acid, boiled, and then titrated in the presence of glycerol for boric acid. A total of 3.3 mmoles of boric acid was found. The formate produced in this reaction was 2.2 mmoles as determined by permanganate titration. The solution in the carbon dioxide absorption traps at the end of the reaction train (see Fig. 1) was similarly found to contain 1.6 mmoles of boric acid. The amount of boric acid in the bubblers was always less than the amount of formate produced in the reaction, but there was no simple relationship. From a Dry-Ice cooled trap containing anhydrous ethereal trimethylamine inserted in the system before the barium hydroxide bubblers, a solid compound could be recovered which gave a white crystalline sublimate melting at 92–95° (lit.[11] for trimethylamine borine, 94–95°).

High Level Preparation of Aqueous Sodium Formate.—In the apparatus shown in Fig. 2, a total of 11.896 g. of isotopic barium carbonate, containing an estimated[12] 203 millicuries of C^{14}, was processed as above, in five runs. From these runs, the recovered barium carbonate weighed 1.947 g. (9.84 mmoles, 16.3%), and contained an estimated 32 millicuries of C^{14}. By titration, the total amount of formic acid produced was 33.35 mmoles (66% based on the absorbed carbon dioxide). The neutralized formate solutions (containing a slight excess of alkali) were combined and vacuum distilled almost to dryness. The residue was taken up in distilled water, centrifuged, and made up to 100.0 ml. From this solution, two 100 λ samples were taken, and each pipetted into a solution of 2.000 g. (29.4 mmoles) of sodium formate in 10 ml. of water. The S-benzylthiuronium salts were then prepared and recrystallized from ethanol. Duplicate assay of each sample of the salt showed an average specific activity of 0.0206 microcuries per mg. This corresponds to a total yield of 129 ± 2 millicuries of sodium formate. Crystallization of the derivatives was so carried out as to produce a considerable fractionation should more than one acidic species be present; however, assay of the crude derivative led to the same result, within experimental error, as assay of the recrystallized salt. If radioactive species other than formate were present in the solution, direct assay of the solution should give a higher value than assay through a formate derivative; both assays, however, gave the same value within experimental error.

Summary

Carbon dioxide has been reduced to formic acid in 69–88% yield by passage of the gas into an ether solution of lithium borohydride at 0°. Carbon-14 dioxide yields formic acid-C^{14} on similar treatment. By the use of this method, 129 millicuries of formic acid-C^{14} as aqueous sodium formate-C^{14} has been prepared.

Ethyl formate-C^{14} has been prepared at the microcurie level by the reaction of sodium formate-C^{14} with diethyl sulfate at 170°.

During the reduction diborane is liberated, and a small amount of methanol-C^{14} is produced. No formaldehyde was detected as a product of the reaction.

OAK RIDGE, TENNESSEE RECEIVED OCTOBER 10, 1949

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[11] Burg and Schlesinger, THIS JOURNAL, **59**, 780 (1937).

[12] The barium carbonate was obtained from the Operations Division of the Oak Ridge National Laboratory, and was assayed by an indirect solid counting method developed and used by that group.

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Application of Polarization Theory to Sorption of Water Vapor by High Polymers[2,3]

BY SAM R. HOOVER AND EDWARD F. MELLON

Introduction

In our studies of water absorption by proteins we found that the sorption of water at high relative humidity depends on the prior sorption on active sorptive groups such as the free amino and peptide groups.[4,5]

This dependence was not only qualitatively true; attempts to fit the data to various possible equations showed that many of our data can be described by the simple relationship $\log a = kp/p_0 + b$ when a = amount absorbed, p/p_0 = relative vapor pressure, and k and b are empirical constants.[5] This equation fitted the data from 30 to 90% relative humidity. Expressed in words, it says that the amount absorbed in this region as the relative humidity increases is proportional to the amount already adsorbed. Moreover, the slope constant k was the same for three proteins and two synthetic polyglycines. As stated previously,[5] "This fact indicates that all the water absorbed in this humidity region is held by hydrogen bonds of about the same strength." These results seemed to be best interpreted as sorption of water in water, and further analysis was made in an attempt to put this idea on a more quantitative basis.

Current treatments of sorption phenomena have been based primarily on the Brunauer–Emmett–Teller (BET) extension of the Langmuir isotherm to multimolecular adsorption,[6,7,8,9] and the Flory–Huggins solution theory.[10,11] The BET theory was developed originally to describe the adsorption at low temperature and pressure of gases on surfaces with succeeding layers held by van der Waals forces. The original two-constant equation for an unlimited number of layers and the modified three-constant equation, wherein n, the number of layers, is introduced, give valuable information in the lower portion of

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Paper V in the series "Water Absorption of Proteins."

[3] Presented at the American Chemical Society meeting in Atlantic City, N. J., September, 1949.

[4] Mellon, Korn and Hoover, THIS JOURNAL, **69**, 827 (1947).

[5] Mellon, Korn and Hoover, *ibid.*, **70**, 3040 (1948).

[6] Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

[7] Bull, *ibid.*, **66**, 1499 (1944).

[8] Dole and McLaren, *ibid.*, **69**, 651 (1947).

[9] Dole, *J. Chem. Phys.*, **16**, 25 (1948).

[10] Simha and Rowen, THIS JOURNAL, **70**, 1663 (1948); Rowen and Simha, *J. Phys. Colloid Chem.*, **53**, 921 (1949).

[11] Cutler and McLaren, *J. Polymer Sci.*, **3**, 792 (1948).

the sorption curve, but do not describe the high relative pressure region in many systems adequately. A number of alternate derivations and modifications of the BET equations have been proposed[12,13,14] which fit the data better at high relative vapor pressures. However, these modified equations are relatively empirical in describing water absorption in the high relative humidity region; and the third constant is essentially a curve-fitting one. The Flory–Huggins theory considers the interaction of solid and vapor to be a solution phenomenon in which polymer segments are equivalent and interchange with vapor molecules. This treatment has been applied with partial success to the higher vapor pressure region but does not describe the lower region at all.[11] Moreover, we believe our demonstration of specific sorptive sites in proteins argues against the concept of a mixing of vapor with *equivalent* polymer segments.

Study of the previous literature showed that isotherm equations have been derived by both de Boer and Zwikker[15] and Bradley[16] for the assumed system of a strongly sorptive polar surface or group which adsorbs a first layer, and subsequent layers which are sorbed because of the dipole induced in the first layer, and propagated similarly through the layers. The equation of de Boer and Zwikker is

$$\ln p_a/K_3p_0 = K_2K_1^a \qquad (1)$$

when a is the amount absorbed at pressure p_a. They found that K_3 is often close to unity and in those cases can be neglected. Bradley used a different derivation and arrived at a similar equation which in our notation is

$$\ln p_0/p_a = K_2K_1^a \qquad (2)$$

In this equation K_2 and K_1 are functions of the field of the sorptive polar group, the dipole moment of the sorbed gas, the polarizability of the gas, and of the temperature. K_1 in addition includes a term which is characteristic of the distribution of the sorbed molecules on the sorptive sites. Later in the same year, Bradley[17] extended his treatment to consider the sorption of gases with permanent dipoles on polar sorbents. He concluded it was necessary to consider the term K_4 as in equation [3].

$$\ln p_0/p_a = K_2K_1^a + K_4 \qquad (3)$$

This term was taken to be approximately zero in the derivation of equation 2. The term K_4 is included to account for the difference between the heat of evaporation from the polarized surface and from the bulk liquid. Brunauer[18] has reviewed the derivation of the polarization isotherm and has criticized severely its application to sorption of gases with *induced dipoles.* He considers its application to molecules with large *permanent dipoles* more reasonable and worthy of further test.

On the basis of the similarity between our conception of the sorption process and the assumptions of the polarization theory, we have investigated the applicability of these equations to our data. The simplest equation, the two-constant equation of Bradley (2), fits throughout the whole range of our data, from 6 to 93% relative humidity. The description of the data was so accurate that we have extended it to water sorption in other high polymer systems.

Experimental Methods and Data

Our methods have been reported previously.[4] They consist in gravimetric determination of water uptake from the atmosphere over saturated salt solutions in evacuated desiccators. Details of the drying conditions, temperature control, and reproducibility of measurements were given. For our previously reported work, from which come most of the data used for the calculations below, three samples were usually run at different times. The standard error of the mean of these three values was less than 0.1 g. per 100 g. in all cases, and less than 0.04 g. per 100 g. in two-thirds of the cases. In our more recent work, duplicates have been considered satisfactory.

Application of Polarization Isotherm

For consistency of notation, we shall use the equation derived by Bradley but with the terminology used here in the preceding discussion. The exponential equation $\ln p_0/p = K_2K_1^a$, (2), which can be readily transformed to

$$\log \log p_0/p = \log K_2 + a \log K_1 \qquad (4)$$

then gives a linear relation for log log p_0/p plotted against a. It must be emphasized here that *the data are not condensed* by use of the polarization isotherm. The log log plot would do so if the abscissa were not expanded to correct for this effect. Comparison of Figs. 1 and 2 shows that the abscissa has been expanded so that the data cover exactly the same horizontal distance in the graphs as originally drawn. The ordinate scale, "sorption, % dry weight," is identical for Figs. 1 and 2.

The theoretically derived function log log p_0/p fits the sigmoid isotherm characteristic of water sorption because, as the log log of a ratio, the two curved regions at high and low relative vapor pressures are converted to a linear function. A simple plot of log log p *vs.* sorption, for example, does not fit the data at all.

The intercept on the pressure axis when $a = 0$ is log K_2, and log K_1 is the slope of the line. Values of the intercept and slope were obtained by calculating the least-square line on the seven points at which our determinations were made. We have previously presented our data on a weight basis, g. of water per 100 or 1000 g. of dry protein, or, for theoretical reasons, as mole of water per

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(12) Anderson, THIS JOURNAL, **68**, 686 (1946).

(13) Cook, *ibid.*, **70**, 2925 (1948).

(14) Ross, *J. Phys. Colloid Chem.*, **53**, 383 (1949).

(15) de Boer and Zwikker, *Z. physik. Chem.*, **B3**, 407 (1929).

(16) Bradley, *J. Chem. Soc.*, 1467 (1936).

(17) Bradley, *J. Chem. Soc.*, 1799 (1936).

(18) Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943; Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

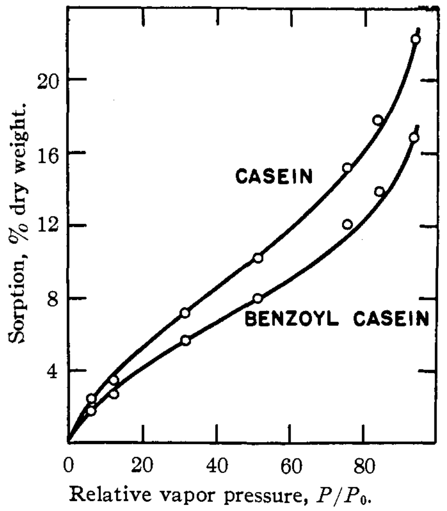

Fig. 1.—Sorption isotherm of water on casein and benzoyl casein at 30°.

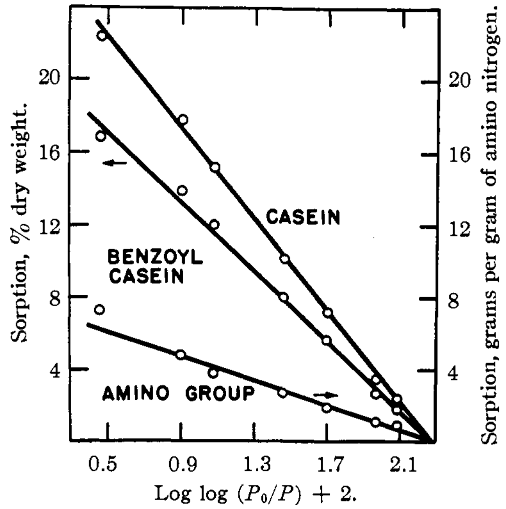

Fig. 2.—Sorption isotherms of water on casein, benzoyl casein and the amino group of casein, plotted according to the polarization theory.

mole of amino or peptide nitrogen. For this paper, all calculations are on the weight basis, g. per 100 g. dry substance, which is the "per cent. regain" as used in the textile industry. A necessary exception will be noted in the derived data for the sorption of the amino group in casein, which is expressed as grams of water per gram of amino nitrogen.

The typical sigmoid isotherm for the sorption of water by organic high polymers is illustrated in Fig. 1 by casein and a benzoylated casein in which 72% of the free amino groups have been substituted.[4] The fit of these data to the linear relationship of log log P_0/P is shown in Fig. 2. The values on the abscissa are plotted as log log $(P_0/P) + 2$ so that all points are of positive sign. The intercept on the pressure axis is about the same for each of these materials and corresponds to a relative vapor pressure of about 0.014. The derived sorption data for the amino group in casein[4] also give a reasonably good straight line in Fig. 2 when plotted as grams of water per gram of amino nitrogen.

Figures 3, 4, 5 and 6 demonstrate similar close agreement of the sorption data to the least square plots of the Bradley isotherms for a variety of materials. The silk and polyglycine curves (Fig. 3) represent sorption on a simple peptide chain, whereas the wool and ovalbumin curves (Fig. 4) describe a composite of sorption on the peptide chain and on polar side groups.

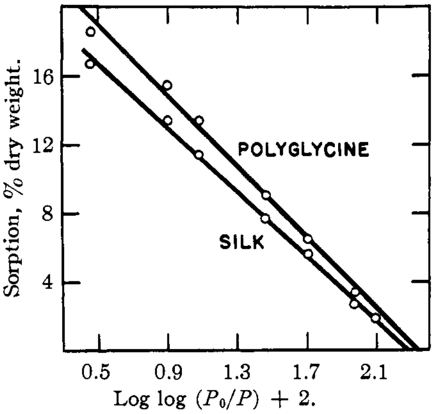

Fig. 3.—Sorption isotherm of water on polyglycine and silk at 30°, plotted according to the polarization theory.

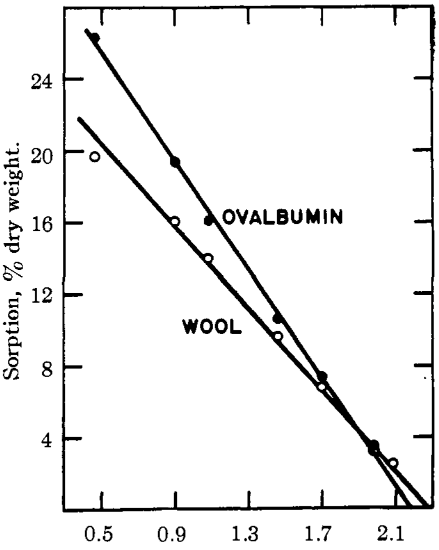

Fig. 4.—Sorption isotherm of water on ovalbumin and wool at 30°, plotted according to the polarization theory.

The sorption data for cotton yarn and mercerized cotton yarn shown in Fig. 5 prove that this closeness of fit is not limited to the proteinaceous materials. The sorption data of Speakman and

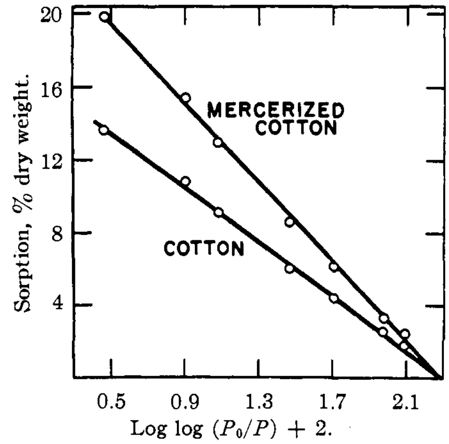

Fig. 5.—Sorption isotherm of water on cotton and mercerized cotton at 30°, plotted according to the polarization theory.

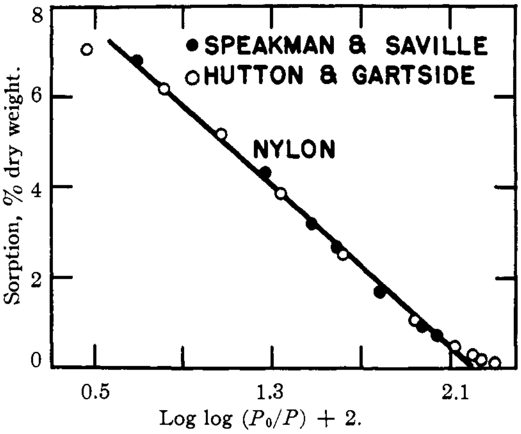

Fig. 6.—Sorption isotherm of water on nylon at 25°, plotted according to the polarization theory.

Saville[19] and Hutton and Gartside [0] on nylon lie on a single straight line plot in Fig. 6. The deviation of these measurements at the end of the relative humidity scale is expected, since the function log log P_0/P necessarily approaches infinity as P approaches zero and negative infinity as P approaches P_0. Therefore, the linear relationship must break down at both ends of the scale.

Effect of Temperature on Polarization Isotherm

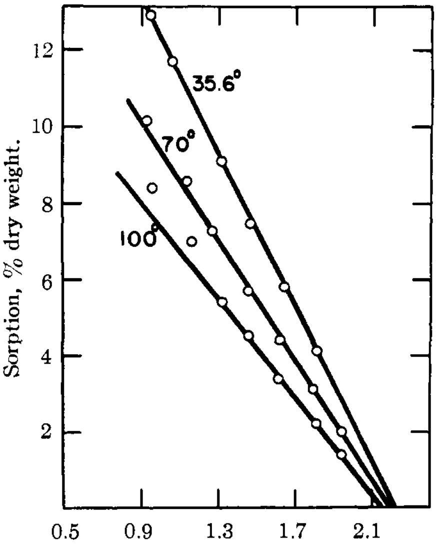

Fig. 7.—Sorption isotherms of water on silk at 35.6°, 70° and 100°, plotted according to the polarization theory: data of Wiegerink.

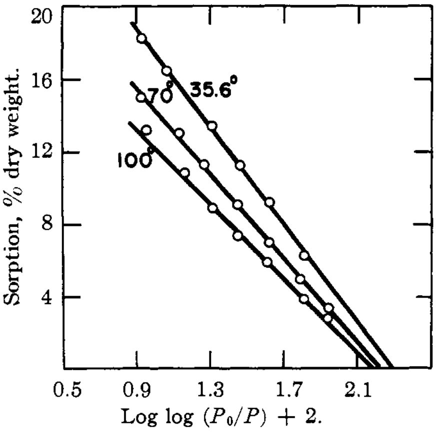

Fig. 8.—Sorption isotherms of water on wool at 35.6°, 70° and 100°, plotted according to the polarization theory data of Wiegerink.

We have not carried out experiments over a sufficient range of temperature to test the temperature dependency of the two constants. However, the measurements of Wiegerink[21] on a variety of textile materials were made over a wide range of temperature, and the polarization isotherm fits his data for wool, silk, and viscose rayon excellently (Figs. 7, 8 and 9). The isotherm plot also gives additional information, for there is a clear indication of additional increase in weight, presumably due to oxidation or hydrolysis, in silk at 100° and high relative humidity. The demonstration of such changes is not new; Speakman and Cooper[22] showed that degradative changes in wool occur at high humidities above 55°, and Hutton and Gartside[23] recently reported similar changes in isoelectric silk even at 25°.

It is apparent that both the slope and intercept constants are dependent on temperature. This is true for Bradley's treatment if the adsorbed material possesses a permanent dipole.[17] In Wiegerink's data on water absorption of textile materials, the major effect is in the slope constant, for the intercepts do not differ greatly. At the

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(19) Speakman and Saville, *J. Textile Inst.*, **37**, P271 (1946).

(20) Hutton and Gartside, *ibid.*, **40**, T171 (1949).

(21) Wiegerink, *J. Research, Nat. Bur. Standards*, **24**, 645 (1940).

(22) Speakman and Cooper, *J. Texile Inst.*, **27**, T191 (1936).

(23) Hutton and Gartside, *ibid.*, **40**, T161 (1949).

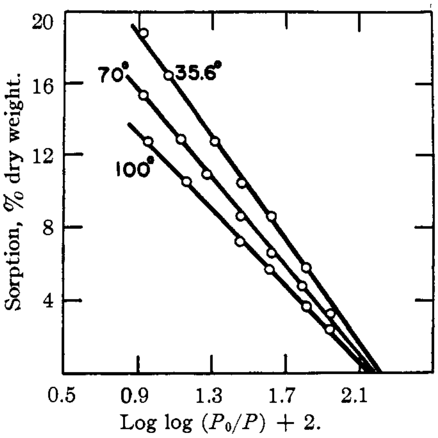

Fig. 9.—Sorption isotherms of water on viscose rayon at 35.6°, 70° and 100°, plotted according to the polarization theory: data of Wiegerink.

three temperatures, the intercept is about the same for the three materials; more extensive data would be required to determine whether an intercept could be established as a "constant" for each temperature.

Discussion

The value of the polarization theory in describing the water absorption of high polymers must now be considered. First, it appears to be established that the simple two-constant linear equation fits the experimental data from $p/p_0 = 0.05$ to 0.95. The average deviations of the data from the calculated linear relationship for the results plotted in Figs. 1–5 are given in Table I, together with the constants of the least-square line from which they were derived. These deviations approach the experimental error of the measurements.

TABLE I

FITTING OF EXPERIMENTAL DATA TO LOG LOG p_0/p = LOG K_1 + a LOG K_2 BY LEAST-SQUARE CALCULATION OF THEORETICAL VALUES

Material	Figure no.	Intercept log K_1[a]	Slope $-\log K_2$	Average deviation of data from theory g./100 g.	%
Casein	2	0.27	0.079	0.25	3.2
Benzoylcasein	2	.28	.104	.34	2.8
Polyglycine	3	.33	.096	.41	4.2
Silk fibroin	3	.29	.107	.20	3.3
Ovalbumin	4	.18	.066	.25	3.0
Wool	4	.28	.088	.44	5.1
Cotton	5	.30	.132	.15	3.8
Mercerized cotton	5	.28	.092	.21	4.2

[a] Expressed as log K_1 + 2 in the text and figures.

The derivation of the two-constant equation is not rigorous, but appears to be reasonable. We are here faced with the embarrassing but unusual circumstance that additional constants can logically be introduced, but are not necessary. We believe it is noteworthy that the theoretical basis used by de Boer and Zwikker and by Bradley in deriving their equations is essentially the same as that reached by us as a conclusion from our data, namely, that sorption on active sites occurs at low vapor pressures and that sorption at higher vapor pressure is due to this prior sorption. Such an idea would not necessarily restrict the treatment to the polarization theory; for example, it is implicit in the BET isotherm. However, *the polarization theory introduces a particular mechanism for the propagation of the dipole forces through the dipolar sorbent, and predicts the exponential pressure function actually observed.*

The polarization isotherm can also be valuable as a means of predicting the isotherm from a minimum of data. If further work shows that the intercept on the pressure axis is a constant at any one temperature for a given polymer, as seems probable, only a single determination of sorption would enable one to draw the whole isotherm with reasonable accuracy. The results on cotton and mercerized cotton illustrate this possibility.

A further contribution of the linear plot lies in the possibility of demonstrating that a portion of the data may be in error. The deviations of the data in Fig. 7 illustrate this point. The magnitude of the change in weight due to degradation can be estimated roughly from the deviations observed. Parenthetically it should be noted here that the original data of Wiegerink fit the linear relation much better than the statistically recalculated curves of his results published by Toner, Bowen and Whitwell.[24] There appears to be a fairly consistent trend of their smoothed curve; in the region around 30% relative humidity it is consistently low for the various textile materials. Thus the usual advantages of a linear over a curvilinear relation can be utilized in studying water sorption of high polymers.

Summary

The equation $\ln p_0/p = K_2K_1^a$ (in which K_1 and K_2 are both dependent on temperature), derived by Bradley to describe the sorption of gases on polar sorbents through dipole propagation, fits the experimental data for the sorption of water on a variety of high polymers. Results on casein, benzoylcasein, silk, polyglycine, wool, ovalbumin, cotton, mercerized cotton, nylon and viscose rayon are presented as straight line functions (log log p_0/p *vs.* a log K_1). The average deviation of the experimental points over the range of 6 to 93% relative humidity is 0.28 g. of water per 100 g. dry weight, or 3.7% for the authors' data on the first eight substances.

The application of this equation to sorption of water on polar groups, and the value of this linear relationship in analyzing sorption data, are discussed.

PHILADELPHIA 18, PA. RECEIVED SEPTEMBER 15, 1949

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(24) Toner, Bowen and Whitwell, *Textile Research J.*, **17**, 7 (1947).