# Heats of Wetting of Polysaccharides. II. A Rule Which Exists Between Adsorption Isotherms and Heats of Wetting of Polysaccharides

By Toshio NAKAGAWA

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## Net Heat of Adsorption

Net heat of adsorption defined by heat of adsorption minus heat of condensation, can be experimentally acquired by means of measuring heats of wetting of dried and partially saturated substance.

Denote the heat of wetting, obtained by throwing one gram of a dry substance into water, by $H$, and that obtained by a partially saturated substance, which consists of one gram of dry substance and $m$ grams of water, by $H(m)$, then $H-H(m)$ gives the net heat of adsorption $N(m)$, generated when one gram of dry substance adsorbs $m$ grams of water.(1)

$$N(m)=H-H(m) \qquad (1)$$

However, it should be remembered, that the processes are tacitly assumed to be reversible ones.

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(1) A. B. Lamb and A. S. Coolidge, *J. Am. Chem. Soc.*, **42**, 1146 (1920).

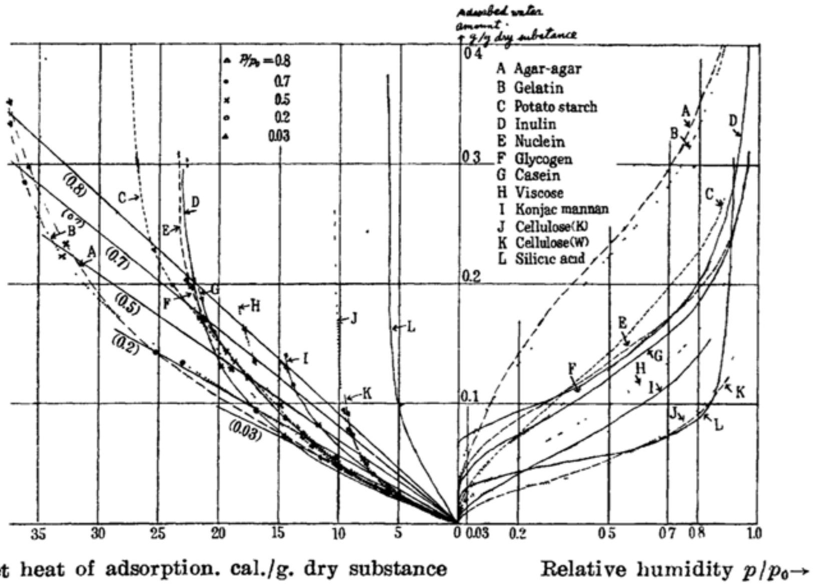

Fig. 1.

## The Rule Found by the Author

The present writer arranged the data concerning heats of wetting, which were reported by J. R. Katz,(2) E. Rosenbohm,(3) A. V. Dumanskii *et al*,(4) and M. Wahba,(5)(6) together with the author's own data, and plotted net heats of adsorption against water amounts adsorbed.

By comparing the curves thus obtained with the adsorption isotherms obtained by Katz,(2) H. Sato,(7) Wahba(6) and the author, it was found that there exists a simple rule, between the net heats of adsorption and water amounts adsorbed among the following substances: starch, inulin, cellulose, viscose, glycogen, konjac mannan, casein, nuclein, gelatin, and agar-agar.

The rule states: "When we bring one gram of each of the above-mentioned substances under the same relative humidity $x(p/p_0)$, generated net heats of adsorption $N(m)$ (heat of adsorption minus heat of condensation) are proportional to the amounts $m$ of water adsorbed, independently of the varieties of substances, in the range of $x$ smaller than 0.8".

The author wishes to expound the rule in further detail. In the right half of Fig. 1. are represented adsorption isotherms taking relative humidity $x$ in abscissa and adsorbed quantity $m$ (g. water/1 g. of dry substance) in coordinate.

The data were gathered from the works of the following investigators, Katz(2) (inulin, cellulose (K), casein, nuclein, gelatin, agar-agar at room temperature), H. Sato(7) (potato starch 20°C), Wahba(6) (cellulose (W), viscose 30°C), and the author (konjac mannan, glycogen 20°).

It should be mentioned here that in this paper Katz's values slightly differ from his original report. Katz obtained the relation between relative humidity and adsorbed water amount, by exposing the samples over sulfuric acid solution with various concentrations. To estimate the water vapor pressure over sulfuric acid solution, he used Regnault's(8) data, but it seems inadequate particularly at a concentration higher than 50 per cent. Relative humidities were therefore amended by Greenewalt's(9) report.

In the left half, net heats of adsorption $N(m)$, obtained using the method discussed above are plotted against adsorbed quantities $m$, taking the former in abscissa, and the latter in coordinate.

The data were collected from the experiments of the following investigators, Rosenbohm(3) (gelatine), Katz(2) (inulin, cellulose (K), casein, nuclein, agar-agar at room temperature), Dumanskii *et al*(4). (potato starch, 30°C), Wahba(5)(6) (cellulose (W), viscose 30°), and the author (konjac mannan, glycogen 30°C).

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

(3) E. Rosenbohm, *Kolloid Beih*, **6**, 177 (1914).

(4) A. V. Dumanskii, Ya. F. Mezhennyi and E. F. Nekryach, *Colloid Zhur.*, **9**, 355 (1917); *Chem. Abs.*, **43**, 6042 (1949).

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

(6) M. Wahba, *J. Phys. Colloid Chem.*, **54**, 1148 (1950).

(7) H. Sato, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 790 (1951).

(8) Regnault, Landolt Tab. 3. Aufl. 166 (1905).

(9) G. H. Greenewalt, *Ind. Eng. Chem.*, **17**, 522 (1925).

The samples used in the two sets of experiments are the same excepting gelatin and starch. In the case of starch, it is ascertained by the author that Sato's sample has almost the same value of heat of wetting as the one used by Dumanskii (Sato's sample 28.2 cal./g., Dumanskii's 28.06 cal./g.).

When we draw a parpendicular line at a certain value of $x$ in the right half of Fig. 1, its intersecting points with adsorption isotherms give the water amounts adsorbed by respective substances. Next we draw horizontal lines from these intersecting points toward the left half of Fig. 1. Intersecting points of these lines with net-heat-of-adsorption curves gives the values of net heats of adsorption, which will be developed when these substances are brought under the same relative humidity $x$. It will be recognized from Fig. 1. that these intersecting points lie on a straight line passing origin.

This rule holds well in the region from very small value of $x$ (0.03) to relatively large value ($x=0.8$). This fact seems to the author too consistent to be considered as merely an accident. The rule cannot hold at any larger value of $x$, exceeding 0.8. The above-mentioned rule can be expressed mathematically as follows:

$$N(m)=a(x)m(x) \qquad (2)$$

where $N(m)$: a function of $m$, and depends also on the kind of substance.

$m(x)$: a function of $x$, and depends on the kind of substance.

$a(x)$: a function of $x$ independently of the variety of substance.

Equation (2) indicates that net heat of adsorption is proportional to $m$ at same $x$, independently of the variety of substance. Heat of adsorption $A(m)$ is also proportional to the adsorbed water amount $m$, because net heat of adsorption is defined by heat of adsorption minus heat of condensation.

$$\text{Thus} \quad A(m)=N(m)+Lm=(a+L)m \qquad (3)$$

$L$: heat of condensation of 1 g. water.

From Fig. 1, values of $a(x)$ are obtained as follows relating to several values of $x$.

| $x$ | 0.03 | 0.2 | 0.5 | 0.7 | 0.8 |
|---|---|---|---|---|---|
| $a(x)$ | 205 | 178 | 145 | 123 | 109 cal./g. water |

For the purpose of comparison, adsorption isotherm and net-heat-of-adsorption curve of silicic acid[(2)] are also represented in Fig. 1. Clearly it does not obey the rule.

It is difficult to explain why the rule holds in the above-mentioned substances, but it is also noticeable that these substances are polysaccharides, proteins, or their relatives.

The approximate value of net heat of adsorption can be obtained by drawing only one adsorption isotherm, in the case of the substance which obeys the rule, so it is interesting to explore what kinds of substances are governed by the rule.

The above-mentioned relation does not hold when $x$ exceeds 0.8. Possibly this fact is due to the rapid increase of different kinds of adsorption in such a high humidity.

To the author, it seems an interesting fact that a regularity is found in the integral rather than in the differential heat of adsorption.

An example of polysaccharide which does not obey the rule, is reported. Namely, comparing the adsorption isotherm of "Künstliche Stärkekörper" obtained by Katz,[(2)] with the net heat of adsorption of the same substance reported by H. Rodewald and his collaborator,[(10)] we find the rule does not hold well. The net heat of adsorption expected from the adsorption isotherm using the above-mentioned rule, is lower than the experimental value.

But there is some reason to think the value given by Rodewald *et al.* is somewhat too high, possibly for the sake of lower experimenting temperature. For example, among the heats of wetting of potato starch reported by them and other more recent investigators, their value alone is somewhat higher than the others.

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|---|---|---|
| H. Rodewald *et al*[(10)]. (1900) | 32.68 cal./gr. | (at 0°C) |
| A. V. Dumanskii *et al*[(4)]. (1947) | 28.06 | (20°) |
| W. G. Schrenk *et al*[(11)]. (1947) | 29.2 | (30°) |
| T. Nakagawa[(12)] (1949) | 28.2 | (30°) |

## Experiments

The samples of glycogen and konjac mannan, of which data are employed in the above discussion are the same ones as glycogen and β-konjac mannan in the preceding report of this series.[(12)]

A sample of each spread in a wide bottle, was put into a desiccator containing sulfuric acid solution with varying concentrations, and exposed for several months until constant weight was reached.

Adsorbed amount was measured as the increase of weight, relating to relative humidity.

Heats of wetting of partially saturated substances were measured using the same apparatus described in the preceding report. In this case, the sample enclosed in an ampoule, was put into the same desiccator that was mentioned above,

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(10) H. Rodewald and A. Kattein, *Z. Phys. Chem.*, **33**, 579 (1900).

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

(12) T. Nakagawa, Preceeding report in this journal.

and the ampoule was sealed off after the adsorption equilibrium had been roughly attained. Net heats of adsorption were then readily calculated.

In Fig. 1, curves thus obtained are represented with those derived from other investigators' data.

## Summary

A simple rule which correlates adsorption isotherms and heats of wetting of polysaccharides was described.

The rule states: " When we bring one gram each of polysaccharides (and several other substances belonging to organic high polymer) under the same relative humidity, generated net heats of adsorption are proportional to the amounts of adsorbed water, independently of the varieties of substances."

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*Department of Chemistry, Faculty of Science,*
*Tokyo University, Tokyo*