Interaction of Dyes with Chitosan Derivatives

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Synopsis

The states of water in N-acylated, both aliphatic and aromatic, chitosan gels were investigated by DSC technique. The amounts of two states of water, freezable and nonfreezable water, were found to depend on the chemical and physical structure of the gels. The interaction between these hydrophobic gels and the dyes which have been designed and prepared to carry the ionic, hydrophilic, and hydrophobic nature was determined in detail. The dyes having $-OH$, $-N(C_4H_9)_2$, and naphthalene nucleus show a remarkable increase of the equilibrium sorption to compare with that of methyl orange. The contribution of the electrostatic, hydrophobic, and hydrogen bonding interaction in the sorption was discussed. The predominant contribution of the hydrophobic interaction in the systems of butyl orange/N-octanoyl chitosan gels has been made clear by means of the temperature dependence of the sorption.

INTRODUCTION

Recently chitin, chitosan, and their derivatives have been investigated to prepare the functional polymeric materials.[1-6] The gels for liquid chromatography, the supporters of immobilized enzyme, and the separation membranes are the pertinent examples. These are expected to develop a new horizon in the utilization of the natural resources. On the other hand, the basic researches of the interaction between those materials and small molecules are rather quite few. We have reported the sorption of D, L-tryptophan and methyl orange by chitosan gels chemically modified with hydrophobic groups.[7,8] The present work is an extension of the same line.

In exhibiting the sorptivity of both the natural and synthetic polymers, water in polymer is known to have an important role.[9,10] The properties of polymer are strongly affected by the state of water in the polymer matrices.[11-13] In the elucidation of the sorption mechanism of small molecules by polymer, the knowledge of the state of water should, thus, afford an important information. In this context the differential scanning calorimetry (DSC) was performed on the sorbed water/chitosan gel systems.

In this investigation, as the sorbate, small molecules, the anionic azo dyes were used. The various azo dyes can be prepared by designing the ionic group, the hydrophobic group, and the groups which have a specific function as, for example, the hydrogen bond formation. Klotz et al. examined the interaction between poly(ethylene imine) having long acylated chain and azo dyes carrying some functional groups as $-OH$, including methyl orange.[14-16] Kozuka et al. investigated the binding of butyl orange with copoly(2-hydroxyethyl methacrylate-N-vinylpyrrolidone) and discussed the importance of the hydrophobic interaction in the binding.[17] Our group has reported the interaction

R = (CH$_2$)$_6$CH$_3$: C$_8$-X

= (CH$_2$)$_{10}$CH$_3$: C$_{12}$-X

= (CH$_2$)$_{16}$CH$_3$: C$_{18}$-X
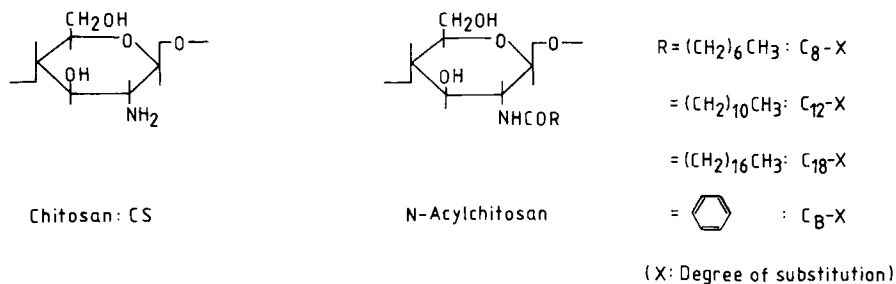
= ⬡ : C$_B$-X

(X: Degree of substitution)

Fig. 1.   Structural formulae of chitosan and N-acylchitosan gels.

between quaternized poly(4-vinylpyridine) and 4-aminoazobenzene and its derivatives, and the fluorine containing azo dyes.[18,19]

A few examples of the interaction of chitosan with azo dyes were reported; the chiral binding of some azo dyes in acetic acid aqueous solution[20] and the metachromasy.[21] As mentioned above in the previous investigation of the sorptivity of methyl orange by chitosan and N-acylchitosan gels, the hydrophobic group of the optimum chain length in the gels was found to give a prominent effect to increase the sorptivity.[8] In the present work, based on these results, the dyes which have a common skeletal structure, phenyl-azo-phenyl, carrying various groups including an additional phenyl group were used to investigate the effect of hydrophobic interaction in chitosan gel matrices on the sorption behavior.

EXPERIMENTAL

Materials

Chitosans which have the degrees of the substitution of amino group, 0.85 (sample I) and 0.77 (sample II) (Kyowa Yushi Co. Ltd.) were used. The flake of chitosan was dissolved in 10% aqueous acetic acid solution with methanol and acylated by carboxylic acid anhydrides. The formed gel was neutralized with 0.1N KOH aqueous solution. The products were washed with water and dried. The diameters of the gels thus formed were 50–300 μm.[7,8] The acylated chitosan derivatives (Fig. 1) were obtained by a conventional method as described in the previous paper.[8] The anhydrides of the carboxylic acids used were octanoic, dodecanoic, octadecanoic, and benzoic. The dyes used have a variety of chemical structures as given in Figure 2. All of the dyes were prepared by the conventional methods from the appropriate diazo and coupling components (analytical grade reagent), or purchased from Tokyo Kasei Co. (guaranteed grade). The method of the purification was prescribed previously.[8]

DSC Measurement

The gels (100 mg) were shaken with distilled water (20 mL) in stoppered glass test tube, 4 days at 30°C. After that, the gels were carefully blotted with filter paper (Whatman Filter Paper 50) to remove the surface water. Fifteen milligrams of the gels were weighed accurately in DSC aluminum pan. The
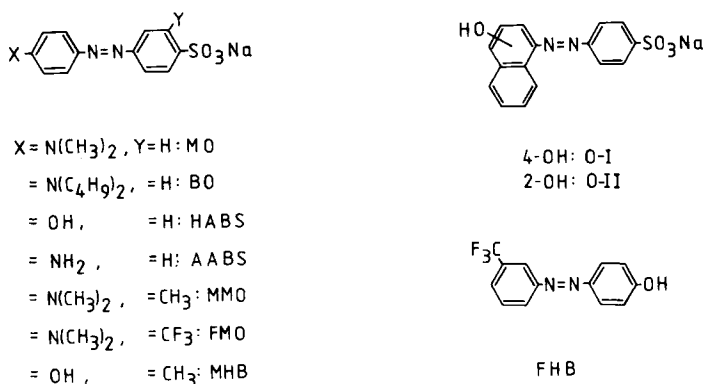
$$X-\text{<benzene>}-N=N-\text{<benzene, Y>}-SO_3Na$$

$X = N(CH_3)_2$, $Y = H : MO$

   $= N(C_4H_9)_2$, $= H : BO$

   $= OH$, $= H : HABS$

   $= NH_2$, $= H : AABS$

   $= N(CH_3)_2$, $= CH_3 : MMO$

   $= N(CH_3)_2$, $= CF_3 : FMO$

   $= OH$, $= CH_3 : MHB$

4-OH : O-I
2-OH : O-II

FHB

Fig. 2. Types of azo dyes used.

water content (g H_2O/g dried polymer) was determined by weighing before and after drying *in vacuo* at 100°C in 2 days. The measurement was performed by means of a differential scanning calorimeter, SSC 575/DSC 10 (Seiko Instrument and Electronics Ltd.). The sample pan was cooled from 300 to 170 K with a speed of 2.5 K min^{-1} and then heated to 300 K with the same speed. From the endothermic peak in the thermogram obtained the amounts of the freezable water were estimated. The rest in the total water content was assigned as the nonfreezable water.

Equilibrium Sorption Measurement

The gels (ca. 10 mg) were equilibrated in the aqueous solution of an appropriate concentration of dye at 30 ± 0.1°C in 4 days. The solutions were kept in stoppered Pyrex test tube and were occasionally shaked. The attainment of the equilibrium sorption was confirmed by a preliminary experiment. The amounts of the sorption were decided by the differences of the initial and final concentrations of the bath determined spectrophotometrically. The characteristics of dyes were given in Table I.

RESULTS AND DISCUSSION

The States of Water in *N*-Acylated Chitosan Gels

In Table II, the solubility of the gels was given. The chitosan and the octanoyl– and dodecanoyl–chitosan gels with the degree of substitution (D.S.) of less than ca. 0.3 are found to dissolve in dilute acetic acid solution. On the other hand, the higher the D.S. of the gels, the lower the solubility in the aqueous acidic solution and is becoming swellable in LiCl/*N*-methylpyrrolidon/*N*,*N*-dimethylacetamide mixture. The gels of D.S. larger than 0.8 are soluble in the mixed solvent. In the cases of the longer octadecanoyl and benzoyl gels, the affinity to the organic solvents becomes larger.

The water content with respect to the D.S. was shown in Figures 3 and 4. In the former figure, the water content (g/g of dried polymer) of CS-I (sample I) and its octanoyl derivatives gives a maximum at D.S. = 0.3 and drastically decreases at D.S. > 0.8. In the case of dodecanoyl derivatives the water

TABLE I
λ_{max} and Extinction Coefficient of Dye Solutions

Dye	MW[a]	$\lambda_{max}/(nm)$	$\epsilon_{\lambda_{max}} \times 10^{-3}/(m^2\ mol^{-1})$
MO	327.3	464	2.67
HABS	300.3	352	2.47
AABS	299.3	387	1.81
BO	411.5	478	3.60
O-I	350.3	477	2.84
O-II	350.3	485	1.46
FHB	288.2	348	3.43
MMO	341.3	461	2.64
FMO	395.3	453	2.45
MHB	314.3	351	2.17

[a] Molecular weight.

TABLE II
Properties of N-Acylchitosan Gels

Sample no.	D.S.[a]	Solubility in[c]	
		10% AcOH	LiCl/NMP/DMA (1/10/10)
CS-I	(0.85)[b]	s	i
CS-II	(0.77)[b]	s	i
C_8-0.1[d]	0.09	s	i
0.3	0.29	s	i
0.4	0.41	sw	sw
0.6	0.58	i	sw
0.8	0.79	i	s
1.0	1.02	i	s
C_{12}-0.1[d]	0.08	s	i
0.3	0.32	s	i
0.45	0.45	sw	sw
0.5	0.54	sw	sw
0.6	0.58	i	sw
0.8	0.81	i	s
0.9	0.94	i	s
C_{18}-0.3[d]	0.30	sw	sw
C_B-0.3[e]	0.32	sw	i
0.5	0.51	i	sw
0.7	0.68	i	s

[a] Degree of substitution of acyl group.
[b] Degree of substitution of amino group.
[c] i = insoluble, s = soluble, sw = swelling.
[d] Prepared from CS-I.
[e] Prepared from CS-II.

content decreases monotonously with increase in D.S. On the other hand, benzoylated CS-II (sample II) has increasing water content at D.S. = 0.3 and decreasing at D.S. = 0.4. Further increase of D.S. = 0.7 was found to keep the same level of the water content.

Figure 5 is an example of the DSC thermogram at the elevating temperature process. A clear distinction of the thermogram of the gels from that of
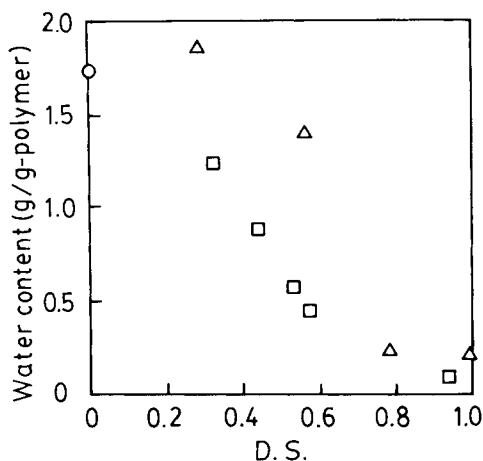
Fig. 3.   Effect of D.S. and chain length on the water content of chitosan and *N*-acylchitosan gels: (○) chitosan (I); (△) octanoylchitosan; (□) dodecanoylchitosan.
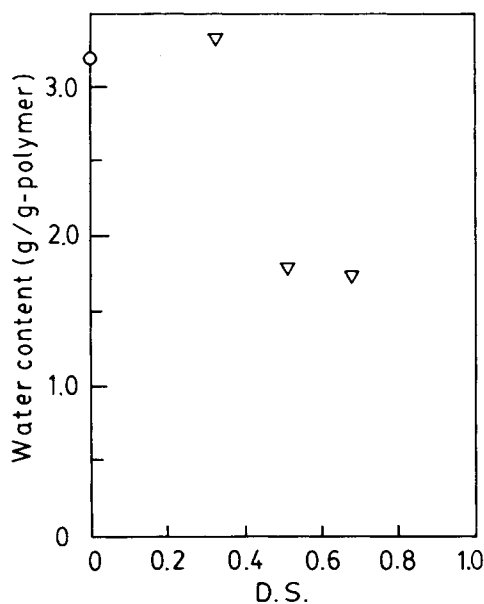

Fig. 4.   Effect of D.S. on the water content of chitosan and benzoylchitosan gels: (○) chitosan (II); (▽) benzoylchitosan.

pure water is the appearance of a shoulder at the lower temperature range in the endothermic peak, which is clear in the cases of chitosan gel and acylated chitosan gels with low D.S. The shoulder suggests the existence of different kind of water species from free water which corresponds to the main peak. The different kind of water species would be assigned as weakly interacted water with the polymer. The phase transition peak from ice to liquid water is extremely small for the gel of D.S. = 1.0. In Figures 6 and 7, the amounts of the freezable and nonfreezable water were given as a function of the degree of substitution of gels.
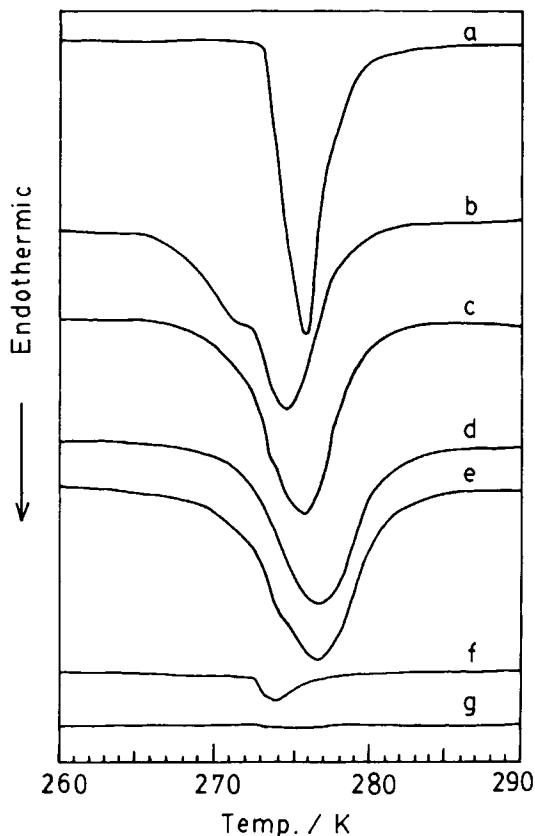
SEO ET AL.

Fig. 5. DSC heating curves of water sorbed by chitosan and octanoylchitosan gels: (a) pure water; (b) chitosan (I); (c) C_8-0.1; (d) C_8-0.4; (e) C_8-0.6; (f) C_8-0.8; (g) C_8-1.0.

For the chitosan gel itself, the higher the amino content, the lower the amounts of the freezable water. The introduction of octanoyl group leads to the increase of the freezable water. The octanoyl chitosan having D.S. = 0.3–0.4, the amount is approximately 1.4 times larger than that of the chitosan. Further increase of the degree of substitution over 0.6 gives the decrease and finally reaches zero at D.S. = 1.0.

On the other hand, in the case of dodecanoyl chitosan, the amounts of freezable water decrease linearly with rise of D.S. In the introduction of benzoyl group, the amounts of the freezable water increases at D.S. = 0.3 and then decreases to the half of the original chitosan at D.S. = 0.5, and further increase of the D.S. does not change the amount of the freezable water.

Concerning the nonfreezable water, the amounts in chitosan gels with different degree of amino content are approximately the same as 5 mol/basemol. The nonfreezable water contents are 4.5–5 mol/basemol and approximately 6.5 mol/basemol, for octanoyl and benzoyl compounds, respectively.

From the results mentioned above, it is supposed that the introduction of long acyl group makes the crystal structure of chitosan gels loose in the beginning, resulting in the increase of the amounts of freezable water. With
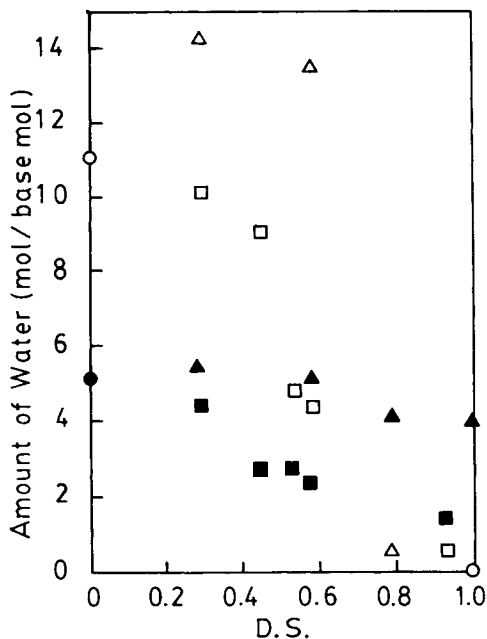
Fig. 6. Effects of D.S. and chain length on the states of water in chitosan and N-acylchitosan gels. Open symbols: freezable water; filled symbols: nonfreezable water. (○) Chitosan (I); (△) octanoylchitosan; (□) dodecanoylchitosan.
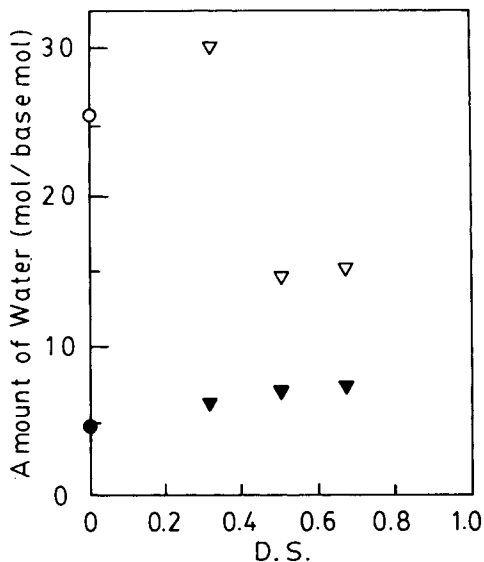

Fig. 7. Effect of D.S. on the states of .water in chitosan and benzoylchitosan gels. Open symbols: freezable water; filled symbols: nonfreezable water. (○) Chitosan (II); (▽) benzoylchitosan.

increasing of the substitution, on the other hand, the more compact structure of the gels due to the stronger interaction between the long acyl groups as well as the increase of the hydrophobicity is formed to give the distinct decrease of the freezable water. In the case of the benzoyl group, the interaction of the π-electron of the phenyl group with water and the bulky structure of this group are supposed to keep a relatively coarse structure.

On the other hand, as the amounts of the nonfreezable water were scarcely affected by the amino group contents and the degree of acyl group substitution, the nonfreezable water is thought to be bound strongly with the hydroxyl group of glucosamine residue in the structural unit of the gels. Accordingly, it is estimated that two to three water molecules are bound with one OH group. The values are larger than the bound water in a noncrystalline area of cellulose (3.6 mol/basemol).[22] A remarkable decrease of the nonfreezable water, approximately 1 mol water/basemol, was found in dodecanoyl compound with the degree of substitution of 0.9, presumably due to the extremely compact and hydrophobic nature of the gel.

Sorption Isotherm of Azo Dyes by Chitosan Gels Having Acyl Chain Groups

Dyes Having Amino and Hydroxyl Groups

The sorption behavior of the chitosan (I) and octanoyl chitosan gels for the azo dyes having the hydrogen bond forming groups is discussed in comparison with that for MO. In Figure 8, HABS having OH group shows higher sorption and AABS having NH_2 group shows lower sorption than MO. In comparing MO with AABS (Fig. 9), chitosan has larger sorptivity for AABS than for MO. On the other hand, C_{18}-0.3 shows the reverse tendency. In the higher concentration range for C_8-0.6, the slope of the isotherm is clearly larger for MO than AABS. In Figure 10, the isotherms for HABS and MO were given. For both of the dyes, the introduction of octanoyl group in chitosan increases the amount of the sorption. In the high concentration for chitosan and C_8-0.6, the slope of the isotherm for HABS is larger than MO; however, the difference is scarcely found for C_8-1.0.
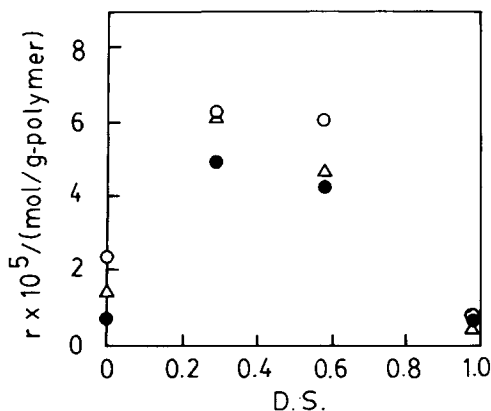

Fig. 8. Effect of D.S. on dye sorption by octanoylchitosan gels. Initial concentration of dye $= 1 \times 10^{-4}$ mol dm^{-3}. ($\bullet$) MO; ($\circ$) HABS; ($\triangle$) AABS.
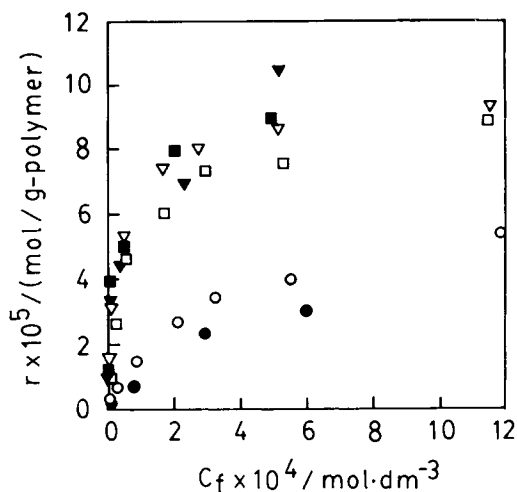
Fig. 9. Sorption isotherms of dyes by *N*-acylchitosan gels. Open symbols: AABS; filled symbols: MO. (○) Chitosan (I); (▽) C_8-0.6; (□) C_{18}-0.3.
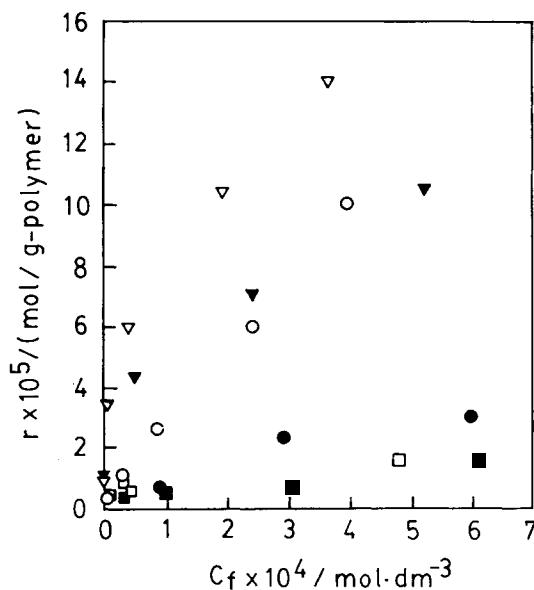

Fig. 10. Sorption isotherms of dyes by octanoylchitosan gels. Open symbols: HABS; filled symbols: MO. (○) Chitosan (I); (▽) C_8-0.6; (□) C_8-1.0.

Looking at the effect of chain length of gels on the sorption of HABS in Figure 11, for the same degree of substitution as 0.3, the amounts of sorption in moles per basemol are found to be almost the same. This indicates the amino content is a dominant factor in the sorptivity of this dye.

Dyes Having Hydrophobic Groups

Figure 12 shows the sorption isotherms of various azo dyes for octanoyl chitosan gels. The amounts of sorption give a maximum at the degree of
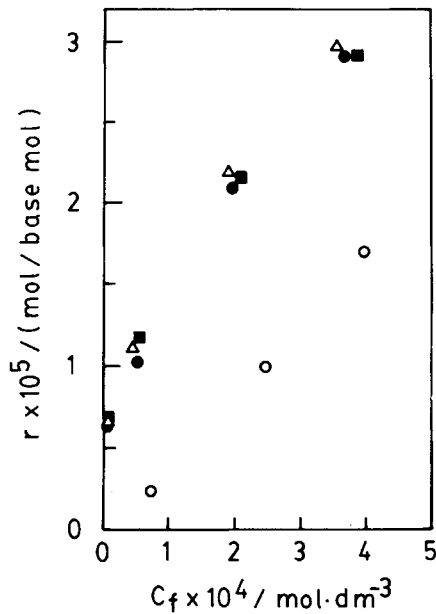
SEO ET AL.

Fig. 11. Sorption isotherms of HABS by *N*-acylchitosan gels. (○) chitosan (I); (△) C_8-0.3; (●) C_{12}-0.3; (■) C_{18}-0.3.
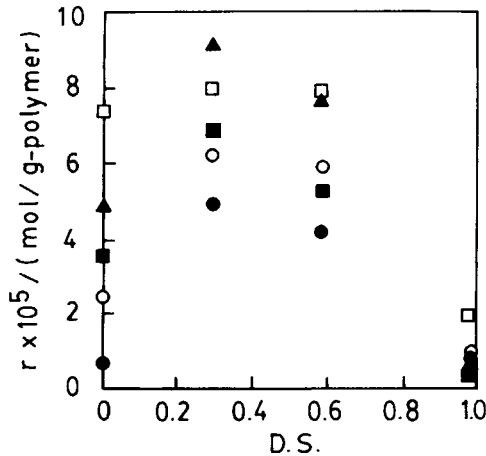

Fig. 12. Effect of D.S. on dye sorption by octanoylchitosan gels. Initial concentration of dye = 1×10^{-4} mol dm^{-3}. (●) MO; (○) HABS; (□) BO; (■) O-I; (▲) O-II.

substitution of 0.3 and then decrease with rise of the degree of substitution. Inspecting the chemical constitution of the dyes, it was clearly found that the larger the hydrophobicity of the dyes, the greater the sorptivity. The larger hydrophobic nature of BO than MO; O-I and O-II than HABS yields a higher degree of the sorption. The reason that the amount of sorption of O-II is higher than that of O-I is attributed to the larger hydrophobic characteristics of the former dye.[23] BO has the larger amounts of sorption than the other dyes, especially for C_{18}-0.3, which has a longer hydrophobic chain (Fig. 13). On
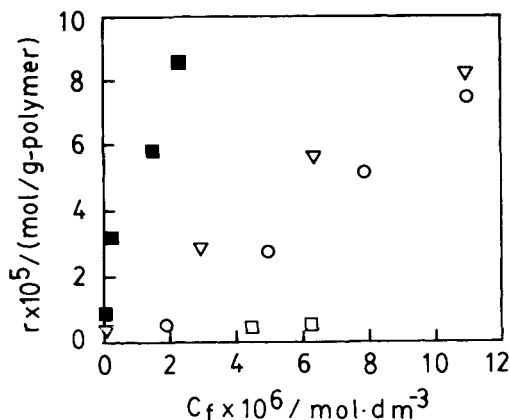
Fig. 13. Sorption isotherms of butyl orange (BO) by N-acylchitosan gels: (○) chitosan (I); (▽) C_8-0.6; (□) C_8-1.0; (■) C_{18}-0.3.
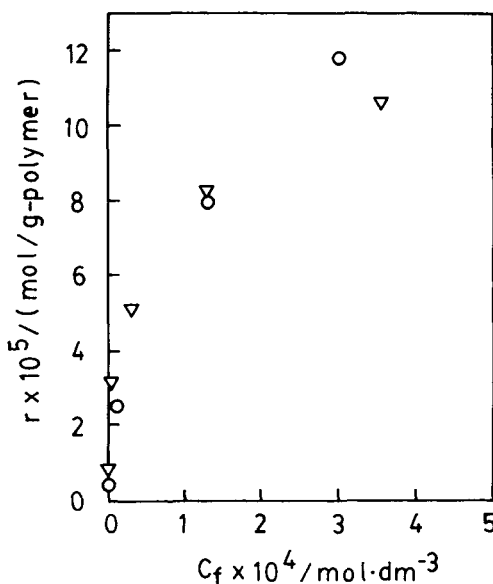

Fig. 14. Sorption isotherms of Orange I (O-I) by octanoylchitosan gel (D.S. = 0.6): (○) chitosan (I); (▽) C_8-0.6.

the other hand, the sorption of O-I by CS-I was found to be the same level of the sorption by C_8-0.6 (Fig. 14). This observation together with the large amounts of BO sorption by CS-I indicates that the chitosan has the hydrophobic region in itself.

The amounts of the sorption of an uncharged azo dyes containing CF_3 group, FHB by octanoyl chitosan gels are shown in Figure 15. It is worthwhile to mention that the sorption of FHB increases with the increase in the degree of substitution up to 1.0 in contrast to the other dyes. This suggests that the C_8-1.0 has a compact structure and exhibits no electrostatic interaction. Furthermore, the highly negative surface potential due to the hydrophobic gel surface[24] repels the azo dye anions.
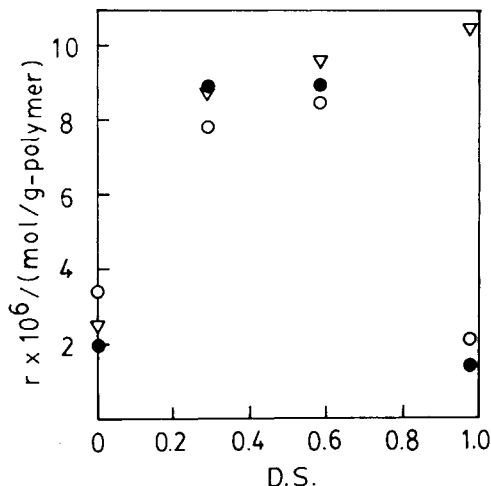
Fig. 15. Effect of D.S. on dye sorption by octanoylchitosan gels. Initial concentration of dye = 1 × 10^{-5} mol dm^{-3}. (●) MO; (○) HABS; (▽) FHB.

Sorption Isotherm of Azo Dyes by Chitosan Gels Having Aromatic Acyl Groups

Figure 16 shows that the sequence of the amounts of sorption by benzoyl chitosan gels for various dyes is almost the same as by octanoyl chitosan gels, given in the previous section. At low degree of substitution of the benzoyl chitosan gel the sorption of MO and HABS is a little lower than C_8-gel; however, the hydrophobic dyes, BO, O-I, and O-II has higher sorption than C_8-gel.

In Figure 17, the sorption isotherms of MO, BO, O-I, and O-II by benzoyl chitosan gel of D.S. = 0.5 were shown. In the low concentration region, the slopes of the isotherms increase in a sequence of MO < O-I < O-II and in the higher concentration region the slope of O-I increases significantly. The
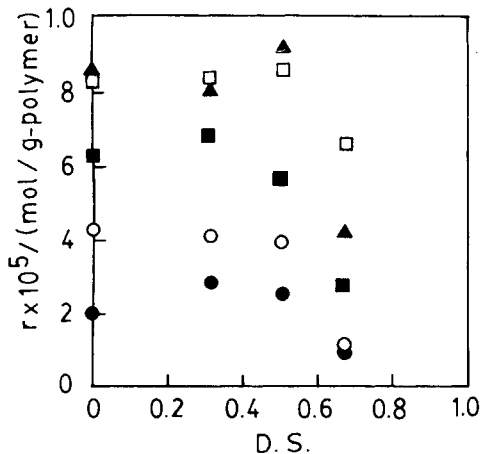

Fig. 16. Effect of D.S. on dye sorption by benzoylchitosan gels. Initial concentration of dye = 1 × 10^{-4} mol dm^{-3}. (●) MO; (○) HABS; (□) BO; (■) O-I; (▲) O-II.
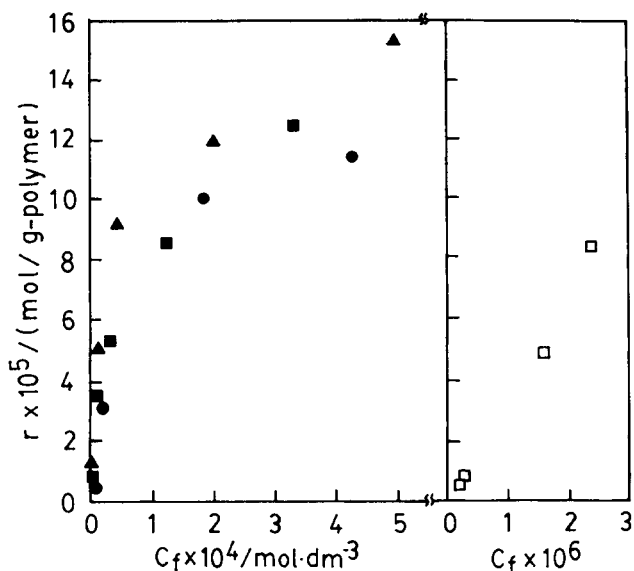
Fig. 17.   Sorption isotherms of dyes by benzoylchitosan gel (D.S. = 0.5): (●) MO; (□) BO; (■) O-I; (▲) O-II.

sorption of BO at low concentration is remarkably large and increases linearly with increasing the concentration. The effects of the substituent groups of dyes on the sorption are found in Table III. It is observed that there are no differences of the sorptivity by C_8-1.0, but clear differences are found by CS-I and C_B-0.5 in a sequence of MMO > FMO > MO, MHB > HABS. This suggests the hydrophobic effects of CH_3 and CF_3 groups.

The Analysis of the Interaction by a Dual Sorption Model

The sorption isotherms obtained were interpreted by means of a dual model[25,26] comprised of the electrostatic (L) and nonelectrostatic interactions (P) as reported in the previous works[8,27]:

$$r = r_P + r_L = K_1 C_f + \frac{S K_2 C_f}{1 + K_2 C_f}$$

TABLE III
Effect of the Substituent Groups of Dye on the Sorption

Sample no. \ Dye	$r \times 10^5$ [a] (mol g^{-1})			$r \times 10^6$ [b] (mol g^{-1})	
	MMO	FMO	MO	MHB	HABS
CS-I	2.99	1.56	0.75	4.50	3.35
C_8-1.0	0.49	0.37	0.40	1.14	2.05
C_B-0.5	4.92	3.17	2.50	7.72	7.25

[a] Initial concentration of dye = 1×10^{-4} mol dm^{-3}.
[b] Initial concentration of dye = 1×10^{-5} mol dm^{-3}.

TABLE IV
Sorption Parameters

Sample no.	Dye	Amino content ($\times 10^3$/mol g^{-1})	pH	$K_1 \times 10^2$ (dm^3 g^{-1})	$K_2 \times 10^{-5}$ (dm^3 mol^{-1})	$S \times 10^5$ (mol g^{-1})
CS-I	MO	4.8	6.4	4.0	0.6	0.5
	HABS		6.7	22.6	0.4	1.0
	AABS		6.6	2.5	0.2	2.0
	BO		6.5	550	0.5	0.5
	O-I		6.7	18.8	0.4	6.6
C_8-0.3	MO	2.9	6.3	9.8	3.8	5.2
	HABS		6.7	28.0	2.1	5.2
C_8-0.6	MO	1.3	6.3	13.2	3.9	3.7
	HABS		6.7	37.3	3.7	4.5
	AABS		6.7	2.3	0.5	6.6
	BO		6.3	500	2.1	3.0
	O-I		6.7	15.2	1.9	5.4
C_8-1.0	MO	0.0	6.0	2.2		
	HABS		6.3	1.1		
	BO		6.4	18.8		
C_{12}-0.3	MO	2.3	6.4	13.3	7.9	3.8
	HABS		6.6	26.6	4.3	3.2
C_{18}-0.3	MO	2.2	6.4	11.3	5.7	4.1
	HABS		6.4	20.7	2.8	4.1
	AABS		6.6	2.2	0.5	6.6
	BO		6.6	2380	76.4	2.9
C_B-0.5	MO	1.3	6.4	21.3	3.4	2.6
	BO		6.5	3480	—	—
	O-I		6.5	18.6	1.1	6.5
	O-II		6.5	9.3	0.8	10.1

where r is the amount of sorption of dye (mol g^{-1} polymer), C_f the external dye concentration (mol dm^{-3}), K_1 the partition constant of the P (partition) mode. K_2 and S are the sorption constant and the saturation value in the L (Langmuir) mode, respectively. The parameters K_1, K_2, and S, which represent the sorption characteristics, were decided by a nonlinear least-square method. For C_8-1.0 and the system of C_B-0.5/BO, the L-mode was assumed to be negligible. The results were compiled in Table IV.

HABS has a larger value of K_1 than MO for all the gels except C_8-1.0. For CS-I, the values is 5.6 times. Considering this value together with the results of Figures 10 and 11, the hydrogen bonding between —NH$_2$ groups of gels and the —OH group of HABS is supposed to contribute to the partition mode sorption. The reason why the introduction of N-acyl group does not result in the increase of K_1 is as follows. The introduction of N-acyl group perturbs the crystalline structure of gels leading to the increase in the possibility of hydrogen bonding and, at the same time, giving the reduction of the effective amino groups.

AABS has small values of K_1 and K_2 and relatively large values of S for all the gels used. It is estimated that AABS has a less hydrophobic nature than MO giving a small value of K_1. The electrostatic repulsion between the dye cation and gels suppresses the hydrogen bond formation. As a result, the contribution of the interaction with the SO$_3^-$ group is dominant, resulting in the increase of the Langmuir site.

BO shows a remarkable increase of K_1 to compare with other dyes, especially, for C_{18}-0.3 having a long alkyl chain. The significant contribution of the hydrophobic interaction is thought to result in the K_1 value of 200 times larger than MO.

It is interesting that K_1 of HABS for CS-I and C_8-0.6 was larger than that of O-I and the value of S was the reverse. For the acyl chitosans having large D.S., both K_1 and S are small. From the above results, it is estimated that, in spite of the higher hydrophobicity of O-I than HABS, the larger size of O-I gives a decrease of the sorption. In the case of C_8-1.0, due to the lack of amino group, the sorption is solely governed by the partition mode. In Table IV, K_1 is generally found to be quite small to compare with other gels. This is attributed to the compact structure with an extremely limited amount of free water caused by the mutual interaction of acyl groups. In the limited water sorption, the more hydrophobic BO is more sorbed than MO and HABS. The fact that K_2 and S are quite small for chitosan is explained by a compact structure due to the high crystallinity of approximately 40% (density ca. 1.4).[28]

It is worthwhile to note the difference of the effects of benzoyl and octanoyl groups on the sorptivity of dyes. In comparing the values of K_1 for C_B-0.5 and C_8-0.6, it is concluded that benzoyl groups cannot interact so firmly as the octanoyl group due to the bulky structure of the phenyl ring. Thus the K_1 value of BO is found to be seven times larger for C_B-0.5 than C_8-0.6.

Temperature Effects on the Sorption

In Figure 18, the temperature dependence of the sorption isotherm was given for the BO/C_8-1.0 system in which the partition mode is predominant. From the van 't Hoff plot (Fig. 19), the thermodynamic parameters were
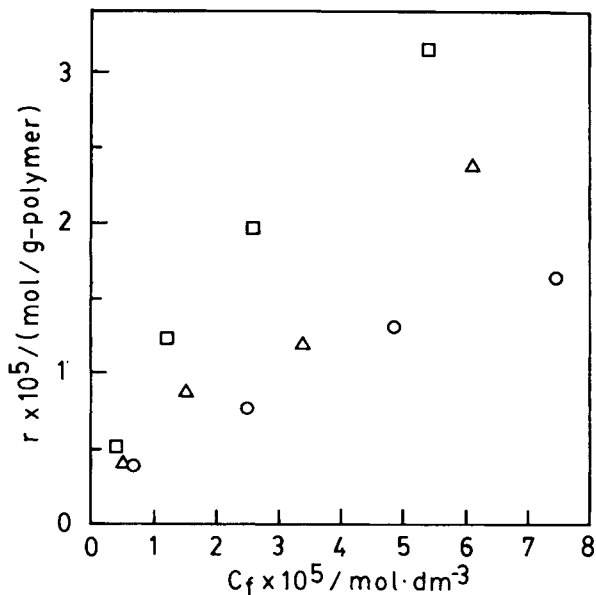

Fig. 18. Effect of temperature on the sorption of BO by octanoylchitosan gel (D.S. = 1.0): (○) 30°C; (△) 40°C; (□) 50°C.
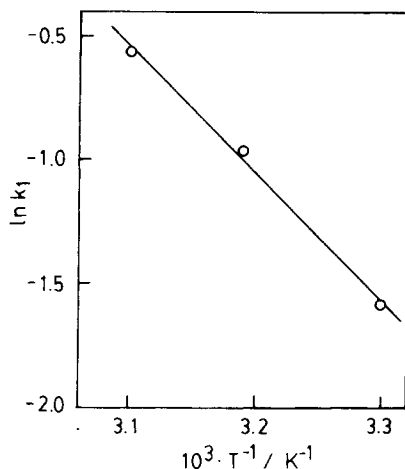
Fig. 19.   van 't Hoff plot of partition constant K_1: dye: BO; gel: C_8-1.0.

TABLE V
Thermodynamic Parameters

Sample no.	Dye	$K_1 \times 10^2$ (dm^3 g^{-1}) [$K_2 \times 10^5$ (dm^3 mol^{-1})]			ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
		303 K	313 K	323 K			
C_8-1.0	BO	20.6	38.2	56.9	3.98^a	42.4	127
C_B-0.7	BO	310		152			
C_B-0.7	O-II	9.3	9.3	8.2			
		(1.4	2.3	1.9)			

^{a}At 303 K.

obtained and given in Table V. It is clear that the sorption is an endothermic process and is governed by the hydrophobic interaction.

On the other hand, in the case of the gels having amino group, e.g., C_B-0.7/BO and C_B-0.7/O-II, the sorption process was found to be slightly exothermic. This is ascribed to the contribution of the sorption mechanism other than the hydrophobic interaction, i.e., the hydrogen bonding mechanism pertaining to the amino group of the gels. The hydrogen bonding with the π-electron of the aromatic ring is thought to be effective in these systems.

CONCLUSION

1. The DSC investigation on the states of water in N-acylchitosan (both aliphatic and aromatic) gels indicated that nonfreezable water content is almost the same level for all the gels investigated irrespective of the chemical constitution. The amount of freezable water gave, on the other hand, a maximum at D.S. = 0.2–0.4 and decreased to zero at D.S. = 1.0.

2. The sorptivity of various dyes having a variety of ionic nature and hydrophobicity by chitosan and its derivatives was investigated in detail. The azo dyes which have —OH and —N(C$_4$H$_9$)$_2$ as a substituent group and naphthol as a component showed an enhanced sorption to compare with that

of MO. The participation of the electrostatic interaction, the hydrophobic interaction, and the hydrogen bonding interaction in binding mechanisms was approved. For the interaction between a hydrophobic dye, BO and a hydrophobic gel, octanoyl chitosan of D.S. = 1.0, the contribution of the hydrophobic interaction derived by an entropy gain was made clear.

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