rene–vinyl acetate (for which $b_1b_2 < 0$) in the light of the equations herein reported.

Acknowledgment.—The author wishes to thank Dr. Roland E. Florin of the Chemistry Department of the University of Nebraska for his helpful criticisms during the early part of this work.

Summary

The copolymerization rate equation and some approximations to it were integrated. Some of the implications of the results were discussed briefly.

CAMBRIDGE 38, MASSACHUSETTS

RECEIVED SEPTEMBER 7, 1949

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Water Sorption by Synthetic High Polymers

BY MALCOLM DOLE* AND I. LUCILLE FALLER[1]

Introduction

It is the purpose of this paper to describe results obtained in studying the sorption of water vapor by synthetic high polymers in order to discover correlations if any between water sorption and the chemical and physical constitution of the polymers. Systematic studies on synthetic polymers over a complete vapor pressure range and at different temperatures as a function of polymer constitution have not often been carried out. By synthetic high polymers we restrict ourselves to synthetic linear polymers. The sorption of water by three dimensional plastics occurs too slowly for equilibrium to be reached even after months of soaking in liquid water; see, for example, the review by Kline, Martin and Crouse.[2] Bull[3] has investigated drawn and undrawn Nylon at 25 and 40° as well as a number of naturally occurring proteins. Mellon, Korn and Hoover[4] have measured the water sorption of casein as a function of the extent of benzoylation of its free amino groups.

The percentage of water sorbed at 81 and 100% relative humidity by N-methylated polydecamethylene sebacamide (10–10 polyamides) has been determined by Baker and Fuller,[5] who found that the amount of water sorbed gradually increased as a function of the N-methylation up to 55% methylation which was as far as their studies were carried. Other measurements of water sorption at 100% relative humidity by N-alkylated polyamides have been reported by Wittbecker, Houtz and Watkins.[6] Apparently the water sorption is reduced as the size and branching of the substituted alkyl group increases. The degree of disorder introduced into the polymer also affects the properties of the material, as indeed is demonstrated by the data reported below.

In the paper by Hauser and McLaren[7] water sorption isotherms are given at 25° for the following sorbents: polyvinyl alcohol, cellulose acetate, Nylon, polyvinyl butyral, rubber hydrochloride and vinylidene chloride–acrylonitrile copolymer. Mention is also made of measurements at 40°.

Theoretical treatment of water sorption data can be usually classified into one of three points of view; first, application of strict adsorption theory such as that of Brunauer, Emmett and Teller[8] (henceforth referred to as BET); second, application of liquid-mixing equations of Flory[9] and Huggins[10]; and third, introduction into the theory of factors to allow for swelling effects. Application of the BET equation has been made by Bull,[3] Dole and McLaren,[11] Pauling[12] and others. Cutler and McLaren[13] have recently interpreted the sorption of water by proteins in terms of the liquid-mixing theory of Huggins.[10] Even more recently Rowen and Simha[14] also advocate the use of Huggins' equation with parameter, μ. An additional term, suggested by Rowen and Simha to account for the contribution to the entropy resulting from elastic deformation, was dropped by them as being of negligible importance, at least for the sorption of water by cellulose. Mellon, Korn and Hoover[4] find that neither the disorientation nor the application of tension affects appreciably sorption by proteins.

White and Eyring[15] have similarly considered the elastic work of swelling, but have combined their swelling theory with adsorption theory to ob-

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* Harvard University Ph.D., 1928.

(1) University Fellow, 1946–1948; present address, Argonne National Laboratory, Chicago.

(2) G. M. Kline, A. R. Martin and W. A. Crouse, *Modern Plastics*, **18**, No. 2, 119 (1940).

(3) H. B. Bull, THIS JOURNAL, **66**, 1499 (1944).

(4) E. F. Mellon, A. H. Korn and S. R. Hoover, *ibid.*, **69**, 827 (1947). See also Mellon, Korn and Hoover, *ibid.*, **70**, 1144, 3040 (1948); **71**, 2761 (1949).

(5) W. O. Baker and C. S. Fuller, *ibid.*, **65**, 1120 (1943).

(6) E. L. Wittbecker, R. C. Houtz and W. W. Watkins, *Ind. Eng. Chem.*, **40**, 875 (1948).

(7) P. M. Hauser and A. D. McLaren, *ibid.*, **40**, 112 (1948).

(8) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

(9) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(10) M. L. Huggins, *Ind. Eng. Chem.*, **35**, 216 (1943); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(11) M. Dole and A. D. McLaren, THIS JOURNAL, **69**, 651 (1947).

(12) L. Pauling, *ibid.*, **67**, 555 (1945).

(13) Janice A. Cutler and A. D. McLaren, *J. Polymer Sci.*, **3**, 792 (1948).

(14) J. W. Rowen and R. Simha, *J. Phys. and Colloid Chem.*, **53**, 921 (1949).

(15) H. J. White and H. Eyring, *Textile Research J.*, **17**, 10 (1947); White and Stam, *ibid.*, **19**, 136 (1949).

tain an equation like the BET equation, but with an additional empirical constant. Dole[16] has examined the statistical thermodynamic basis of adsorption and has suggested various equations applicable to the sorption of vapors by high polymers.[17]

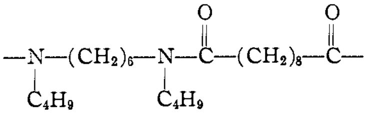
In this paper we report data for the sorption of water vapor at various relative humidities for a number of N-isobutylated 6–10 polyamides, polyvinylmethoxyacetals, and for certain polyesters and polyvinylpyrrolidone.

Experimental Procedure and Results

The experimental technique was essentially the same as that used by Bull.[3] The materials used and their sources were as follows:

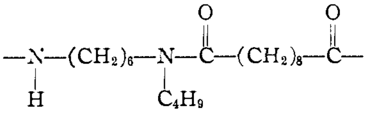
Polyhexamethylene sebacamide (6–10 polyamide); also described as 0/0/100 6–10 polyamide (labelled "A" in Table I).

Poly-N,N′-isobutylhexamethylene sebacamide ("C" in Table I), described as 100/0/0 6–10 polyamide whose repeating unit is



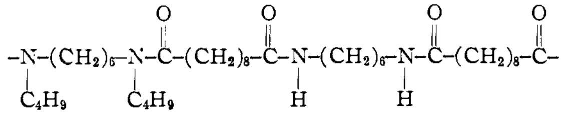
$$-\underset{C_4H_9}{\underset{|}{N}}-(CH_2)_6-\underset{C_4H_9}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-$$

Poly - N - isobutylhexamethylene sebacamide ("B" in Table I); described as 0/100/0 6–10 polyamide whose repeating unit is



$$-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{C_4H_9}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-$$

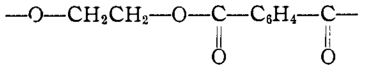
Poly-N,N′-isobutylhexamethylene sebacamide, polyhexamethylene sebacamide copolymer (50 mole per cent. of each) described as 50/0/50 6–10 polyamide ("D" in Table I) whose repeating unit is



$$-\underset{C_4H_9}{\underset{|}{N}}-(CH_2)_6-\underset{C_4H_9}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-$$

Preparation and properties of the isobutylated 6-10 polyamides are described in a paper by Wittbecker, Houtz and Watkins.[18]

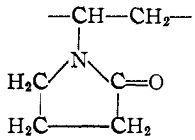
Polyethylene terephthalate whose repeating unit is



$$-O-CH_2CH_2-O-\underset{O}{\underset{\|}{C}}-C_6H_4-\underset{O}{\underset{\|}{C}}-$$

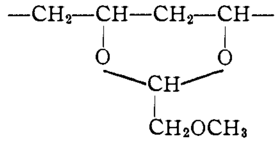
All the above compounds were generously supplied by the Rayon Technical Division of E. I. du Pont de Nemours and Company.

Polyvinylpyrrolidone, labelled "K" in Table I, whose repeating unit is



was kindly supplied by the Bell Telephone Laboratories and by the General Aniline and Film Corporation.

Polyvinylmethoxyacetals: these compounds were made from polyvinyl alcohol and methoxyacetaldehyde.[19] Three different polymers were chosen for study; those having 86, 72 and 48% of the hydroxyl groups (labelled "G," "F" and "E," respectively, in Table I) of the polyvinyl alcohol replaced by the methoxyacetal group. The coagulation temperatures of these substances in water were 35, 36 and 52°, respectively. The substituted group has the structure



These polymers were kindly given to us by the Visking Corporation.

Polyhexamethylene adipate and polyhexamethylene sebacate, labelled "H" and "I" in Table I. These polyesters were kindly prepared for us in the Northwestern Laboratories by Mr. H. E. Vinsinger using pure monomers donated by the Chemical Department, Experimental Station of E. I. du Pont de Nemours and Company. All of the above materials were used as received without further purification.

The accuracy of the experimental results is limited by the weighing error at very low vapor pressures, assuming that true equilibrium has been obtained. Although a semi-micro magnetically damped balance accurate to 0.03 mg. was used, the error in the amount of water sorbed may amount to as much as 15% at the lowest relative humidities. On repeating the sorption experiments, the data usually agreed within a few per cent. No evidence of hysteresis was noted in any experiments. Figure 1 includes all the data obtained in the experiments on the 0/100/0 polyamide at three temperatures 15, 25 and 40°. As the change in sorption with temperature was hardly greater than the fluctuations of individual values, we have decided to report in the case of the polyamides and the polyvinylmethoxyacetals sorption values averaged over the three temperatures. The polyester and polyvinylpyrrolidone data were obtained only at one temperature, 25°.

In Table I we have collected all of the experimental results obtained in the sorption studies. These are values taken at "rounded-off" values of the relative vapor pressure from plots of the actual data such as Fig. (1) and represent, therefore, "smoothed" results.

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[16] M. Dole, *J. Chem. Phys.*, **16**, 25 (1948); see also T. L. Hill, *ibid.*, **14**, 263 (1946).

[17] M. Dole, *J. Colloid Sci.*, **3**, 411 (1948); *Ann. N. Y. Acad. Sci.*, **51**, 705 (1949).

[18] E. L. Wittbecker, R. C. Houtz and W. W. Watkins, *Ind. Eng. Chem.*, **40**, 875 (1948).

[19] K. F. Beal and C. J. B. Thor, *J. Polymer Sci.*, **1**, 540 (1946).

TABLE I

SORPTION OF WATER BY SYNTHETIC HIGH POLYMERS AVERAGED TO 25°

(Moles of water per 100 g. of polymer)

Substance → Rel. partial press. of water	A	B	C	D	E	F	G	H	I		K
0.05	0.010	0.012	0.009	0.088	0.040	0.030	0.020	0.002	0.001	0.001	0.117
.1	.019	.025	.015	.013	.070	.055	.038	.004	.002	.003	.197
.2	.035	.047	.027	.024	.125	.085	.060	.007	.004	.005	.340
.3	.050	.068	.040	.033	.180	.125	.078	.009	.006	.008	.518
.4	.065	.093	.052	.042	.245	.180	.096	.012	.007	.011	.738
.5	.081	.120	.066	.052	.340	.240	.122	.015	.008	.014	.987
.6	.097	.152	.081	.064	.485	.340	.171	.019	.010	.018	1.295
.7	.114	.188	.099	.082	.740	.600	.271	.023	.012	.022	1.723
.8	.135	.232	.120	.104	1.340	1.500	.482	.028	.014	.027	2.433
.9	.166	.282	.150	.129	2.350	3.46	.905	.034	.017	.033	3.770
.95		.316	.180	.146	3.010		1.260	.037	.018	.037	

Symbol	Compound	Symbol	Compound
A	0/0/100 6–10 polyamide	G	Polyvinylmethoxyacetal 86% combination
B	0/100/0 6–10 polyamide	H	Polyhexamethylene adipate
C	100/0/0 6–10 polyamide	I	Polyhexamethylene sebacate
D	50/0/50 6–10 polyamide	J	Polyethylene terephthalate
E	Polyvinylmethoxyacetal 48% combination	K	Polyvinylpyrrolidone
F	Polyvinylmethoxyacetal 72% combination		

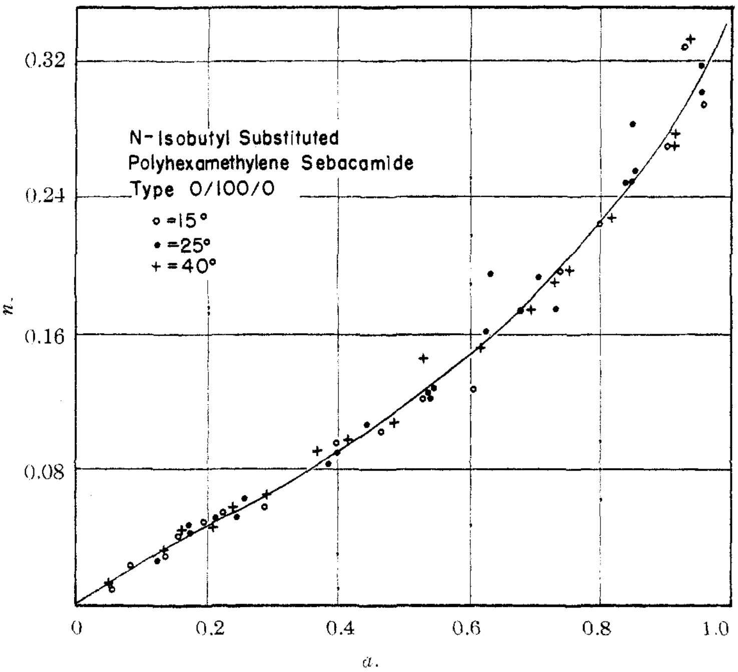

Fig. 1.—Sorption of water in moles per 100 g. polymer.

Theoretical Interpretation of Data

Isobutylated Polyamides.—Figure 2 shows the trend in the water sorption of the four types of the 6–10 polyamides with vapor pressure at 25°. As mentioned above the trend with temperature was less than individual fluctuations; hence, a precise calculation of the temperature coefficient cannot be made. In general, the trend was in the direction of a slightly smaller adsorption at the higher temperature.

Like most other water sorption systems, BET[20] plots of the polyamide data show the usual behavior of following the linear relation up to a relative vapor pressure (a) of about 0.4, and then deviating from the curve positively (the value of $a/N(1 - a)$ is too high or N, the sorption, is too low for the theory to be valid). Usually, a sufficient number of points on the straight line was obtained for an extrapolation to be made to unit activity where $N(1 - a)/a$ becomes equal to N_s. Table II contains values of N_s calculated on the basis of moles of water sorbed per mole of carbonyl group in the polyamide.

The striking fact of Table II is the small magnitude of the N_s values; thus, on the basis of the application of the BET equation, it would appear that only 5 to 13% of the possible sorption sites can be occupied by a water molecule. We are here assuming that one peptide bond or carbonyl group can sorb only one water molecule in the first layer. Sponsler, Bath and Ellis[21] and Pauling[12] have suggested that, in the case of the proteins, water sorption occurs on the free amino groups of the side chains

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(20) In the use of BET and other equations, the symbol N means moles of water sorbed per mole of carbonyl group, N_s means moles of sorption sites per mole of carbonyl group and c_1 is the ratio of the partition function of the sorbed molecule to that of the molecule in the pure liquid state, see references (16) and (17).

(21) O. L. Sponsler, J. D. Bath and J. W. Ellis, *J. Phys. Chem.*, **44**, 996 (1940).

TABLE II

MOLES OF SORPTION SITES PER MOLE OF CARBONYL GROUP IN THE 6–10 SUBSTITUTED POLYAMIDES

Compound	N_s, BET
0/0/100	0.076
0/100/0	.131
100/0/0	.083
50/0/50	.054

of such protein constituents as arginine or lysine or on hydroxyl or carboxyl groups in side chains of other amino acid residues. In our polyamides we have no side chains, but we do have end-groups which might serve as more favorable water sorption sites than the carbonyl groups in the chain. Thanks to information received from the Rayon Technical Division of E. I. du Pont de Nemours and Company, the number of NH_2 and COOH ends per 100 g. of polymer is known in the case of the 0/0/100 material. It amounts to 0.002 mole of NH_2 and 0.016 mole of COOH per 100 g. Adding we obtain 0.018 and multiplying by 1.41 to convert to moles per mole of carbonyl, we obtain 0.025 or about one-third of the value for N_s for the 0/0/100 polyamide given in Table II. Thus, the end-groups can account for an appreciable fraction of the sorption, but not all of it. In the case of the isobutylated 6–10 polyamides listed in Table II, measurements of the intrinsic viscosity by scientists of the Rayon Technical Division of E. I. du Pont de Nemours and Company indicated a number average molecular weight between 20,000 and 30,000. Thus the 0/100/0, 100/0/0 and 50/0/50 polymers had intrinsic viscosities of 1.17, 0.95 and 1.00, respectively. An intrinsic viscosity of unity corresponds to a number average molecular weight of about 26,000 in the case of N-alkyl polyamides of similar type. (The intrinsic viscosities were not directly calibrated by end-group determinations on our polyamides.) We can make a reasonable estimate that the 0/100/0, 100/0/0 and 50/0/50 6–10 isobutylated polyamides have about 0.007, 0.010 and 0.008 mole of end-groups per mole of carbonyl, respectively. If these numbers are subtracted from N_s, then the moles of sorption sites not on end-groups are 0.051, 0.124, 0.073 and 0.046 for the four polymers of Table II. The 0/0/100 and the 50/0/50 polymers are thus shown to have nearly the same value of sorption sites not on end-groups. The conclusion is that the peptide bond is capable of absorbing water even though there be no hydrogen attached to the amino groups, as is the case of the 100/0/0 material.

Further evidence that the peptide bond is capable of sorbing water is seen in the data for water sorption by polyvinylpyrrolidone discussed below.

Having concluded that the peptide bond is capable of sorbing water, we must next explain why so few of the peptide bonds serve as sorption sites. As has been suggested by others in the past[22] crystalline regions of high polymers cannot sorb water; in fact, the extent of water sorption is suggested as a measure of the extent of crystallinity of the polymer. Such a definition of crystallinity is vague and difficult to treat theoretically; yet there is undoubtedly a strong connection between water sorption and the magnitude of internal binding between chains or the crystallinity of the polymer. This is seen by comparing the water sorption of the 50/0/50 and the 0/100/0 isobutylated 6–10 polyamides. Although both have exactly the same chemical composition, the 0/100/0 polymer sorbs roughly twice as much water as the 50/0/50 compound. We attribute this to the fact that in the 50/0/50 polymer longer sequences of unsubstituted imino groups along the chain are permitted than in the case of the 0/100/0 material where the substituted (S) and the unsubstituted (U) nitrogens must follow the sequence SUSU or SSUUSSUU or combinations of these two sequences along the chain. A long sequence of unsubstituted nitrogens such as UUUU which is possible in the 50/0/50 polymer would permit the development of greater crystallinity than in the 0/100/0 polyamide. This is also seen in the fact that the 50/0/50 polymer has a melting point of 150° as compared to that of 75° for the 0/100/0 polymer.

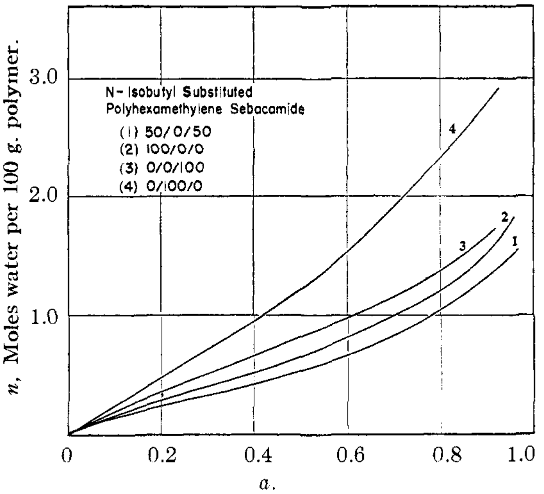

Fig. 2.

In sharp contrast to the polyamides, our data indicate that polyvinylpyrrolidone, which is water soluble, has one water sorption site per peptide bond. As there are no amino or carboxyl end-groups in this material, there is no uncertainty about the relative degree of water sorption on the ends of the long chain molecules as compared to sorption on polar groups in the chain. Furthermore, as there are no hydrogen atoms attached to the nitrogen atoms of the peptide bond, we do not have to postulate sorption through hydrogen bond action of an imino or amino hydrogen. Possibly

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(22) See particularly the publication of P. H. Hermans, "Contributions to the Physics of Cellulose Fibers," Elsevier Publishing Co., New York, N. Y., 1946.

the bulkiness of the side chain and the existence of the ring are responsible for the accessibility of the peptide bonds to water molecules on sorption.

For comparison with water sorption data on the 6–6 and 6–10 polyamides, we determined the water sorption isotherms at 25° for the 6–6 and 6–10 polyesters, and in addition, measurements were made on polyethylene terephthalate. Agreement obtained with the BET theory was about the same as with the polyamides. Calculations of N_s are given in Table III where N_s values for the 6–6 and 6–10 polyamides are also listed for comparison.

TABLE III

MOLES OF SORPTION SITES PER MOLE OF CARBONYL GROUP AT 25°

Substance	N_s
Polyhexamethylene adipate (6–6)	0.012
Polyhexamethylene sebacate (6–10)	.009
Polyethylene terephthalate	.010
Polyhexamethylene adipamide[3] (6–6)	.117
Polyhexamethylene sebacamide (6–10)	.076

It is immediately apparent that water sorption by the polyesters is much less than that of the polyamides and, in fact, of about the same order of magnitude as the number of end-groups per mole of carbonyl. The number average molecular weight of the polyethylene terephthalate is estimated to be about 40,000 ± 10,000 which corresponds to 0.05 mole of end-groups per mole of carbonyl group. Subtracting this number from the 0.010 of Table III, we obtained 0.005, or only 0.5% of the carbonyl–ester linkages serve as sorption sites. This number is zero within the limits of uncertainty of the data and theory. The number average molecular weight is not known for our samples of the 6–6 and 6–10 polyesters, but it is likely that water sorption along the chains in the polyesters is not possible.

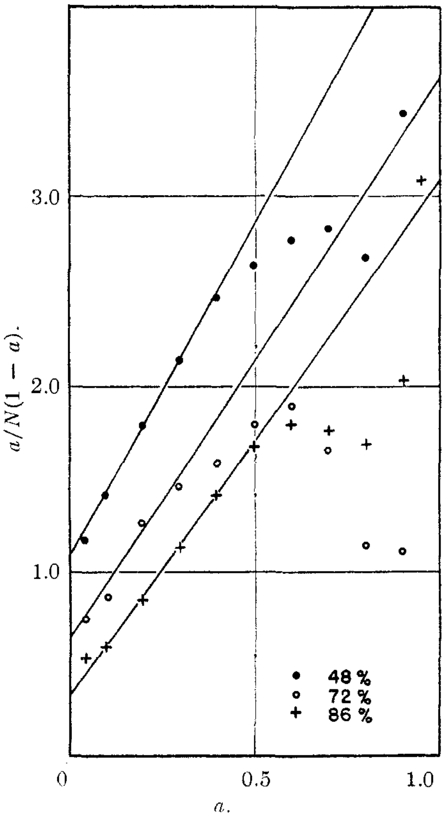

Fig. 3.—BET plot of the water sorption data for the polyvinylmethoxyacetals.

The polyvinylmethoxyacetals are interesting polymers as they have the property of being soluble in water at 0°, but precipitating at higher temperatures. BET plots of the three polyvinylmethoxyacetals are given in Fig. 3 where, contrary to the usual behavior, the data fall below the straight line at the higher vapor pressures. Such a deviation from the BET curve is in the direction of too much sorption of water. Not only does the slope of the BET function, $a/N(1 - a)$, decrease with rising relative vapor pressure, but in some cases the slope actually becomes negative. As the slope of the BET curve is given by the expression

$$(c_1 - 1)/c_1N_s$$

the slope can decrease by N_s increasing or by c_1 decreasing. It can only become negative by c_1 becoming less than unity. It is illuminating to plot the data in such a way that the number of sorption sites can be calculated from values in the high or low relative vapor pressure regions.[17] Thus if a/N is plotted as a function of the water activity, the slope will be positive and equal to $1/N_s$ in the region where monolayer sorption predominates, the region of validity of the Langmuir equation

$$\frac{1}{c_1N_s} + \frac{a}{N_s} = \frac{a}{N} \qquad (1)$$

or will be negative and equal to $1/N_s$ in the region where sorption on higher layers predominates, the region where the following "modified Raoult's law" equation seems to approach validity[17]

$$\frac{1}{cN_s} - \frac{a}{N_s} = \frac{a}{N} \qquad (2)$$

We shall assume that the limiting slope as a goes to zero represents the "Langmuir slope" and that the limiting slope as a goes to unity represents the "modified Raoult's law slope." The polyvinylmethoxyacetal data are plotted according to this scheme in Fig. 4 where N is the number of moles of water sorbed per mole of uncombined OH group in the polymer.

TABLE IV

MOLES OF SORPTION SITES PER MOLE OF UNSUBSTITUTED HYDROXYL GROUP IN POLYVINYLMETHOXYACETALS

% Substn.	BET	N_s, Langmuir	N_s, modified Raoult's law
48	0.22	0.28	0.83
72	.28	.36	1.18
86	.32	.59	1.00

Estimates of N_s are given in Table IV; unfortunately, not too great reliability can be accorded these estimates because of the uncertainty in the data at the highest and lowest vapor pressure regions. The BET and Langmuir values for the 48 and 72% substituted materials agree roughly so that we can probably believe that the order of magnitude is correct. The N_s data as obtained from the modified Raoult's law are least reliable; they suggest that the polymers change their structure as they swell in such a direction as to make all of the OH groups accessible for water sorption. At the present time we shall accept this suggestion as being the correct explanation for the anomalous behavior of the polyvinylmethoxyacetals in sorbing water.

Acknowledgments.—This work is part of a general program of study of the thermodynamics of high polymers, for which grants have been gratefully received from Visking Corporation, the Rayon Technical Division of E. I. du Pont de Nemours and Company, the Richardson Company and the Research Corporation (Frederick Gardner Cottrell Grant). We are particularly indebted to Dr. C. E. Black III of the Rayon Technical Division of E. I. du Pont de Nemours and Company and Dr. C. J. B. Thor of the Visking Corporation for helpful coöperation and advice.

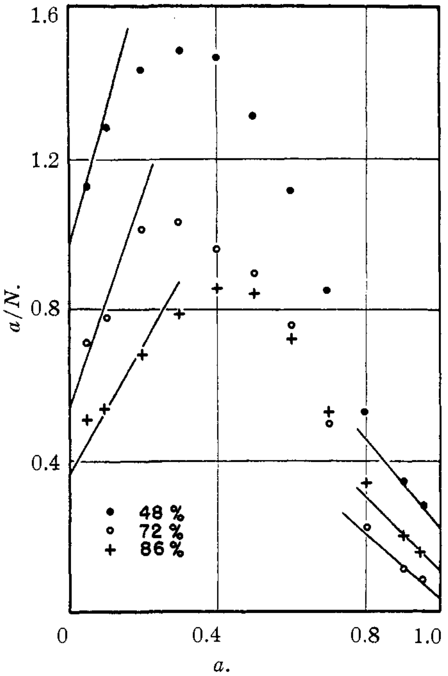

Fig. 4.—Langmuir and modified Raoult's law plot of the water sorption data for the polyvinylmethoxyacetals.

Summary

Water sorption data at 25° are given for eleven synthetic linear polymers, 0/0/100 polyhexamethylene sebacamide, 0/100/0 N-isobutylated polyhexamethylene sebacamide, 100/0/0 N,N'-isobutylated polyhexamethylene sebacamide, 50/0/50 polyhexamethylene sebacamide, N,N'-isobutylated polyhexamethylene sebacamide copolymer, 48, 72 and 86% substituted polyvinylmethoxyacetal, polyhexamethylene adipate and sebacate, polyethylene terephthalate and polyvinylpyrrolidone. The data are interpreted in the light of the BET and other sorption theories. Sorption by the polyesters is so small that it probably occurs only on end-groups. Sorption by polyvinylpyrrolidone is so great that probably every peptide bond serves as a sorption site. Sorption by the polyamides is small and greatly affected by the extent of disorder in the solid. The polyvinylmethoxyacetals sorb water to a much larger extent than expected at high vapor pressures of the water, thus leading us to suggest that more sorption sites become available at higher relative humidities.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 1, 1949

[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

On the Nature of Thermochromism

BY W. T. GRUBB* AND G. B. KISTIAKOWSKY†

A number of organic compounds undergo color changes with temperature which are so noticeable that a special name, thermochromism, has been given to the phenomenon. The compounds showing it are some of the substituted ethylenes, with multiple or fused aromatic rings as substituents. Padova[1] proposed that an association–dissociation equilibrium was responsible for the phenomenon and attempted to prove it by molecular weight measurements. Bergmann and Corte[2] demonstrated that Padova's experiments were in error and Bergmann and Engel[3] and others suggested that the formation of diradicals by a partial dissociation of the ethylenic double bond was the cause of thermochromism and supported this proposal by studies of the chemical behavior of such compounds. Probably still stronger chemical evidence was adduced by Schoenberg[4] as support for the existence of an equilibrium between normal ethylenes and betaine-like structures, with

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* Harvard University Ph.D. 1949.

† Harvard University Faculty 1930–.

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