Water Vapor Adsorption of Hydrophilic Polymers

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1. Introduction

In most chemical systems, the fraction of the molecules on a surface and the free-energy difference between the surface and the bulk material are relatively small. But if we consider systems in which the surface effects are dominant, attention is devoted principally to systems in which the molecules of gas are concentrated on the surface of a solid. The molecules are said to be adsorbed on the solid surface, and this process is called adsorption. The distinction between adsorption and absorption (penetration of one component throughout the body of a second) is not always clear out and noncommittal word sorption is used. There are two categories of adsorption, *physisorption* – the essentially physical forces are holding gas molecules to the solid, and *chemisorption* – chemical bonds serve this function[3]. Most frequently, adsorption studies are isothermal measuring and data consists of the amount of adsorbate (substance that adsorbs) by a given weight of adsorbent (underlying material) as a function of gas pressure. Therefore, a great variety of adsorption process was presented. For many chemisorptions that lead ultimately to a monolayer (monomolecular) adsorption, one can find a good linear relationship with Langmuir isotherm.

However, physical adsorption isotherms are sigmoidal-shaped (S-shaped) curves and other theories had to be developed, to explain the more complete adsorption process that leads to multilayer formation. The most important is due to Brunauer, Emmett and Teller that leads to an isotherm expression, abbreviated as the *BET isotherm*. More about both of these theories can be found in references[2,4].

2. Modified BET equation

Recently very interesting type of adsorption had certainly became adsorption of water (water vapor) by hydrophilic polymers. It is needed to investigate what is affecting water adsorbability by polymer.

Gocho et al.[5] used vinyl acetate (VAc) and vinyl alcohol (VA) copolymer in order to investigate the relationship between the water uptake of copolymer and its functional groups, their continuity or alternately repeating of different groups or the higher order structure. To explain the sigmoidal sorption isotherms of water by this copolymer (or other hydrophilic polymers), Langmuir adsorption together with Flory-Huggins mixing theories (LFH model) [5] or BET adsorption could be used but their application in this case seems to be unrealistic because they had been developed for solid surfaces.

According to the LFH model water molecules are adsorbed by the polar groups on the polymer chains obeying Langmuir adsorption equation[3,4] and after covering all polar sites, they are sorbed as the solvent obeying Flory-Huggins mixing equation[5]. On the other hand, according to BET equation, water molecules are first adsorbed on the solid surface, which is called first layer and the second layer is formed on the first layer as further adsorption is continued. If the adsorption is continued to the finite nth layer it is called multilayer adsorption.

In the interpretation of the BET equation extended to the polymer/water system, the nth layers correspond to the water molecules successively condensed on the first layer (called water mixed with polymer in FH equation). If hydrophilic polymer adsorbs water without any crosslinking, it will

be dissolved as polymer solution and LFH equation and infinite BET equation ($n \to \infty$) are applicable. On the other hand, if the polymer is crosslinked they will be swollen, number of adsorbed layers is limited and polymer solids become gel material.

Gocho et al. modified BET adsorption equation in order to examine sorption isotherms for system VAc/VA copolymer/Water because this copolymer has two different kinds of energy levels for adsorption sites (one for hydroxyl groups and the other one for acetoxyl groups).

$$V = \frac{V_m Kx[1-(n+1)x^n + nx^{n+1}]}{(1-x)[1+(K-1)x-Kx^{n+1}]} \quad (1),$$

where V is total amount of adsorbed water (g/g polymer), V_m is total amount of the adsorbed water at the first layer (g/g polymer), n is total number of layers adsorbed K is constant of equilibrium between water vapor and adsorbed water, x corresponds to the relative vapor pressure.

$$x = \frac{p}{p_0} \quad (2)$$

If $n=1$ Eq.(1) is called the Langmuir adsorption isotherm, and in the case of $n \to \infty$ the infinite BET adsorption isotherm.

3. Sorption isotherms of PVAc/PVA Copolymers

In order to investigate water sorption, Gocho et al. prepare two kinds of PVAc/PVA copolymer samples[5]. The first were homogenously acetylated samples, PVA acetylated by anhydrated acetic acid. Obtained polymer films were called R-series. The second were heterogeneously acetated sample, block copolymer of poly VA and poly VAc/VA These block copolymer films were called B-series.

Vinyl alcohol contents of R and B-series are shown in Table 1.

Sorption isotherm measurement was performed on samples, which were completely dried, and after that in weighing bottles placed in desiccator. The humidities in desiccator were controlled and after 30 days the weight of the samples was measured at $20 \pm 0.2°C$ every two days until the weight change became within $\pm$ 0.5%.

Applying Eq.(1) to the experimental data, the nonlinear regressions were performed (Figs. 1 and 2) and for both series the increase in vinyl alcohol content also represents the increase in water gain.
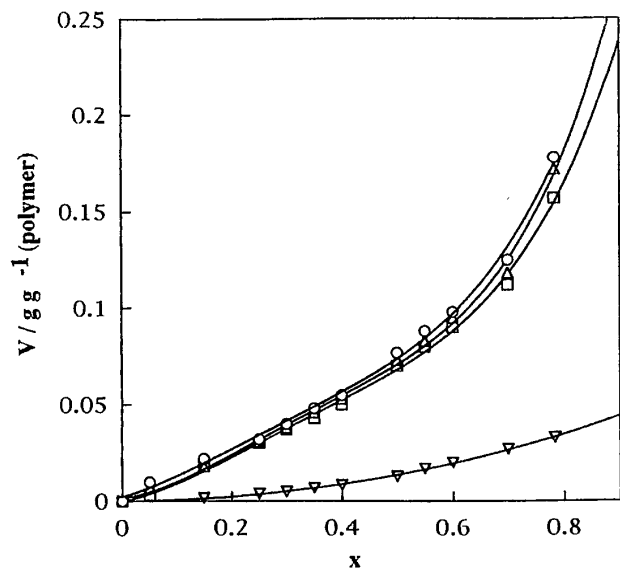

FIG. 1. The amount of water content in the homogeneously acetylated VAC/VA copolymer, V, represented by the weight of sorbed water (g) per weight of dried polymer (g) as a function of relative vapor pressure x $=p/p_0$ and application of modified BET equation, where vinyl alcohol contents in mol fraction are 0.812 (R1, ○), 0.773 (R2, △), 0.706(R3 □), and 0.206 (R4, ▽), respectively.

Samples R1 , R2 and R3 were dissolved in water, which corresponded to that V increased infinitely at $x = 1$. On the other hand, samples R4, B1, B2 and B3 were swollen in water which corresponded that

TABLE 1
Parameters of BET Equation

Sample	R1	R2	R3	R3	B1	B2	B3
$X_{VA}{}^{a}$	0.812	0.773	0.706	0.206	0.705	0.613	0.384
V_m (g/g)	0.048	0.047	0.045	0.020	0.020	0.016	0.015
K	3.4	3.1	3.0	0.49	27	8.1	2.6

^{a} X_{VA} is the mole fraction of vinyl alcohol in poly(vinyl acetate) and poly(vinyl alcohol) copolymer.

their V should have finite value at $\chi = 1$.

Eq. (1) was used to estimate the parameters of V_m and K, which are also shown in Table 1. In Fig. 3 the densities of R and B series are plotted as a function of vinyl alcohol content and the one of B-series is larger. Extrapolation has shown that, for R-series if the $\chi_{VA}=1$ density would be ca. 1.26 g/cm^3, which corresponds to a density of perfectly amorphous PVA.

In addition, BET theory[3] provides the estimation of K values of hydroxyl groups (K_A) and those of acetoxyl groups (K_B). For R-series these values were $K_A=4.1$,

$K_B=0.33$ due to the fact that R-series samples show amorphous characteristics.

On the other hand, in the B-series (heterogeneously acetylated sample), according to the Fig. 3, vinyl alcohol groups take part in crystal formation. When calculated K_A values for B1, B2 and B3 samples were ca. 38, 13 and 6.2, respectively and compared to those of R-series were very high. The number of adsorption sites in case of B1 is less than one-half that of R3, where the VA content is very similar. This showed that hydroxyl groups are taking part in crystallization.
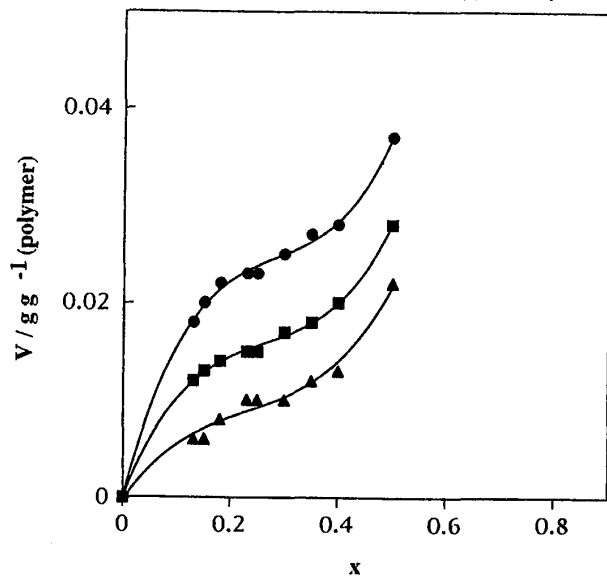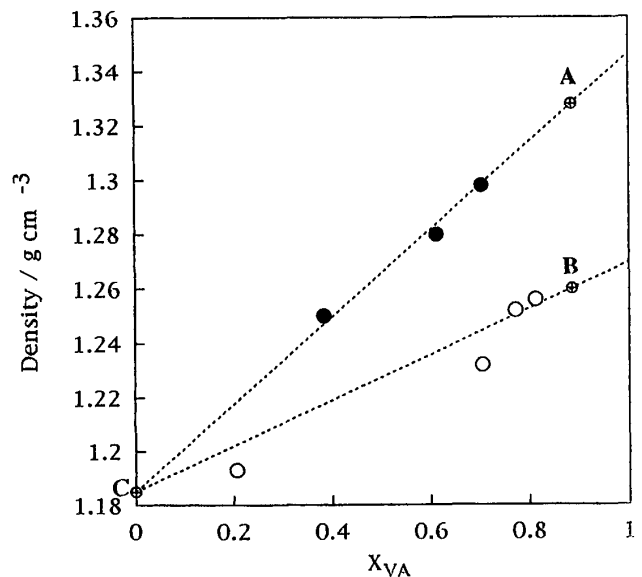

FIG. 2. The amount of water content in the heterogeneously acetylated VAc/VA copolymer, V, represented by the weight of sorbed water (g) per weight of dried polymer (g) as a function of relative vapor pressure $\chi = p/p_0$ and the application of the modified BET equation, where vinyl alcohol contents in mole fraction are 0.705 (B1, ●), 0.613 (B2, ■), and 0.384 (B3, ▲), respectively.

FIG. 3. Densities of the VAc/VA copolymers as a function of mol fraction of vinyl alcohol χ_{VA}, where point A indicates the density where the degree of crystallinity is 100%, point B 0%, and point C is the density of poly(vinyl acetate), (●) represents heterogeneously acetylated PVA and (○) homogeneously acetylated VAc/VA copolymers.

From this observation, it has been pointed out that the surface energy of polymer crystal is much higher than that of an amorphous region, as in the case of PVA the surface of crystal has a high energy level[5].

Beside that, Gocho et al. presented a proper modification of classical adsorption theories as Langmuir and BET ones, which can be applied to the problems of multilayer adsorption.

4. References

1. Franks, F., *"Water in Disperse Systems"*, Plenum Press, New York and London, 1975.

2. Conder, J., R., Young, C., L., *"Physico-chemical Measurements by Gas Chromatography"*, John Wiley and Sons, Chichester, New York, Brisbane, Toronto, 1979.

3. Gordon, M., B., *"Physical Chemistry"*, McGraw-Hill Kogakusha, Tokyo, 1973.

4. Atkins, P., *"Physical Chemistry"*, W. H. Freeman and Company, New York, 1994.

5. Gocho, H., Tanioka, A., Nakajima, T., *Sorption Isotherm Analysis of Water by Hydrophilic Polymer Composed of Different Adsorption Sites Using Modified BET Equation*, Journal of Colloid and Interface Science **200**, 155-160 (1998).