

Gel-Water Relationships in Hydrophilic Polymers: Thermodynamics of Sorption of Water Vapor

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Synopsis

A thermodynamic study was conducted of water vapor adsorption on four hydrophilic polymers (agar, carboxymethyl cellulose, gelatin, and maize starch) at 12 and 25°C. Monolayer coverage amounted, after correction for crystallinity, respectively, to 0.93, 1.46, 0.51, and 0.77 mol water/mol monomer. Evidence is adduced from the Bradley equation and thermodynamic data to indicate that at least during coverage with the second layer of water, the energy of adsorption is greater than that due to condensation alone. Differences in the amount of sorption and in the trend of values of ΔS° and $\Delta \bar{H}^\circ$ with the amount of sorbed water are related with differences in the strength of intermolecular association as affected by steric hindrances.

INTRODUCTION

The interrelationship of water with hydrophilic polymer in a gel is not clear. Some investigators^{1,2} consider that water in a gel exists in a semi-rigid state, roughly intermediate between that of liquid water and that of ice, and Forslind³ has estimated that water about a clay crystal is more or less rigid "over distances of some 300 Å units." On the other hand, Pauling⁴ has assumed that only a monolayer of water on the surface of a protein molecule is held more tightly than the molecules of liquid water. Similarly, Kavanau⁵ has concluded that bound water is at least one molecule thick on the polymer surface, but he is noncommittal about the structure of water beyond the unimolecular layer.

Perhaps more insight into gel-water relationships can be attained if a concerted attack is made on these problems in several different gels by different methods of study. In the present instance, a comparative study of four different types of hydrophilic gel substances has been undertaken: agar, carboxymethyl cellulose (CMC), maize starch, and gelatin. Agar is a galactoglycan with occasional sulfate ester ($-\text{OSO}_3\text{H}$) groups; CMC is a carboxymethyl ether ($-\text{OCH}_2\text{COOH}$) of cellulose, with a usual degree of substitution (DS) of 0.4-1.4 in the commercial product; starch has three hydroxyl groups ($-\text{OH}$) per monomer unit; and gelatin consists of different amino acids, some of which may have polar and some nonpolar side chains, linked successively by peptide bonds. The first phase of this

study examines the thermodynamics of water vapor sorption for the dry polymer. Despite the industrial importance of gels of agar, CMC, and native *A*-starch, thermodynamic sorption data are not available for these materials.

EXPERIMENTAL

Materials

Commercial specimens of maize starch (Corn Products Refining Co.), CMC (Hercules Powder Co. 9M31F), and gelatin (Knox Gelatine, Inc.) were used directly. Washed agar was prepared by suspending 2% commercial agar (Difco Laboratories) in distilled water and steaming it at 120°C for 10 min. After being cooled, it was cut into 1-cm³ disks. These were washed in distilled water for 3 days, frozen at -15°C, lyophilized, and then ground to pass a 60-mesh screen. Titration of the acidified agar gave a relatively low DS value of 5×10^{-3} . The DS of acid-washed CMC by titration was 0.98, so that approximately one carboxymethyl group, on the average, was present on each monomer. Maize starch has an amylose content of 26%.

Measurement of Water Vapor Sorption

The apparatus and the method of measurement have been described earlier.^{6,7} About 0.5 g of sample was sieved through a 60-mesh screen and then dried at room temperature and 10^{-4} mm Hg pressure until reaching a constant dry weight.

Estimation of Crystallinity

Because only the amorphous regions are accessible for water vapor uptake, crystallinity was estimated approximately from x-ray diffraction of the polymer substance. After subtraction of the background due to air scattering, amorphous and crystalline areas were measured on photometered x-ray films.^{8,9} The arbitrary range of $\theta = 2.6$ – 12.5° was used because the largest crystalline peaks of the four polymers appear in this region.

RESULTS

The adsorption isotherms are shown in Figures 1–4. (The average error between gravimetric and manometric determinations was 4%.) Initially, after a week of drying under 10^{-4} mm Hg pressure at room temperature, there was relatively little moisture remaining in any of the polymers. At the different values of P/P_0 the amount of water adsorbed by agar and CMC is essentially equivalent, and this amount is definitely greater than the amount adsorbed by gelatin, which in general is slightly greater than that adsorbed by maize starch. The uptake of water by gelatin amounts to about 80% of the values recorded by Bull.¹⁰

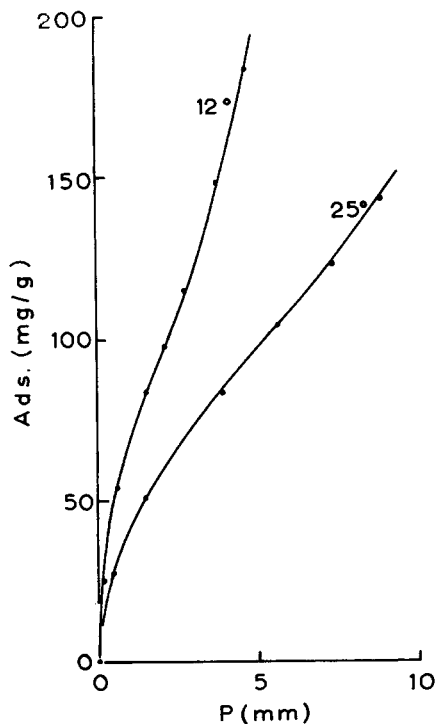


Fig. 1. Adsorption isotherms of water on agar.

The standard differential thermodynamic functions for adsorption at 25°C, calculated from the adsorption isotherms, are presented in Figures 5-8. The equations used here for calculation of the standard differential free energy, $\Delta\bar{F}^\circ$, the differential enthalpy of adsorption, $\Delta\bar{H}^\circ$, and the standard differential entropy of adsorption, $\Delta\bar{S}^\circ$, have been given by Volman et al.⁷ The parallelism between entropy and enthalpy curves, reported by Everett,¹¹ Law,¹² and Bettelheim and Volman¹³ occurs in these

TABLE I
Characteristics of the Dry Polymers

Polymer	B.E.T. constants			V_m , mole H ₂ O/mole monomer	X-ray crystal- linity, %	V_m , mole H ₂ O/mole monomer (corrected for crys- tallinity)
	C	$E_A - E_L$	V_m , mg/g			
Agar	21.4	1.83	93.3	0.80	14	0.93
CMC	21.0	1.81	95	1.21	17	1.46
Gelatin	16.6	1.68	74	0.42	18	0.51
Starch	18.6	1.74	75	0.66	14	0.77

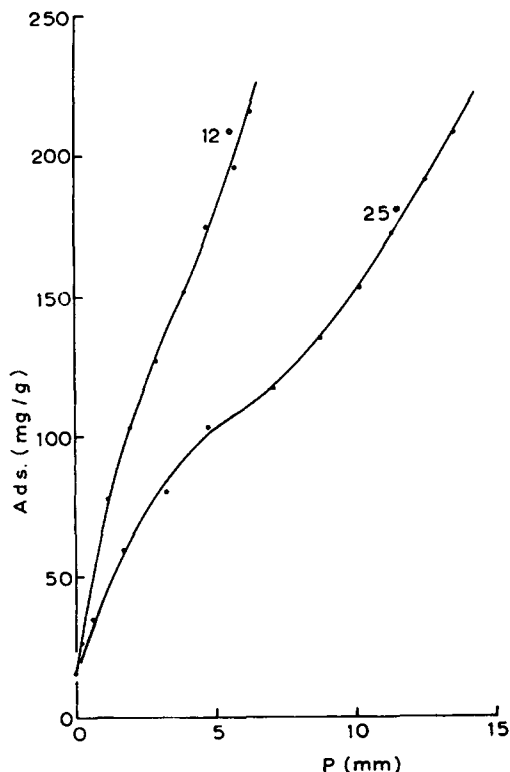


Fig. 2. Adsorption isotherms of water on carboxymethyl cellulose.

polymers also. In all samples, the standard differential free energy decreases gradually with the increase of adsorbed water.

The B.E.T. constants, V_m , C , and $E_A - E_L$, calculated from isotherms at 25°C, are listed in Table I. All the B.E.T. plots are rectilinear up to $P/P_0 = 0.30$. Crystallinity, as estimated by the x-ray diffraction method, is also given in Table I. The data do not seem to show any pronounced differences in crystallinity among the samples. As might be expected for good gel-formers, the relative amount of crystallinity for all is rather low.

DISCUSSION

The B.E.T. constants are particularly useful with respect to monolayer values.¹⁴ The monolayer in maize starch (*A*-starch) is complete at a binding of $2/3$ mole of water per mole of monomer, somewhat more than occurs in the monolayer of *A*-dextrin.⁷ When the fraction crystallinity is taken into account, nearly $4/5$ mole water/mole of monomer (0.77) is adsorbed, but some of this water is taken up in the crystalline regions.^{15,16} Approximately the same amount of water is adsorbed during monolayer

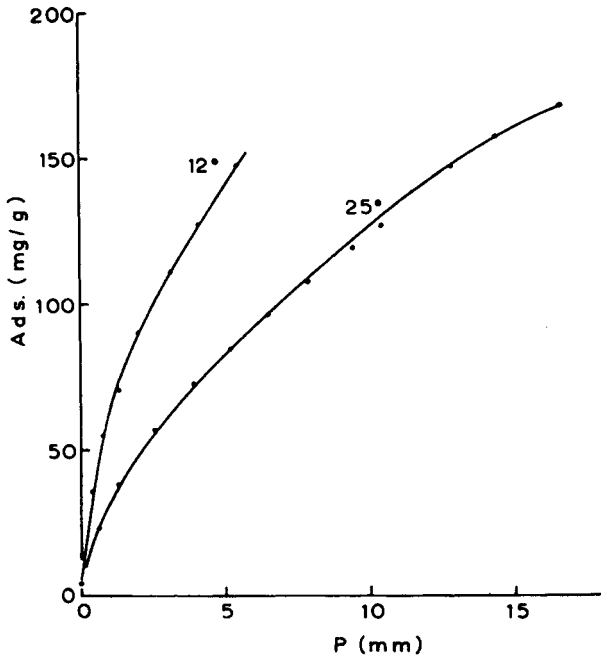


Fig. 3. Adsorption isotherms of water on gelatin.

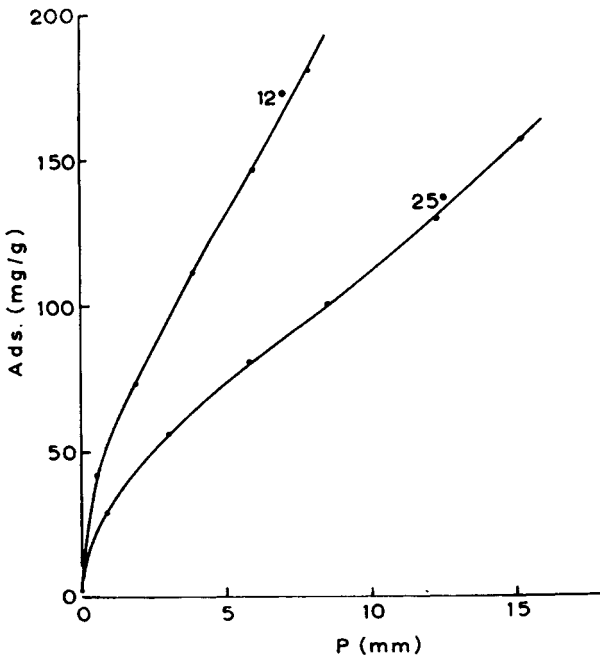


Fig. 4. Adsorption isotherms of water on maize starch.

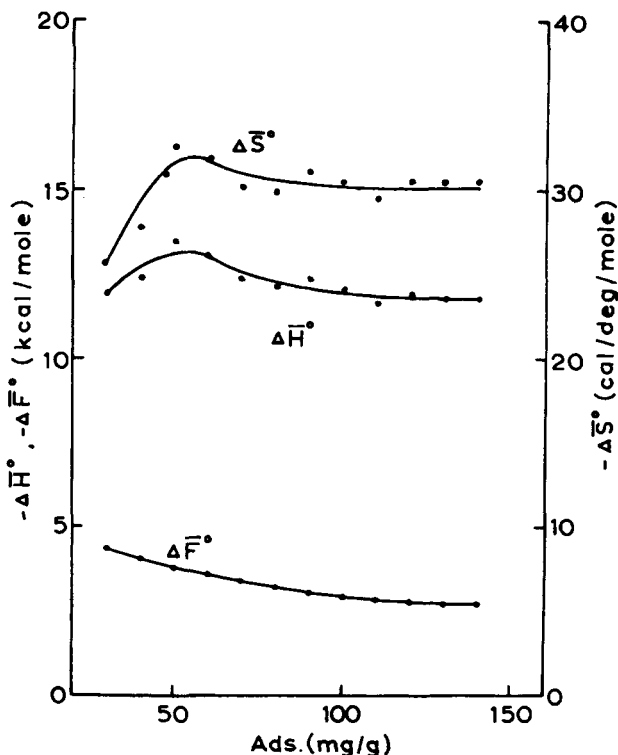


Fig. 5. Standard differential thermodynamic functions for adsorption of water vapor on agar.

formation in *B*-starch.^{17,18} However, there are three free OH groups per monomer in starch. It appears then that statistically only one of these is available for bonding with water. Possibly two OH groups per monomer participate in intramolecular or in noncrystalline intermolecular hydrogen bonding. It is interesting to note that there are two intramolecular hydrogen bonds in sucrose¹⁹ and in cyclohexamylose.²⁵

The value of V_m for gelatin, when corrected for crystallinity, is 0.51 mol water/mol monomer, approximately the same as that calculated on the basis of Bull's¹⁰ data: 0.46 mol water/mol monomer. This value agrees very closely with the percentage of amino acids (46%) which bear hydrophilic side groups. Although it might seem that the carboxyl and imido groups at the peptide bond could also participate in binding water, Pauling⁴ concluded that these groups are almost completely (94%) tied up by hydrogen bonding with other such groups, with a very low residual attraction for water.

The structure of agar is not fully characterized. However, the principal component, agarose, which is present in an amount from 50 to 90%, is composed essentially of alternating units of D-galactopyranose and 3,6-anhydro-L-galactopyranose.²⁰ Thus, in principle, this polysaccharide

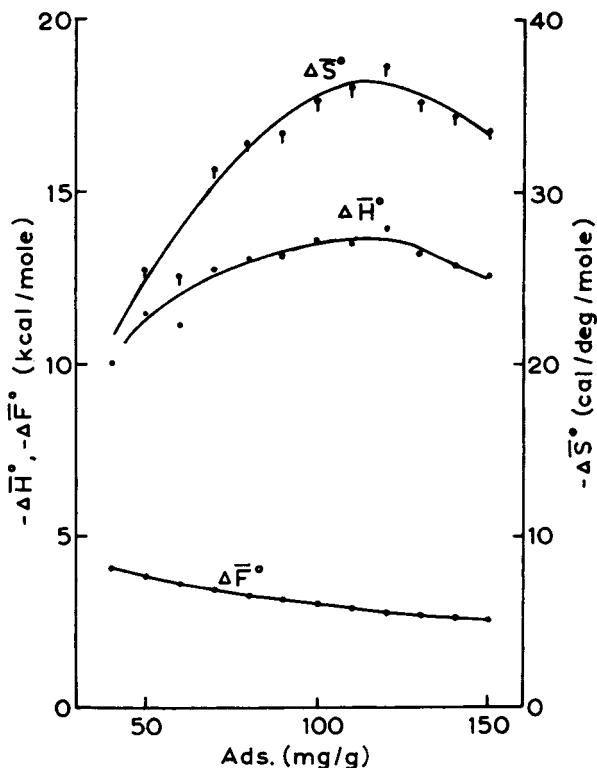


Fig. 6. Standard differential thermodynamic functions for adsorption of water vapor on carboxymethyl cellulose.

resembles starch in presenting hydroxyl groups to its environment, but fewer such groups are present ($5/6$ of the number in starch). The higher affinity for water of agar, *vis-à-vis* starch, might be ascribed to steric properties which perhaps prevent extensive intra- or interchain bonding. The 3,6-anhydro bridge may act as a steric hindrance to molecular association.

The greatest amount of coverage is attained by CMC, the monolayer of which contains 50% more water per monomer than agar and almost 100% more than starch. It would seem reasonable to ascribe this higher affinity for water to the presence of the carboxymethyl group. Such a bulky group could prevent intermolecular association between adjoining molecules. It could also prevent intramolecular bonding, such as has been reported between adjoining monomers in cellobiose.²¹ In the charged state, this group could repel similarly charged groups and simultaneously attract dipoles of water.

Another conclusion of interest from the B.E.T. constants is that the net heat of adsorption ($E_A - E_L$) is greater in agar and CMC than in starch or gelatin. This difference may be related to the greater affinity

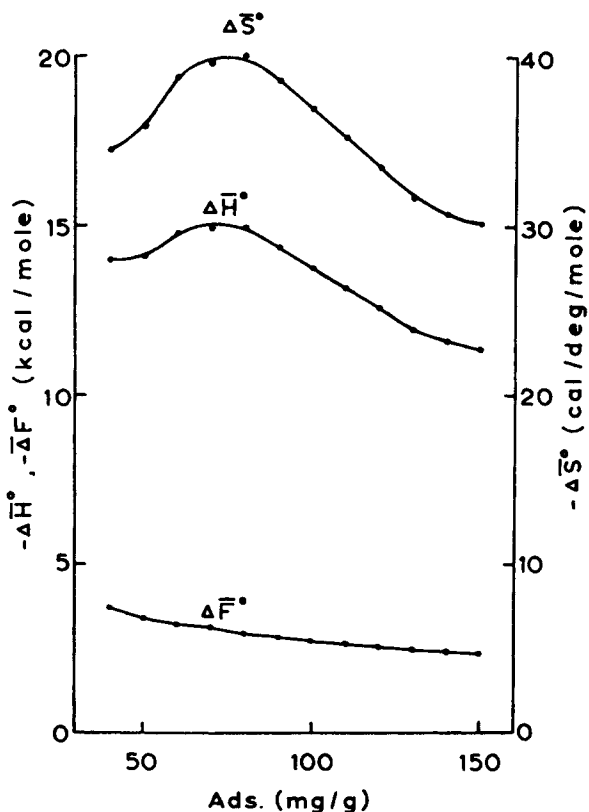


Fig. 7. Standard differential thermodynamic functions for adsorption of water vapor on gelatin.

of the first two polymers for water. The question of the state of water beyond the first adsorbed layer is not answered by the B.E.T. data. The theory of Brunauer, Emmett, and Teller²² is based on adsorption of non-polar gases, and layers beyond the monolayer are assumed to be condensed as in any liquid. They pointed out, however, that "if the adsorbed gas has a large permanent dipole it is possible that many layers may be successively polarized by the mechanism of DeBoer and Zwicker. This case has been treated by Bradley (1936)."

If the equation of Bradley²³ be used, it is found that the values of a versus $\log(\log P_0/P)$ tend to fall on a straight line, even at the highest values of P/P_0 used here. This is in accord with Bradley's prediction of the formation of a polymolecular film of permanent dipoles (as in water). A similar rectilinear relationship has been shown by Ling.²⁴ Note that the B.E.T. equation gives a nonrectilinear plot at the higher values of P/P_0 , indicating that the B.E.T. theory is not correct for layers beyond the monolayer. The thermodynamic data are in agreement with the Bradley analysis. With the values of $\Delta\bar{S}^\circ$ for condensation of water vapor to

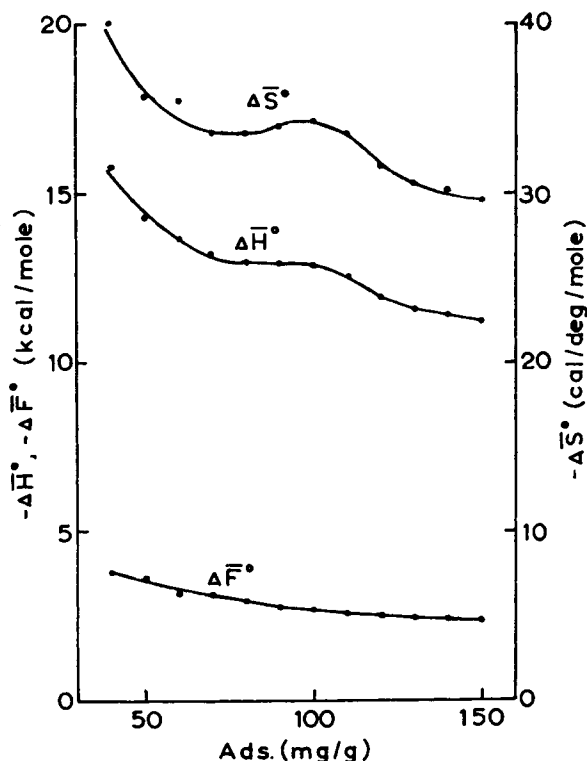


Fig. 8. Standard differential thermodynamic functions for adsorption of water vapor on maize starch.

liquid at 25°C being -28.39 cal/deg/mol, $\Delta\bar{F}^\circ$ at 25°C being -2.05 kcal/mol, and $\Delta\bar{H}^\circ$ at 25°C being -10.52 kcal/mol, it is noteworthy that these values are exceeded in all the polymers even at 150 mg water/g polymer. This suggests that energies greater than that of condensation are still involved in the formation of the 2nd layer of water.

The high $\Delta\bar{S}^\circ$ peak at 70–80 mg/g in gelatin corresponds approximately to the completion of the monolayer in that material. A similarly high peak at adsorption values just below 40 mg/g in starch can be related to the uptake of water of crystallization, which was confirmed by x-ray diffraction and hence is a contribution of configurational entropy. The deviation of individual points from the smoothed trend line are ascribable to the experimental error.

An especially interesting feature distinguishes the $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ curves of agar and CMC from those of gelatin and starch. In the latter two polymers, these curves begin at relatively high levels for low adsorption values and, after more moisture has been adsorbed, they decline to rather low levels. In the former two polymers, however, although the curves begin at relatively low levels for low values of adsorption, they then remain more or less constant (agar) or even rise to higher levels (CMC) as more moisture

is adsorbed. This difference suggests an important difference in the mechanism of adsorption: in gelatin and starch no new polymer substance is made accessible after the monolayer is covered, so that as more water is taken up, less and less attractive force for additional sorption is manifested. In agar and particularly in CMC, new surfaces seem to be exposed continually as the polymer network swells, probably due to the breaking of polymer-polymer bonds which, because of the steric hindrances described earlier, are less firm than those in gelatin and starch.

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