Carbohydrate Polymers 41 (2000) 87–90

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Effect of polymer chain end on sorption isotherm of water by chitosan

H. Gocho[a], H. Shimizu[b], A. Tanioka[c,*], T.-J. Chou[c], T. Nakajima[d]

[a]*Department of Food and Nutrition, Seitoku Junior College of Nutrition, 1-4-6 Nishi Shinkoiwa, Katsushika-ku, Tokyo 124-8530, Japan*
[b]*Faculty of Education, Utsunomiya University, 350 Minemachi, Utsunomiya-city, Tochigi 321-8505, Japan*
[c]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan*
[d]*Doctoral Course of Science for Living System, Showa Women's University, 1-7-57 Taishido, Setagaya-ku, Tokyo 154, Japan*

Received 8 October 1998; accepted 16 December 1998

Abstract

In this study, the sorption isotherms of water vapor by chitosans with various molecular weights were measured. The BET adsorption theory was modified for the system that has several different kinds of energy levels in the water adsorption sites, i.e. a hydroxyl group, an amino group, the polymer chain end, etc. and applied it to the experimental results in order to examine the effect of the polymer chain end on the sorption isotherm of water–chitosan using the parameters which represented the total number of adsorption sites, V_m, the interaction energy between water and the adsorption sites, K, and the number of adsorbed layers, n. V_m and K increased as the molecular weight decreased, and n remained constant. It has been proved that the increase in V_m and K were caused by the hydrophilic groups in the polymer chain end. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Sorption isotherm of water; Water vapor; Chitosan; BET equation; Logarithmic viscosity number; Polymer chain end

1. Introduction

A sorption isotherm of water by glassy polymers show a sigmoid curve; i.e. concave on the low pressure side and convex on the high pressure side of the pressure axis (Fukuda, 1997; Fukuda, Miyagawa & Kawai, 1995; Hinatsu, Mizuhara & Takenaka, 1994; Isasi, Cesteros & Katime, 1994; Nakajima & Gocho, 1978; Nakajima, Hattori & Uno, 1976; Nakajima, Katano & Isobe, 1976; Nakajima, Tamaru & Hattori, 1981). The sigmoid curve is explained by the model based on the Brunauer, Emett and Teller's multilayer adsorption theory (BET) (Barrer, 1990; Brunauer, Emmett & Teller, 1938; Timmermann, 1989; Young & Crowell, 1962). In the case of a polymer film, water molecules penetrate into the polymer matrix so that water adsorption occurs not only on the polymer chain of the film surface, but also on the inside polymer chain, that is, water is dissolved in the polymer matrix as a solvent (Flory, 1953; Takizawa, 1967). For the first layer based on the BET equation, the water molecules that are adsorbed by the polar groups around the polymer chains, and the nth layers except for the first layer correspond to the water molecules successively condensed on the first layer. If hydrophilic polymers without any cross-linking adsorb water, it will be dissolved as a polymer solution. In this case, the BET infinite equation ($n \rightarrow \infty$) is applicable. On the contrary, if polymers are cross-linked, they cannot be dissolved by water adsorption, but are swollen. In this case, the number of adsorbed layers is limited and polymer solids turn into gel materials.

In the previous papers, the BET adsorption equation of the nth layer was modified for the system that has different kinds of energy levels in the water adsorption sites (Gocho, Tanioka & Nakajima, 1998). This was applied to the systems consisting of the water-block copolymer of poly-(vinyl alcohol) and poly(vinyl acetate vinyl alcohol), the water-random copolymer of acrylonitrile and acrylamide, the water-grafted poly(acrilonitrile) by acrylamide, and the water-blend polymer of poly(acrilonitrile) and poly (acrylamide). Applying the nth layer BET equation to those experimental results, the total number of adsorption sites in the adsorbent, V_m, the interaction energy between water and adsorption sites, K, and the number of adsorbed layers, n, in the modified BET equation were calculated. It was proven that these parameters could well explain the heterogeneity of these complexed polymers.

In this study, we applied the modified BET equation to water–chitosan system and discussed the effect of the chitosan's molecular weight on the sorption isotherm of water by examining the V_m, K, n parameters as a function of the logarithmic viscosity number.

---

* Corresponding author. Tel.: + 81-3-5734-2426; fax: + 81-3-5734-2876.

E-mail address: atanioka@o.cc.titech.ac.jp (A. Tanioka)

PII: S0144-8617(99)00113-7

Table 1
Viscosity and amine contents of chitosans

	Chitosan 10	Chitosan 30	Chitosan 50	Chitosan 90
Viscosity[a]	2.49	3.76	4.64	5.25
Amine content[b]	180	186	193	205

[a] Viscosity: logarithmic viscosity number.

[b] Amine content: mg of HCl necessary for neutralizing 1 g chitosan.

2. Experimental

2.1. Samples

Chitosans used in this study, each of which has a different molecular weight (abbreviated as Chitosan 10, Chitosan 30, Chitosan 50 and Chitosan 90), were supplied by Kyowa Yushi Co., Ltd. These samples were purified in a 1.5% acetic acid aqueous solution and 5% NaOH aqueous solution. The precipitated samples were rinsed in water and subsequently in ethanol and ethyl ether before drying in air. Infrared spectra of the purified chitosans were measured by the KBr method. Stretching vibrations of the OH and NH bonds were found between 3300 and 3500 cm^{-1}, bending vibrations of the NH bond between 1590 and 1650 cm^{-1}, and stretching vibrations of CN at 1410 cm^{-1} and between 1020 and 1220 cm^{-1}, which were assigned to the vibration modes of chitosan.

2.2. Measurements of viscosity

The logarithmic viscosity number of each chitosan sample was measured using an Ostwald-type viscometer. Chitosan (80 mg) was dissolved in 100 ml of 1.5% acetic acid aqueous solution for 24 h and then the measurement was carried out in a thermostated water bath at 25°C. The determined logarithimic viscosity numbers are shown in Table 1 with the amine content which denotes the amount (mg) of HCl necessary for neutralizing 1 g of chitosan.

2.3. Measurements of sorption isotherm (Nakajima & Gocho, 1978)

Completely dried samples in weighing bottles were placed in a desiccator for 10 days where the humidities were controlled by various saturated aqueous salt solutions. The weighing bottles with samples were removed from the desiccator for quickly weighing. After weighing, the bottles were placed back in the desiccator. After 10 days, they were again weighed. After that, this procedure was repeated every 2 or 3 days until the weight change was within ± 0.05%. The measurement temperature was 20 ± 0.2°C. The water content in the polymer (water regain), V, was represented by the weight of sorbed water (g) per weight of dried polymer (g) as a function of relative vapor pressure, x.

3. Results and discussion

In Fig. 1, the sorption isotherms for water vapor of various chitosans are shown at 20°C. These curves show the sigmoid shape which is characteristic of a glassy polymer-organic or water vapor system. The amount of adsorbed

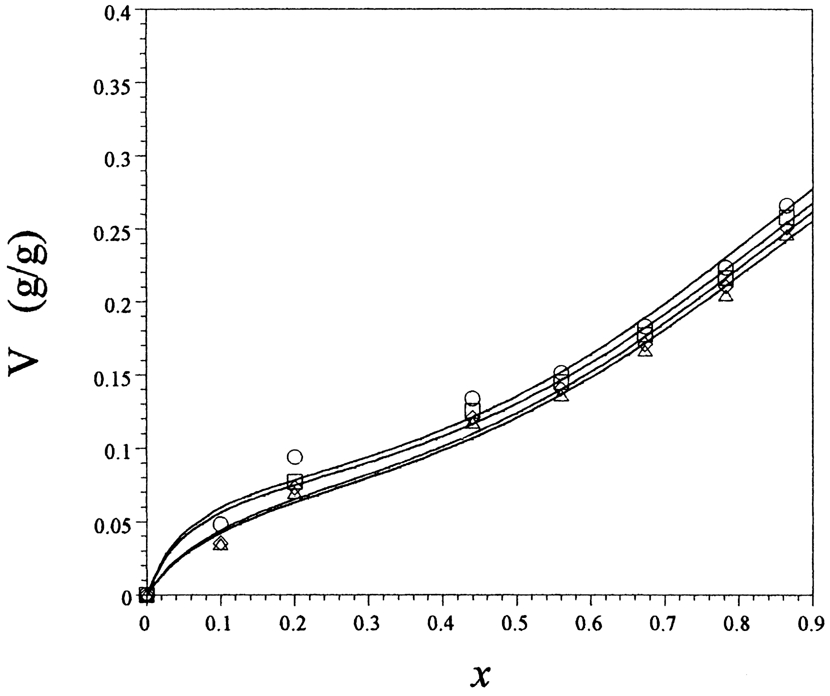

Fig. 1. The water content in the chitosans, V, represented by the weight of sorbed water (g) per weight of dried polymer (g) as a function of relative vapor pressure $x = p/p_0$ and application of the modified BET equation, where chitosan 10 is represented by (○); chitosan 30 (□); chitosan 50 (▽); and chitosan 90 (△).

Table 2
Parameters of the modified BET equation

	Chitosan 10	Chitosan 30	Chitosan 50	Chitosan 90
V_m	0.071	0.068	0.067	0.066
K	31.2	28.4	13.9	13.2
n	8	8	8	8

water varied with the viscosity change, though the difference among the sorption isotherms is very small; i.e. the smaller the viscosity, the larger the amount of adsorbed water. In the previous papers, the BET equation has been modified for the system that has several different energy levels for the adsorption sites.

Assuming that chitosan has the N_m adsorption sites which can be divided into ℓ different energy levels as (Barrer, 1990; Brunauer et al., 1938; Gocho et al., 1998; Timmermann, 1989; Young & Crowell, 1962)

$$\begin{array}{l} \varepsilon_1(N_{ml}) \\ \varepsilon_2(N_{m2}) \\ \quad\vdots \\ \varepsilon_k(N_{mk}) \\ \quad\vdots \\ \varepsilon_l(N_{m\ell}) \end{array} \tag{1}$$

where N_{mk} is the number of sites which have an ε_k energy level (k-level), and

$$N_m = \sum_{k=1}^{\ell} N_{mk}, \tag{2}$$

the total amount of adsorbed water V (g/g-polymer) with the total amount of the adsorbed water for the first layer V_m (g/g-polymer) is represented as follows:

$$V = \frac{V_m K x[1 - (n+1)x^n + nx^{n+1}]}{(1-x)[1 + (K-1)x - Kx^{n+1}]} \tag{3}$$

where x corresponds to the relative vapor pressure ($= p/p_0$), and

$$K = \sum_{k=1}^{\ell} f_{mk}(0) C_{1k} \tag{4}$$

In Eq. (4), $f_{mk}(0)$ is the fraction of the unadsorbed site in the k-level, N_{mk} (0) is the total number of unadsorbed sites, N_m (0), C_{1k} corresponds to the energy parameter C in the original BET equation.

$$f_{mk}(0) = \frac{N_{mk}(0)}{\sum_{k=1}^{\ell} N_{mk}(0)} = \frac{N_{mk}(0)}{N_m(0)} \tag{5}$$

and

$$\sum_{k=1}^{\ell} f_{mk}(0) = 1 \tag{6}$$

As three predominant adsorption sites such as the hydroxyl group (HD), amino group (AM) and polymer chain end (CE) exist at least in chitosan, Eq. (4) can be rewritten as follows:

$$K = f_{mHD} C_{1HD} + f_{mAM} C_{1AM} + f_{mCE} C_{1CE} \tag{7}$$

The polymer chain end is supposed to be composed of a hydroxyl group or aldehyde group. It has been considered that the energy parameter contributing from the polymer chain end, i.e. the third term on the right hand side of Eq. (7), can be neglected because of the small amount of f_{mCE} (Nakajima, Sugai & Ito, 1980; Nikolaev, Prokopov, Shul'gina & Vinogradov, 1987; Sakurai, Minami & Takahashi, 1984; Peniche-Covas, Arguelles-Monal & San Roman, 1995). Applying Eq. (3) to the experimental data, the non-linear regressions were performed in order to determine the parameters V_m, K and n, and the correlation coefficient was within 0.95. The theoretically predicted curves are shown as the solid lines in Fig. 1 and the calculated V_m, K and n are listed in Table 2. The total amount of the adsorbed water at the first layer, V_m, increases with a viscosity decrease. As the molecular weight of chitosan cannot be exactly determined, the logarithmic viscosity number was examined instead. Usually, the viscosity is directly related to the molecular weight (Bueche, 1970). In this experiment, the viscosities are of the order of Chitosan 10 < Chitosan 30 < Chitosan 50 < Chitosan 90, which corresponds to the molecular weight. The lower the molecular weight, the larger the amount of the polymer chain end per unit weight. An increase in V_m with a viscosity decrease corresponds to the increase in the polymer chain end. Therefore, this result shows that the third term on the right hand side of Eq. (7) cannot be ignored. The energy parameter, K, decreased with an increase in viscosity. As shown in Table 1, the amine content increases with the increase in viscosity. The hydration enthalpies are 70.3 and 23.9 kJ/mol for the amino and hydroxyl groups, respectively. Taking the hydration enthalpy into account, the K value has to increase with an increase in the amine content based on Eq. (7), because the energy parameter C of the amino group is larger than that of the hydroxyl group, and the amount of the amino group (corresponding to the amino content) increases with a molecular weight increase. However, these results are contradicting, and therefore, we cannot determine the reason for the decrease in K with molecular weight on the amine content. The polymer chain end of the chitosan molecule is composed of hydroxyl or aldehyde groups as mentioned above. As the molecular weight decreases, the number of polymer chain ends per unit weight increases. Therefore, the adsorption sites are newly produced with decrease in molecular weight. This is the reason why the molecular weight decrease induces an increase in the energy parameter K value. The n value remains constant for all the samples. As the chitosan is a crystalline polymer, the effect of crystallinity cannot be neglected. Upon absorbing water, chitosan can swell, but it will stop to some extent, which means that the cross-links by crystallites prevent further chitosan swelling.

References

Barrer, R. M. (1990). *Journal of the Chemical Society, Faraday Transactions*, *86*, 1123.

Brunauer, S., Emmett, P. H., & Teller, E. (1938). *Journal of the American Chemical Society*, *60*, 309.

Bueche, F. (1970). *Physical properties of polymers*, New York: Wiley.

Flory, P. J. (1953). *Principles of polymer chemistry*, Ithaca, NY: Cornell University Press.

Fukuda, M., Miyagawa, M., & Kawai, H. (1995). *Sen-i Gakkaishi*, *51*, 72.

Fukuda, M. (1997). *Sen-i Gakkaishi*, *53*, 313.

Gocho, H., Tanioka, A., & Nakajima, T. (1998). *Journal of Colloid and Interface Sciences*, *200*, 155.

Hinatsu, J. T., Mizuhara, M., & Takenaka, H. (1994). *Journal of the Electrochemical Society*, *141*, 1493.

Isasi, J. R., Cesteros, L. C., & Katime, I. (1994). *Macromolecules*, *27*, 2200.

Nakajima, T., & Gocho, H. (1978). *Nihon Kagakukaishi*, *10*, 1435.

Nakajima, T., Hattori, H., & Uno, A. (1976). *Sen-i Gakkaishi*, *32*, 535.

Nakajima, T., Katano, H., & Isobe, E. (1976). *Sen-i Gakkaishi*, *32*, 31.

Nakajima, T., Tamaru, H., & Hattori, H. (1981). *Sen-i Gakkaishi*, *37*, 342.

Nakajima, T., Sugai, K., & Ito, Y. (1980). *Koubunshi Ronbunnshu*, *37*, 705.

Nikolaev, A. F., Prokopov, A. A., Shul'gina, E. S., & Vinogradov, M. V. (1987). *Journal of Applied Chemistry*, USSR, *60*, 209.

Peniche-Covas, C., Arguelles-Monal, W., & San Roman, J. (1995). *Polymer International*, *38*, 45.

Sakurai, K., Minami, A., & Takahashi, T. (1984). *Sen-i Gakkaishi*, *40*, 425.

Takizawa, A. (1967). *Journal of Physical Chemistry*, *71*, 1161.

Timmermann, E. O. (1989). *Journal of the Chemical Society, Faraday Transactions*, *85*, 1631.

Young, D. M., & Crowell, A. D. (1962). *The physical adsorption of gases*, London: Butterworth.