Sorption of Methyl Orange by Chitosan Gels Having Hydrophobic Groups

TOSHIHIRO SEO, TAKAKI KANBARA, and TOSHIRO IIJIMA,

Department of Polymer Science, Tokyo, Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Synopsis

The equilibrium sorption of methyl orange by chitosan and its acyl (octanoyl, dodecanoyl, and octadecanoyl) derivatives was investigated. In general, a greater of substitution and a longer chain length increase the sorption of the dye; however, there are optimum degrees of substitution and chain length to enhance the sorptivity. The sorption isotherms were interpreted by means of a dual mechanism which comprises partition and Langmuir sorption modes.

INTRODUCTION

Chitosan (1), obtained by the deacetylation of chitin, is an aminopolysaccharide which constitutes a useful natural polymer resource. Chitosan has been used as a coagulant,[1] for example, for waste treatment. Recently, some interesting works have been presented[2-6] in which the utility of chitosan as a source of value-added polymers with selective sorption functions has been explored.

In our previous work, *N*-acylchitosan gel (2) was prepared, and we investigated the selective sorption of D- and L-tryptophan from aqueous solution.[7] The introduction of a hydrophobic group was found to increase the sorptivity and to enhance the preferential sorption of the L-isomer:

1

2

To elucidate the mechanism of the sorption of small molecules by chitosan gels having hydrophobic groups, the equilibrium sorption isotherm of an anionic dye, methyl orange, was investigated in the present work. This dye has been widely used to explore the hydrophobic domains formed by cationic polymers.[8,9]

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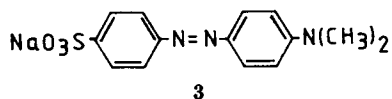
EXPERIMENTAL

Materials

The chitosan used was kindly supplied by Kyowa Yushi Co. The chitosan flake was dissolved in 10% acetic acid and methanol and then acylated by carboxylic anhydrides. The acylated chitosan gel was soaked in water and neutralized by 0.1N KOH ethanol solution. The product was washed with water and dried. The gel particles obtained were of diameter 50–300 μm.

The carboxylic anhydrides used were octanoic, decanoic, and octadecanoic derivatives. Methyl orange (MO) was purchased from Merck Co. as indicator reagent and recrystallized from water.

Equilibrium Sorption Measurement

The sorption equilibrium of MO was determined by soaking the gel particles in aqueous MO solution of 1×10^{-6}–6×10^{-4} mol dm^{-3} at 30°C in Pyrex stoppered tubes. The equilibrium time of 4 days was decided by a preliminary experiment. The amount of MO sorbed was determined spectrophotometrically by measuring the intitial and final concentration of the dye bath solution.

Preparation and Characteristics of *N*-Acylchitosan Gels

The preparation conditions and the characteristics of *N*-acylchitosan are given in Table I. Octanoyl chitosan was obtained by reaction at room temperature for 20 h. Dodecanoyl chitosan was prepared by reaction at 50°C for 2 h, followed by standing until the degree of substitution (DS) reached a value of up to 1.0. Octadecanoyl chitosan was obtained at higher temperature, but the degree of substitution did not exceed 0.4. In Table I, chitosan is

TABLE I
Preparation and Characterization of *N*-Acylchitosan Gels

Sample no.	[(RCO)$_2$O]/[GlcN]	Temp (°C)/time (h)	DS[a]	Solubility in[b]		$W_p(\%)$[c]
				10% AcOH	LiCl/NMP/DMA (1/10/10)	
CS				s	i	63.8
C$_8$-0.3	0.3	25/20	0.29	s	i	60.8
C$_8$-0.6	0.7		0.58	i	sw	51.2
C$_8$-1.0	2.0		0.98	i	s	16.7
C$_{12}$-0.3	0.8	50/2 + 25/18	0.32	s	i	52.4
C$_{12}$-0.5	0.8		0.45	sw	sw	47.4
C$_{12}$-0.8	4.0		0.81	i	s	11.8
C$_{18}$-0.3	2.0	70/3 + 50/17	0.30	sw	sw	49.4
C$_{18}$-0.4	2.0	78/3 + 50/17	0.42	sw	sw	47.7

[a] Degree of substitution of acyl group.
[b] i = insoluble, s = soluble, sw = swelling.
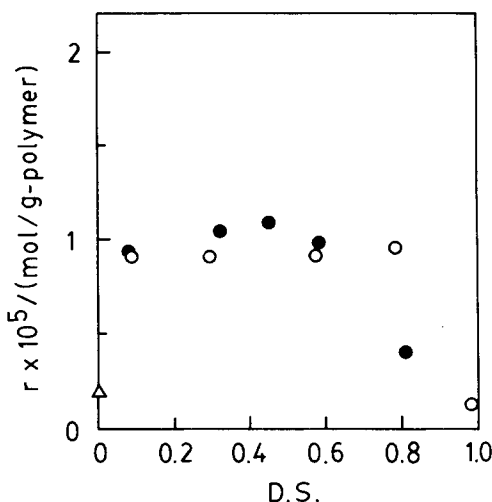[c] Water content.

Fig. 1. Equilibrium sorption of methyl orange by N-acylchitosan gels. Initial concentration of MO = 1×10^{-5} mol dm^{-3}: ($\triangle$) chitosan; ($\bigcirc$) octanoylchitosan; ($\bullet$) dodecanoylchitosan

represented as CS. For the chemically modified chitosan, for example, C$_8$-0.3 means the octanoyl chitosan having the degree of substitution of 0.3.

The products having a hydrophobic group of DS greater than 0.3 were found to be sparingly soluble in acetic acid, but to have increased solubility in the mixed solvent LiCl/N-methylpyrrolidone/N,N-dimethylacetamide. The water regain was found to decrease with an increase of the hydrophobic chain length, and of the degree of substitution. The dodecanoyl chitosan (DS = 1.0) gave a water regain of approximately 12%, as compared with the nonsubstituted chitosan which had a water regain of 64%.

RESULTS AND DISCUSSION

The Sorptivity of Methyl Orange by N-Acylchitosan Gels

Figure 1 shows the equilibrium sorption, r (the number of moles of dye bound per g of polymer), of MO in aqueous solution at pH 6 by N-acylchitosans having two different chain lengths with various DS. The introduction of a longer acyl group of DS = 0.3–0.6 increases the uptake of dye approximately five times as compared with that of the original chitosan, and the dye uptake then decreases clearly above a DS of 0.6. The octanoylchitosan gels of DS = 0.3 and 0.6 exhibited a sharp increase of the isotherm in the low concentration region as compared with the chitosan shown in Figure 2, where C_f is the equilibrium dye bath concentration.

In Figure 3, the sorption isotherms for gels of DS = 0.3 with various lengths of acyl chain are given. The amounts of dye sorbed were approximately five times larger than for the original chitosan, irrespective of the chain length.

The effects of electrostatic interaction with the amino group on the sorption of MO were investigated in aqueous solution (pH 6.0–6.4) and phosphate buffer solution (4.8–5.9 and 8.0) of ionic strength $\mu = 0.01$, and the results are given in Figures 4–7. For the gels of DS = 0.3 and 0.6, the sorption increases,
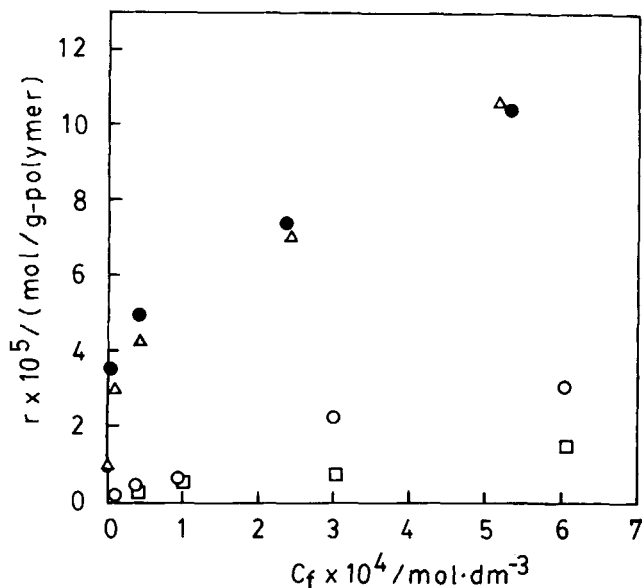
Fig. 2. Effect of DS on the sorption of methyl orange by octanoylchitosan gels. DS: (○) 0.0; (●) 0.3; (△) 0.6; (□) 1.0.

six and five times, respectively, in an acidic condition (pH 4.6) as compared with neutral dyeing, while it decreases slightly in the alkaline buffer solution. From these results it is estimated that the pKa of the ionogenic group $-NH_2$ is approximately 6,[2] and at lower pH the electrostatic interaction with the dye anion becomes significant as the DS decreases. In the case of the gels of DS = 1.0, the amounts of sorption were found to be slightly influenced by pH.
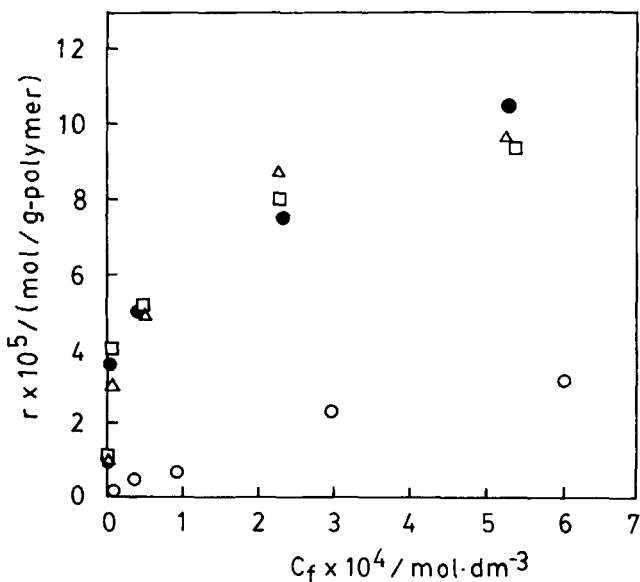

Fig. 3. Effect of chain length on the sorption of methyl orange by N-acylchitosan gels: (○) chitosan; (●) octanoylchitosan; (△) dodecanoylchitosan; (□) octadecanoylchitosan.
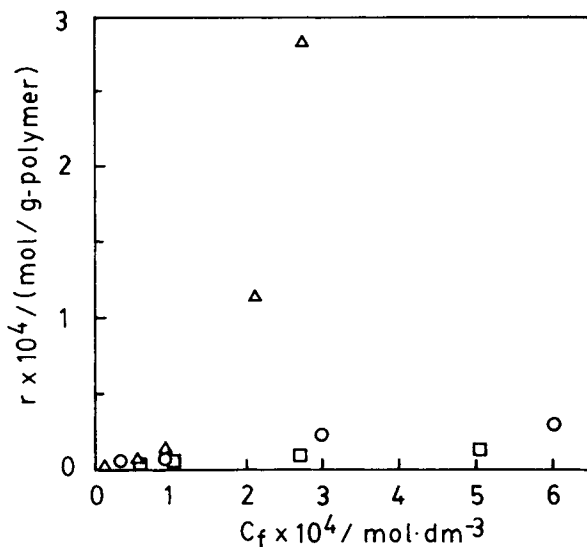
Fig. 4. Effect of pH on the sorption of methyl orange by chitosan gel. pH: (△) 5.9 (phosphate buffer solution); (○) 6.4 (aqueous solution); (□) 8.0 (phosphate buffer solution).

At pH 4.8 the sorption was enhanced about two times as compared with that at pH 6.3. This indicates that the amide groups in the gels are protonated at pH 4.8. On the other hand, in the sorption by chitosan in the lower pH region, the phosphate ion is believed to compete with the dye anion for the charged amino group.

The sorption isotherms of chitosan and octanoyl chitosan (DS = 0.3) gels in acidic conditions at different ionic strengths are given in Figure 8. An increase of the ionic strength decreases the sorption of MO to approximately 20%, for
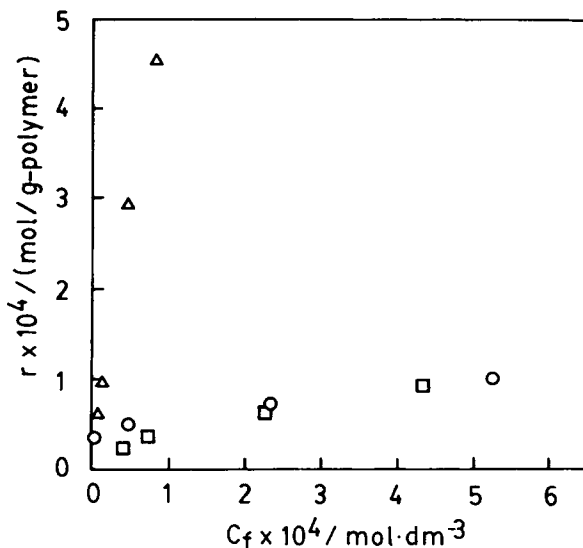

Fig. 5. Effect of pH on the sorption of methyl orange by octanoylchitosan gel (DS = 0.3). pH: (△) 5.8 (phosphate buffer solution); (○) 6.3 (aqueous solution); (□) 8.0 (phosphate buffer solution).
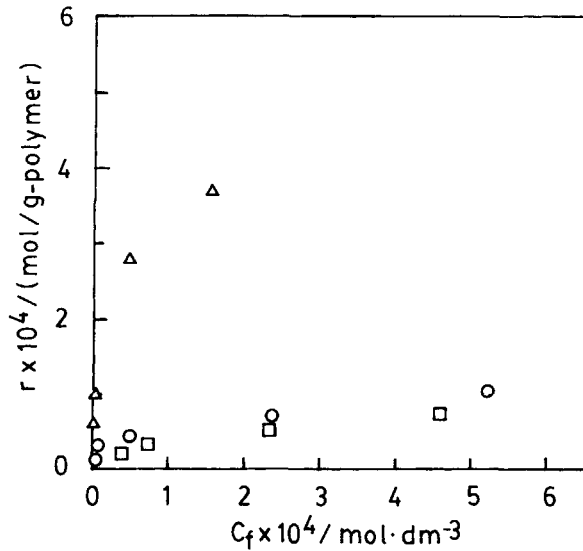
Fig. 6.   Effect of pH on the sorption of methyl orange by octanoylchitosan gel (DS = 0.6). pH:
(△) 5.5 (phosphate buffer solution); (○) 6.3 (aqueous solution); (□) 8.0 (phosphate buffer solution).

chitosan, whereas 60–70% of the sorption was retained for the hydrophobic
gels. This is explained in the following manner. In the case of the sorption by
chitosan in which the electrostastic interaction is dominant, the salt added
exhibits a screening effect on the charged group, but in the case of the
sorption by the hydrophobic gels the salting out effect leads to an increase of
the sorption.

Interpretation of the Data by Means of a Dual Sorption Model

In the analysis of the sorption isotherms, eq. (1) derived by a dual sorption
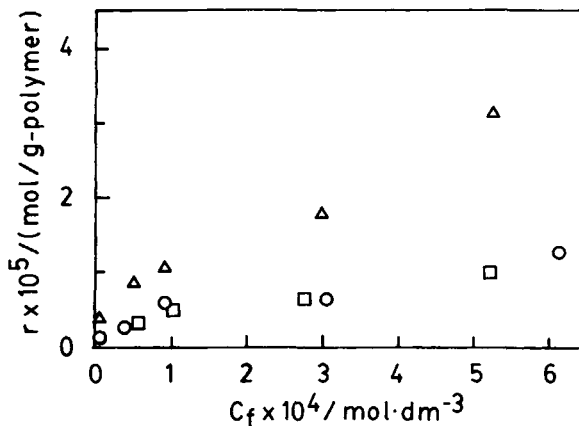model was used. The model consists of two modes of the sorption, i.e.,

Fig. 7.   Effect of pH on the sorption of methyl orange by octanoylchitosan gel (DS = 1.0). pH:
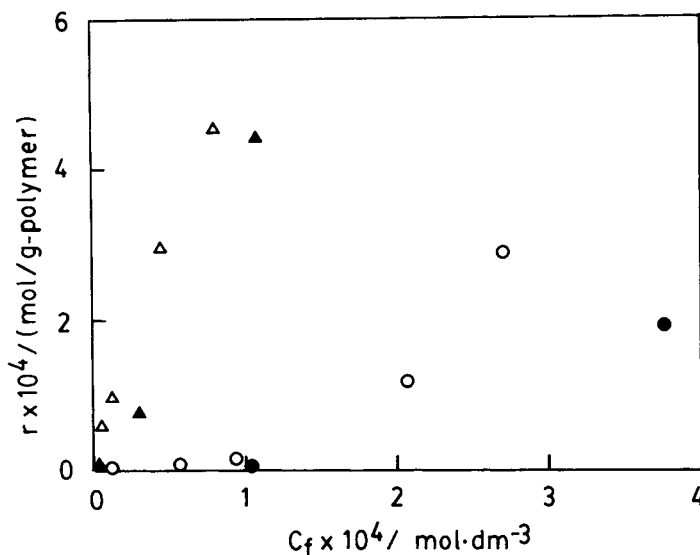(△) 4.8 (phosphate buffer solution); (○) 6.0 (aqueous solution); (□) 8.0 (phosphate buffer solution).

Fig. 8. Effect of ionic strength on the sorption of methyl orange. μ: ($\circ$) 0.01, ($\bullet$) 0.1 for chitosan gel; ($\triangle$) 0.01, ($\blacktriangle$) 0.1 for octanoylchitosan gel (DS = 0.3).

electrostatic (Langmuir) and nonelectrostatic (partition) modes[10-12]:

$$r = r_1 + r_2 = K_1 C_f + \frac{SK_2C_f}{1 + K_2C_f} \qquad (1)$$

where r is the total amount sorbed (mol g^{-1} polymer), C_f is the external dye concentration (mol dm^{-3}), K_1 is the partition coefficient (dm^3 g^{-1} polymer), K_2 is the equilibrium constant of the Langmuir sorption (dm^3 mol^{-1}), and S is the saturation value of the Langmuir sorption (mol g^{-1} polymer), respectively. With use of the nonlinear least-squares method for analysis of the sorption data, K_1, K_2, and S were determined. In the case of the octanoyl chitosan gel of DS = 1.0, K_1 was determined, assuming that the Langmuir mode does not participate.

An example of the analysis of the sorption isotherm is given in Figure 9 for the octanoyl chitosan gel–MO systems. The agreement between the experimental and calculated results is quite good. The dual sorption parameters thus obtained are compiled in Table II.

Inspecting the table, it is found that the value of S is far less than that of the amino content for all the gels used. This is attributed to a quite limited availability of the amino groups for the electrostatic interaction. The octanoyl chitosan gels of DS = 0.3 and 0.6 have far longer values of K_1, K_2, and S as compared with chitosan. This behavior suggests that the sorption based upon a partition mode is caused mainly by a hydrophobic interaction due to the acyl groups introduced. The role of a hydrogen bond with the amino group in the sorption is thought to be minor. The long acyl chain may also influence the sorption by the Langmuir mode.

However, in the upper limit of substitution, DS = 1.0, K_1 is extremely small. This is ascribed to the compact structure of the highly substituted gel
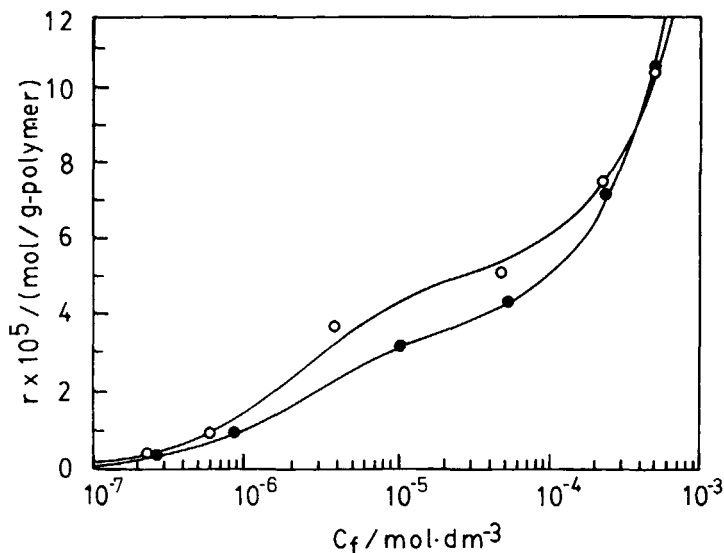
Fig. 9. Equilibrium sorption of methyl orange by octanoylchitosan gels. DS: (○) 0.3: (●) 0.6; (—) calculated by eq. (1).

caused by the interaction between acyl groups. The compact structure makes the region available for the interaction much smaller. The low values of K_2 and S in chitosan are attributed to the high crystallinity of this material, i.e., 40%,[13] which should decrease the effective concentration of amino groups for the electrostatic interaction.

Concerning the effect of the chain length, it was found that the dodecanoyl derivative has larger values of K_1 and K_2 than the octanoyl derivative, although the acyl group content is lower. On the other hand, taking into account the acyl group content, K_1 and K_2 for octadecanoyl and dodecanoyl chitosans are considered to be very similar. From the above considerations, it is concluded that the increase of the chain length from C_8 to C_{12} brings about

TABLE II
Sorption Parameters

Sample no.	DS	Amino content $(\times 10^3/\text{mol g}^{-1})$	Acyl content $(\times 10^3/\text{mol g}^{-1})$	pH	K_1 $(\times 10^2/ \text{L g}^{-1})$	K_2 $(\times 10^{-5}/ \text{L mol}^{-1})$	S $(\times 10^5/ \text{mol g}^{-1})$
CS		4.8	0.0	6.4	4.0	0.6	0.5
				8.0	1.7	0.1	0.5
C_8-0.3	0.29	2.9	1.5	6.3	9.8	3.8	5.2
				8.0	9.1	0.1	6.3
C_8-0.6	0.58	1.3	2.4	6.3	13.2	3.9	3.7
				8.0	11.9	0.8	2.0
C_8-1.0	0.98	0.0	4.8	6.0	2.2		
				8.0	1.5		
C_{12}-0.3	0.32	2.3	1.4	6.4	13.3	7.9	3.8
C_{18}-0.3	0.30	2.2	1.2	6.4	11.3	5.7	4.1

the improvement of the sorptivity, but a further increase of the carbon number does not affect the results.

With change of pH from 6.3 to 8.0, K_1 and S scarcely change, in marked contrast to the significant decrease of K_2 for all the gels used. The change of the sorption behavior with pH should be explained by the structure of the gels, and by the ionic strength of the medium, in addition to the decrease of the electrostatic interaction with the amino group.

CONCLUSION

The introduction of a long acyl group into chitosan gel at a degree of substitution of 0.3–0.6 gives both an increase of the sorptivity due to hydrophobic interaction, and an increase of the effective sites for electrostatic interaction. An increase of the chain length up to the carbon number of 12 was found to be effective in increasing the sorptivity. The hydrophobic groups in the gels decreased the effects of pH and ionic strength on the sorption.

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