouple with 36 pairs of junctions
S	ampoule containing sample (usually ahout 0.8 g.)
A	rod grasping ampoule
B	brass rod with keen needle
H	electric heater with resistance about 4.7 Ω
L	glass stirrer
R	string

The actual procedure of measurement is as follows. The apparatus is arranged as illustrated in Fig. 1a. When the thermal equilibrium is roughly attained, L is started. Potential difference at the ends of the thermocouple is recorded once every minute. The temperature in D_1 rises slowly because of the mechanical work of the stirrer (AB in Fig. 2). When the temperature-time curve results in a straight line, S is broken. The temperature is elevated rapidly owing to the heat of wetting (BC in Fig. 2), but in a short time returns again to a straight line (CD). When an amount of electric current is passed for a certain time through H, the temperature-time curve behaves as before (DEF).

Extrapolating these two straight lines (CD, EF), we can get temperature elevation S_1 by the heat of wetting and S_2 by the electrical work, and calculate the heat of wetting by comparing S_1 and S_2.

When the heat generation is relatively slow, necessary correction is given to S_1 and S_2. However in this experiment these corrections were usually small, and in most cases unnecessary.

If the value of an evacuated sample is to be obtained we put the sample in a thin walled ampoule S', evacuate under 1/1000 mm. Hg, and fuse off the neck, which remains an L-shaped

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(1) H. Rodewald and A. Kattein, *Z. phys. Chem.*, **33**, 579 (1900).

(2) J. R. Katz, *Kolloid. Beih.*, **9**, 1 (1917).

(3) W. G. Schrenk, A. C. Andrews and H. H. King, *Ind. Eng. Chem.*, **39**, 113, (1947).

(4) A. V. Dumanskii, Ya. F. Mezhennyi and E. F. Nekryach, *Kolloid. Zhur.*, **9**, 335 (1947); *Chem. Abst.*, **43**, 6042 (1949).

(5) M. Wahba, *J. Phys. Colloid. Chem.*, **52**, 1197 (1948).

(6) W. Harkins and Roy Dahlstrom, *Ind. Eng. Chem.*, **22**, 897 (1930).

hook. The rod A is removed and S' is fixed tightly to B, as shown in Fig. 1b. By pulling up the string R fastened to the hook, we can break the neck and bring out the sample into the water. In this case, heat development is somewhat slower, but the measurement can be performed without difficulty.

The accuracy of the apparatus was estimated in taking account of the sensibility of the potentiometer, and the exactness in determining electrical work. This is calculated to be about one per cent.

Furthermore, it is also deduced that the measured heat amount in the calorimeter has always uncertainty amounting to 0.05 cal., and this means, when we measure the heat smaller than 5 cal., the accuracy becomes less than one per cent.

The experimental values endorse the above presumption.

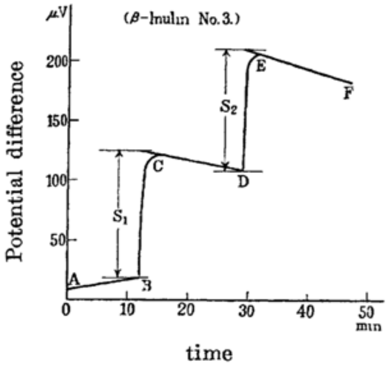

Fig. 2.

(1) Native potato starch: Native potato starch was dried in Abderhalden's desiccator under reduced pressure (2/100 mm. Hg.) so long as to reach constant weight.

(2) Potato starch in the form of paste: 6.5 g of native potato starch was mixed with 3 cc. of water, heated to 100°C. and dried at 100°C. Starch so treated was called by Katz "Verkleisterte" starch. It swelled to give paste when immersed into water.

(3) Retrograded potato starch: Potato starch paste was laid under saturated water vapor for a long time (from 22 to 162 days). Retrograded starch did not make paste.

(4) Potato amylose: Potato amylose was isolated by Schoch's method.(7) Potato starch was autoclaved with water for 3 hours at 110°C. To the 3 percent solution thus treated, excess amount of n-butanol was added and filtered. The filtrate which contained amylopectin, served as the source of the sample (6). Filtered precipitate was dissolved in hot water; then the solution was poured into a large amount of methanol, precipitating amylose. The resulting precipitate was filtered, washed with methanol and dried. This substance swelled well in cold water, dissolved partly in cold and perfectly in hot water, giving blue color with iodine.

(5) Retrograded amylose: The above-mentioned amylose was exposed to saturated water vapor for 25 days. The sample swelled in cold water but less than sample (4), and dissolved in hot water with difficulty.

(6) Potato amylopectin: The solution containing amylopectin (cf. sample (4)) was mixed with a large amount of methanol, the resulting precipitate was centrifuged, washed and dried. This sample swelled and partly dissolved in cold water. Iodine color was reddish violet.

(7) Retrograded amylopectin: Exposure of sample (6) to saturated water vapor for 29 days, gave retrograded amylopectin which swelled a little in cold water, but was entirely insoluble. This was confirmed by addition of iodine to the supernatant, which gave no color reaction.

(8) β-Inulin: "Takeda's" inulin was dissolved in hot water with active charcoal and filtered. The filtrate was cooled and frozen with freezing mixture; then melted. It remained a deposit. The precipitate was recrystallized three more times. β-Inulin is insoluble in cold water.

(9) α-Inulin: β-Inulin was dissolved in hot water, the solution was poured into a large amount of alcohol, the precipitate was centrifuged, washed and dried. α-Inulin dissolves in cold water.

(10) Retrograded inulin: α-Inulin was exposed to saturated water vapor for 10 days. This was insoluble in cold water.

(11) Konjac powder: Native konjac powder sold as "special grade", was dried under reduced pressure. This powder swells and dissolves in cold water. However, as the dissolution needed a very long time, it dissolved imperfectly in the course of the heat measurement.

(12) α-Konjac mannan: Native konjac powder was dissolved in cold water by shaking, and the solution filtered with cloth was mixed with alcohol. The resulting precipitate, after being washed and dried surves as the sample. α-Konjac mannan swelled and dissolved in cold water, but the perfect dissolution was not attained in the course of measurement because of slowness of the reaction.

(13) β-Konjac mannan: One per cent solution of α-konjac mannan was heated with $Ba(OH)_2$, and filtered. The deposit was treated with one per cent acetic acid solution for several days to remove Ba, then washed with water. The sample swelled a little in water, but did not dissolve even when boiled.

(14) Glycogen: "Takeda's" glycogen was dissolved in water, precipitated with alcohol, dissolved in water again, electrodialized, then precipitated with alcohol containing a trace of potassium acetate and washed thoroughly with alcohol. Glycogen dissolved well in cold water and gave a slightly turbid solution.

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(7) T. J. Schoch, "Advances in Carbohydrate Chemistry." Vol. I. The fractionation of starch.

Results and Discussion

The results obtained are shown in Table 1. Each value is the mean of two or three experiments.

Table 1

		Heat of wetting cal./g.	
		in the presence of air	evacuated
1	Native potato starch	28.2	27.2
2	Potato starch paste	24.6	
3	Retrograded potato starch	25.6 (22 days) 25.5 (162 days)	
4	Potato amylose	22.8	
5	Retrograded amylose	23.5	
6	Potato amylopectin	21.2	
7	Retrograded amylopectin	21.8	
8	β-Inulin	23.1	23.2
9	α-Inulin	17.9	
10	Retrograded inulin	21.2	
11	Konjac powder	21.3	
12	α-Konjac mannan	23.7	
13	β-Konjac mannan	16.2	16.7
14	Glycogen	23.5	

We see that the heats of wetting of polysaccharides lie in the range from 10 to 30 calories per gram of dried substance. The value of native potato starch (28.2 cal./g.) is in good accordance with that of Schrenk *et al*(3). (29.1) and Dumanskii *et al*(4). (28.06). The elevation of drying temperature from 34° to 64° or 100°C caused no decrease of weight and no change of heat-of-wetting exceeding experimental error (0.2 cal.). It is somewhat interesting that potato starch gives a higher value than either of its fractions (potato amylose, potato amylopectin.)

Inulin gives 23.1 cal./g. in agreement with Katz's(2) result. Heats of wetting of evacuated samples were also measured in three cases, namely potato starch, inulin and konjac mannan, but no or little effects were observed.

It seems to the present writer that there exists no correlation explicitly between the heat of wetting and the molecular constitution of polysaccharides.

Summary

Heats of wetting of various polysaccharides, such as potato starch, potato amylose, potato amylopectin, inulin, glycogen, and konjac mannan were measured, but no correlation between heat of wetting and molecular constitution was found.

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