

Functional Monomers and Polymers. LXX. On the Adsorption of Iodine onto Chitosan

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Synopsis

The ability of adsorbing iodine in different organic solutions by chitosan was studied by sorption isotherm measurements. The ability was found to be larger in polar solvents than in nonpolar solvents. The form of the chitosan samples, such as film, powder, and flake, had no influence on the adsorption behavior. On the other hand, chitin had only small adsorbing ability of iodine. It is concluded that the adsorption of iodine is caused by charge-transfer complexes between amino groups of chitosan and iodine molecules, but their structure differs from that of inclusion compounds as seen in amylose-iodine complexes. The adsorption was also studied on chitosan films with different degrees of acetylation.

INTRODUCTION

Chitosan is the acid-soluble, deacetylated derivative of chitin, a naturally occurring polysaccharide found in fungi and arthropods, and is readily prepared by the reaction of chitin with aqueous sodium hydroxide solution. Recently, both chitin and chitosan have found applicability to inorganic chromatography, and much attention has been paid to the binding of metal ions. However, only little attention has been devoted to their adsorption of halogens.

Several studies concerning the reaction of chitosan with iodine have been reported. By treating iodine-potassium iodide, chitosan hydrochloride becomes soluble in the concentrated calcium chloride solution to yield a dark-brown precipitate.¹ Certain color reactions between chitosan and iodine are known as the chitosan test for the detection of partially deacetylated chitin and chitosan.² Recently, the preparation technique for the chitosan-iodine adduct was described.³

There appear to be two types of iodine adsorption on the polymers: one is an inclusion compound in which iodine molecules are included in host molecules such as amylose⁴ or poly(vinyl alcohol),⁵ and the other is the charge-transfer complexes between iodine and a polymer such as nylon 6.⁶ It should be noted that both chitin and chitosan are linear in structure, which differs from polymers such as amylose, which has a helical structure; nevertheless, chitosan displayed excellent adsorption of iodine. We therefore studied the adsorption characteristics of iodine onto chitosan in detail. The present paper deals particularly with the sorption isotherm measurements of iodine and the properties of the polysaccharide-iodine complexes.

EXPERIMENTAL

Chitin (6.80% N) and chitosan (8.15% N, viscosity 440 cP in 0.5% solution of 0.25*N* acetic acid at 20°C) were supplied by Nippon Tennen Gas Kogyo Co. Ltd. The chitosan film was prepared by pouring an aqueous acetic acid solution of chitosan on a glass plate (15 μm thick) maintained at about 60°C, followed by immersing it in 10% aqueous sodium hydroxide solution.⁷

The concentration of iodine solutions was determined by titrating with aqueous sodium thiosulfate. Only in the case of acetone solution, a precisely weighed amount of iodine was dissolved in the solvent. The adsorption of iodine was performed by immersing precisely weighed chitin or chitosan (about 0.1 g) in 200 ml iodine solution in different concentrations for five days at 30°C. Then, the iodine-adsorbed films were wiped with a filter paper and dried thoroughly under reduced pressure. In the case of flake or powdery samples, the adducts were thoroughly washed with water and dried under reduced pressure. The amount of adsorbed iodine was estimated from the increase in the weight of chitosan or chitin after treatment.

Ultraviolet and visible spectra of various iodine solutions as well as iodine adsorbed chitosan films were measured by using a Union SM-401 spectrometer with a 10-mm quartz cell in the region from 200 to 600 nm at 25°C.

The reacylation reaction of chitosan film was carried out by treating with acetic acid and dicyclohexylcarbodiimide in aqueous DMF solution at room temperature. The amino group content in the acetylated chitosans thus obtained was determined by elemental analysis. The adsorption of iodine was performed similarly by immersing precisely weighed polysaccharides (about 0.1 g) in 200 ml of an aqueous iodine-potassium iodide solution (0.0149 mole/l.) for five days at 30°C.

RESULTS AND DISCUSSION

Adsorption of Iodine Onto Chitin and Chitosan

To reach equilibrium of the adsorption of iodine onto chitosan film required about three days, and in the case of chitosan flake it took about two days. The chitosan film indicated larger and more rapid adsorption of iodine than the chitosan flake (Fig. 1).

Figure 2 shows the relationship of the amount of iodine adsorbed on the chitosan film with the iodine concentration in an aqueous potassium iodide solution. The sorption isotherm relationship gave a straight line which showed a gentle slope within the iodine concentration measured. This fact suggests that the iodine adsorption takes place even in an extremely low concentration of iodine, and the ability for adsorbing iodine is substantially high within the iodine concentrations in question. In very low iodine concentration (0.0029 mole/l.), even about 40% of iodine could be adsorbed on the chitosan film. The colorless, transparent chitosan film turns black as the adsorption of iodine proceeds. When the iodine-adsorbed films were washed with water, the excess amount of iodine tended to be removed: The decrease in the amount of iodine was higher when the films had been adsorbed with iodine in higher concentration, as seen in Figure 2. It can be assumed therefore that not all the iodine molecules were strongly bound to the chitosan molecules.

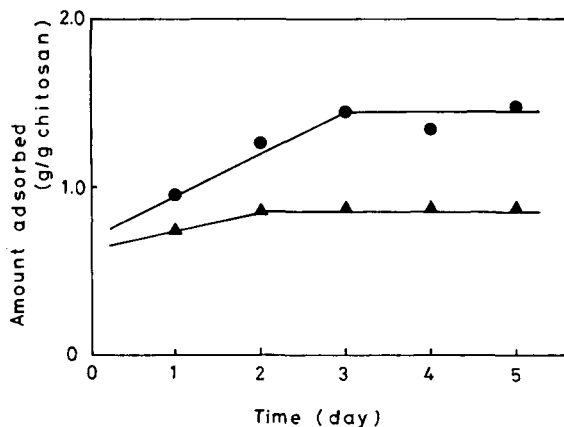


Fig. 1. Plots of reaction time vs. adsorption amount of iodine. Adsorbed in aqueous I_2 -KI solution (0.146 mole/l.) at $30^\circ C$: (●) chitosan film; (▲) chitosan flake.

Figure 3 shows sorption isotherm curves for both chitin and chitosan in flake or powder form in aqueous potassium iodide solution. Chitosan in flake or powder seems also to have high adsorption ability and shows similar sorption isotherm curves to the chitosan film. On the other hand, chitin in flake or powder did not exhibit such high adsorption ability as chitosan and caused no color change.

The effect of solvents used for adsorption experiments is shown in Figure 4. All the experiments carried out in organic solvents were done by immersing chitosan film in the iodine solutions. When ethanol and acetone were used as solvents, adsorption was found to be as high as that carried out in aqueous po-

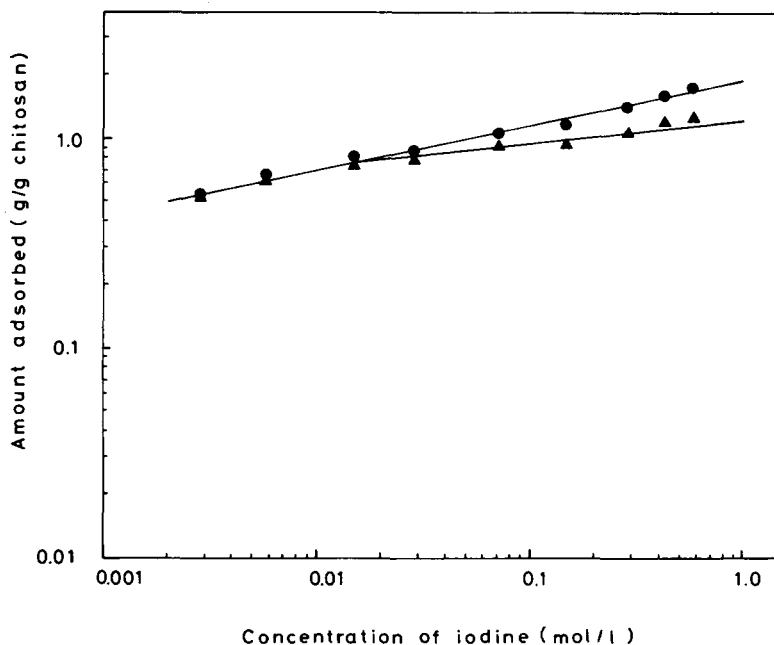


Fig. 2. Adsorption of iodine by chitosan film. Adsorbed in aqueous I_2 -KI solution at $30^\circ C$ for five days: (●) unwashed; (▲) washed with water for 30 min.

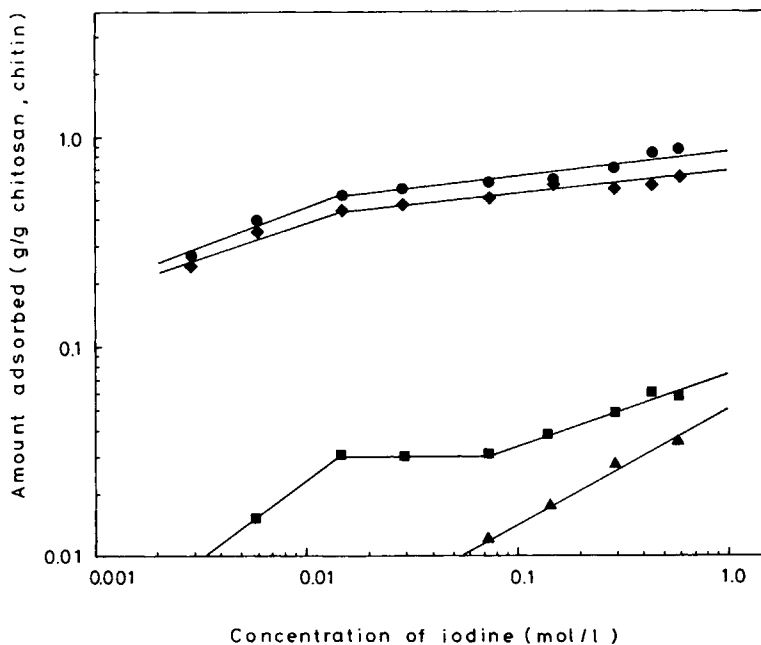


Fig. 3. Adsorption of iodine by chitin and chitosan. Adsorbed in I_2 -KI solution at $30^\circ C$ for five days: (●) chitosan flake; (◆) chitosan powder; (■) chitin flake; (▲) chitin powder.

tassium iodide solution. The iodine-adsorbed chitosan films tended to swell when the adsorption was carried out at a higher iodine concentration in these organic solvents. In benzene or chloroform solution, ability of adsorbing iodine

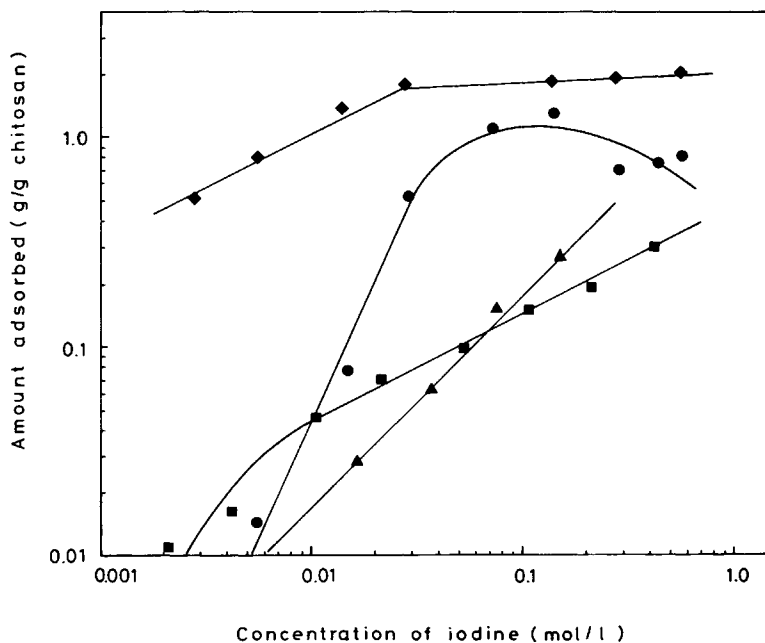


Fig. 4. Adsorption of iodine by the chitosan film in various iodine solutions. Adsorbed at $30^\circ C$ for five days: (◆) I_2 -ethanol; (●) I_2 -acetone; (▲) I_2 -chloroform; (■) I_2 -benzene.

was substantially low, and the sorption isotherm curves tended to be linear (Fig. 4). Such difference in the adsorption ability for different solvents has been also found in the case of nylon 6 film.⁶ From these observations it can be assumed that the adsorption ability depends on the difference in the swelling behavior of the chitosan films and on the dissolved state of the iodine molecules in the solvents.

Absorption Maximum in Visible and UV Spectra

It is known for polymer-iodine inclusion compounds in general that the structure of the polyiodine chain in amylose⁴ and poly(vinyl alcohol)⁵ canals causes a shift in the absorption maximum of about 600 nm to a longer wavelength with increase in the length of the polyiodine chains.⁸⁻¹⁰

Table I shows the absorption maxima of different iodine solutions and the iodine-adsorbed chitosan films in both the visible and UV regions. The iodine-adsorbed chitosan films showed no absorption maxima at about 600 nm. From this fact it appears that no adducts of the inclusion type could be formed between chitosan and iodine under the conditions used. The absorption maxima are found to be independent of the kind of solvent in which chitosan-iodine adducts were formed. The iodine-adsorbed chitosan films showed absorption maxima at about 296 and 365 nm, which differs markedly from those of iodine vapor (about 500 nm).¹¹ From these results it can be assumed that iodine molecules form a certain complex with chitosan, without forming polyiodine structure as seen in generally occurring iodine inclusion compounds.

It is known that the iodine molecules form the $n-\sigma$ and $\pi-\sigma$ type of charge-transfer complexes.¹² A complex found in the iodine-adsorbed nylon films has been explained to be formed by the complexation of iodine with amide groups in nylon.⁶ It can be assumed, therefore, that the iodine molecules form an $n-\sigma$

TABLE I
Maximum Wavelength of Various Iodine Solutions and Iodine-Adsorbed Chitosan Films in Visible and UV Regions

Samples		λ_{\max} , nm ^a	
Aqueous KI solution	(227)		
Iodine solutions			
H ₂ O ^b	(227)	288	352
Acetone			365
Ethanol	(235)		448
Benzene		298	504
Chloroform	(244)		514
Chitosan film after treating in aq. KI solution	(235)		
Iodine-adsorbed chitosan films in			
H ₂ O ^b	(222)	296	366
Acetone	(232)	295	365
Ethanol	(215)	295	366
Benzene	(225)	296	365
Chloroform	(226)	297	365

^a The values in parentheses are not exact because of too strong an absorption of the samples.

^b Aqueous I₂-KI solution was used.

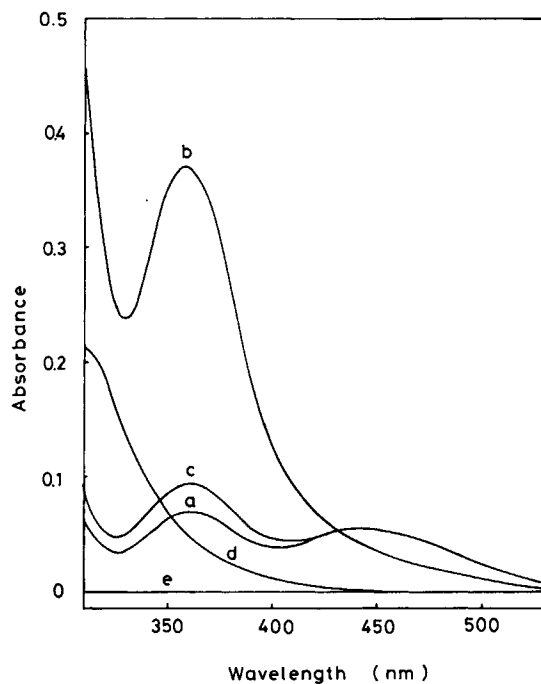


Fig. 5. Visible absorption measured at 25°C in methanol: (a) iodine (6.17×10^{-5} mole/l.); (b) iodine (6.17×10^{-5} mole/l.) and D-glucosamine (2.01×10^{-4} mole/l.); (c) iodine (6.17×10^{-5}) and N-acetyl-D-glucosamine (1.93×10^{-4} mole/l.); (d) D-glucosamine (2.01×10^{-4} mole/l.); (e) N-acetyl-D-glucosamine (1.93×10^{-4} mole/l.).

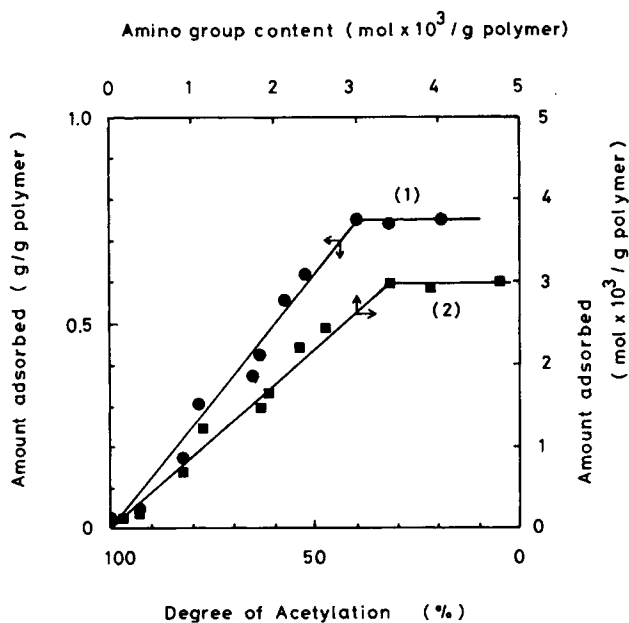


Fig. 6. Adsorption of iodine by a series of polysaccharides. Adsorbed in a 0.015M aqueous I_2 -KI solution at 30°C for five days.

type of charge-transfer complex with the amino groups in chitosan. The absorption bands of the complexes are found to be independent of the solvent in which the chitosan-iodine adducts are formed, and the absorption maxima at about 296 and 365 nm are comparable to those of nylon film, which has an absorption maxima at about 297 and 366 nm.⁶

Figure 5 shows the spectrophotometric results of D-glucosamine and N-acetyl-D-glucosamine, which can be regarded as the monomeric models of chitosan and chitin, respectively. By adding D-glucosamine and N-acetyl-D-glucosamine to a methanol solution of iodine, the absorbance of the visible spectra at 360 nm due to iodine tended to increase, which was larger in the former case. On the other hand, the absorbance at 450 nm tended to decrease only in the case of D-glucosamine. These results indicate that the iodine molecules form complexes with D-glucosamine and N-acetyl-D-glucosamine in methanol solution. It can be expected that a similar complex forms in chitin and chitosan. In spite of the increase in the absorbance at 360 nm in the model compounds, very low adsorption of iodine was found in the case of chitin. This should be ascribed to the fact that chitin exists in a stable form by forming hydrogen bonds intermolecularly through amide groups¹³ so that its ability to form complexes with iodine could be expected to be lower.

Adsorption of Iodine on Chitosan with Different Degree of Acetylation

The chitosan films were then acetylated again by acetic acid in the presence of dicyclohexylcarbodiimide in aqueous DMF solution, and polysaccharide films having different degrees of acetylation were obtained (Table II). Curve 1 in Figure 6 shows the relationship of the iodine amount adsorbed to the amino content of the polysaccharides, which suggests the formation of charge-transfer complexes between amino groups of the polysaccharide and iodine. Curve 2 in this figure shows plots of the iodine amount adsorbed in moles versus moles of amino groups present. A complex of about one amino group of the polysaccharide to one iodine molecule can be formed for the polysaccharides, the acet-

TABLE II
Acetylation Reaction on the Chitosan Films^a

Sample no.	Molar ratios used ^b		Time, min	Amino group content of products, % ^c
	Acetic acid/ chitosan	DCC/ chitosan		
1	4	4	30	68.5
2	3	3	50	61.0
3	5	5	30	48.2
4	5	5	45	42.9
5	5	5	60	36.7
6	10	10	30	34.8
7	5	5	45	22.3
8	10	10	60	17.7
9	10	10	360	7.4
10	10	10	4320	3.7

^a Acetylation was carried out in aqueous DMF (DMF/H₂O = 4/1) at room temperature; 100 ml of the solvent was used throughout the experiments.

^b Chitosan was measured in ground moles; $(1.79-2.81) \times 10^{-3}$ mole chitosan was used.

^c Determined by elementary analysis.

ylation degree of which is over 40. The result was also supported by UV and visible spectral measurements. It was found that the polysaccharides did adsorb no more iodine when their degree of acetylation was above 96.3%. It can be concluded that both acetamide and hydroxyl groups in the polysaccharides are incapable of adsorbing iodine. As can be seen from the figure, the ability of the polysaccharides to adsorb iodine tends to saturate when the amino contents are over 60%. This may be caused by structural problems, which will be elucidated in the future.

Thus, the ability to adsorb iodine was found to be influenced by the kind of solvents used and was substantially low in nonpolar solvents. It became evident that such adsorption of iodine was caused by the formation of charge-transfer complexes between the amino groups of chitosan and iodine molecules, but the structure of the complexes differs from that of the inclusion compounds seen in amylose-iodine complexes.

Studies on the structure and crystallinity of chitosan and chitosan-iodine complexes are now in progress and will be reported in the near future.

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