

Fundamental Adsorption Properties of Chitosan Gel Particles Prepared by Suspension Evaporation Method

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ABSTRACT: Chitosan gel particles were prepared by the suspension evaporation method, and their fundamental adsorption properties have been investigated. The chitosan gel particles were spherical in shape, 150 μm in diameter, and had large macropores, about 2 μm in diameter, formed by the polymer networks. The adsorption properties were evaluated from an interaction viewpoint using anionic surfactants having various numbers of carbon atoms, ethylbenzenesulfonate (EBS), octylbenzenesulfonate (OBS), and dodecylbenzenesulfonate (DBS). The pK_a values of the amino groups within the gel particles were remarkably small compared with those of chitosan polymer. EBS, with its short hydrophobic chain, was adsorbed mainly by an electrostatic

interaction in the pH range 3.0 to 6.0, where the amino groups were dissociated. On the contrary, the adsorption of OBS and DBS, with their relatively long hydrophobic chains, took place via an electrostatic interaction in the pH range 3.0 to 5.0, and then by a hydrophobic interaction in the presence of an electrostatic interaction in the pH range 5.0 to 8.0. We conclude that an electrostatic interaction is essential, even for the adsorption of surfactants having strong hydrophobic interactions. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 901–906, 2002

Key words: adsorption; gels; polysaccharides; surfactants

INTRODUCTION

Chitin, poly (*N*-acetyl-D-glucosamine), is one of the most abundant biopolymers that is extracted from the outer shell of arthropods, and a partial or full *N*-deacetylation of chitin can easily provide chitosan, poly (D-glucosamine), as shown in Figure 1. Owing to their nontoxicity, biocompatibility, and biodegradability, chitin and chitosan are being explored to investigate their potential use in polymer systems. Chitin shows high crystallinity, and has a nonreactive nature. On the other hand, chitosan dissolves in water, and acts as a polyelectrolyte at low pH owing to its amino groups. Thus, chitosan is potentially more easily applied to many engineering fields than chitin. Recently, many researchers have begun to investigate and to utilize chitosan as an adsorbent, because of its high affinity for metal ions,^{1–4} proteins,^{5–7} and dyes.^{8–10} Furthermore, chitosan is expected to be classed as a functional material, because of the specific properties mentioned above.

There are several approaches to derive a high functionality from chitosan. One approach is by chemical modification. Because chitosan has a high reactive primary amino group as well as primary and secondary

hydroxyl groups, a high functionality of chitosan is achieved simply by introducing a specific functional group into the chitosan structure. Inukai et al. reported on the adsorption of semimetals on branched saccharide chitosan gels, in which a series of saccharides was introduced into chitosan resins, or beads. They showed that Ge(IV) was selectively adsorbed onto these gels owing to a complex formation between the Ge(IV) and the hydroxyl groups of the saccharides.⁴ Seo et al. investigated the effect of hydrophobic interaction in the adsorption behavior of dyes on *N*-acylated chitosan gels that were chemically modified with various types of hydrophobic groups. They showed that *N*-octanoyl chitosan gels had a high adsorption capacity for butyl orange, because of the contribution of a hydrophobic interaction between the gels and the butyl orange.⁹

Another approach is to control the micro- and macrostructure of the chitosan gel itself, without any chemical modification. The structure of chitosan gels can be varied, depending upon the preparation method used. Although the adsorption ability and the corresponding behavior are strongly influenced by the structure of the gels, few studies have attempted to control the structure of the gels. Adachi et al. reported on the preparation of chitosan gel particles using the suspension evaporation method. The chitosan gel particles had a unique structure, consisting of large macropores, and a network structure formed on the surface of the gel particles.¹¹ These novel chitosan gel

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particles possessed various chemical and physical properties obtained by controlling the operating conditions during gelation, and thus have the potential for use as highly functional materials. However, there have been few studies concerning the adsorption ability and the behavior of chitosan gel particles that have a specific network structure.

In the present work, the fundamental adsorption properties of chitosan gel particles prepared by the suspension evaporation method have been evaluated. The chitosan gel particles were prepared in a hydrophobic solvent to endow a specific property. Three surfactants, ethylbenzenesulfonate (EBS), octylbenzenesulfonate (OBS), and dodecylbenzenesulfonate (DBS), were selected as the model adsorbates. They are typical univalent anionic surfactants with similar chemical structures. Their adsorption behaviors were investigated under various solution conditions, and these were clarified from the viewpoint of the interaction (electrostatic and hydrophobic) between the gel particles and the surfactant.

EXPERIMENTAL

Materials

Chitosan flakes (Dainichiseika Color & Chemicals Mfg. Co., Ltd.) were used as the starting material without any further purification. The degree of deacetylation was determined to be 84% by the colloidal titration method.

Polyoxyethylene nonylphenol (Nonipol 130, Sanyo Chemical Industries Co., Ltd.), decahydronaphthalene (Decalin, Nacalai Tesque Co., Ltd.), *N,N*-dimethylformamide (DMF, Nacalai Tesque Co., Ltd.), and hexamethylenediisocyanate (HMDI, Tokyo Kasei Kogyo Co., Ltd.) were used in the gelation of the chitosan without any further purification.

Sodium ethylbenzenesulfonate (EBS, Tokyo Kasei Kogyo Co., Ltd.), sodium octylbenzenesulfonate (OBS, Tokyo Kasei Kogyo Co., Ltd.), and sodium dodecylbenzenesulfonate (DBS, Tokyo Kasei Kogyo Co., Ltd.) were used as the model adsorbates, and their chemical structures are shown in Figure 2. These surfactants have similar molecular structures that consist of a univalent anionic site and a linear hydrocarbon chain with various number of carbon atoms.

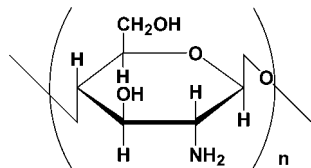


Figure 1 The unit molecular structure of chitosan.

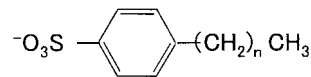


Figure 2 The molecular structure of the surfactants used: $n = 1$, ethylbenzenesulfonate (EBS); $n = 7$, octylbenzenesulfonate (OBS); and $n = 11$, dodecylbenzenesulfonate (DBS).

Preparation of the chitosan gel particles

The chitosan gel particles were prepared by the suspension evaporation method, as reported by Adachi et al. as follows. Chitosan flakes (5.0 g) and adipic acid (5.2 g) were dissolved in distilled water (500 mL), and left overnight with stirring. Then the chitosan solution was filtered through a glass fiber filter to remove any insoluble matter. After Decalin (800 mL) and Nonipol 130 (5 g) were introduced into a Teflon[®]-coated stainless steel vessel (170 mm height \times 130 mm i.d.), the chitosan solution (50 mL) was poured into the vessel, and the solution was stirred at 2000 rpm using a four-blade paddle for 1 h at a temperature of 353 K under a nitrogen atmosphere. The gel particles formed were thoroughly washed with acetone, and then rinsed overnight with a large volume of a methanol/3 M NaOH mixture at 308 K. The gel particles were then suspended in a DMF/acetone mixture, and an appropriate amount of HMDI was added to initiate crosslinking.

We prepared various types of chitosan gel particles by adjusting the amount of the HMDI. The volume of HMDI per unit volume (in mL) of gel particles was 0, 8, 30, and 100 μ L. The gel particles obtained were denoted as Sa0, Sa08, Sa30, and Sa100, respectively. These chitosan gel particles were thoroughly washed with acetone and dried at 353 K for 24 h.

Measurements

The morphology and the surface structure of the chitosan gel particles obtained were studied *in vacuo* using a SEM after having been first deposited with platinum.

The ion (anion) exchange capacity and acidity constant, pK_a , of the amino groups in the chitosan gel particles were determined using acid-base titration on 3 mL gel particles dispersed in aqueous 0.1 M NaCl solution. The pK_a of the original chitosan polymers dissolved in aqueous solutions was also determined in the same manner.

The equilibrium adsorption of the surfactants was measured by the following method. The dried chitosan gel particles (5 mg) were introduced into the surfactant solution (50 mL), and then the mixture was shaken at 298 K for 1 day. The initial concentration of the surfactant solutions was varied from 10^{-4} to 10^{-3} M. In the experiments on the pH dependency of the adsorption (see later), the initial concentration of sur-

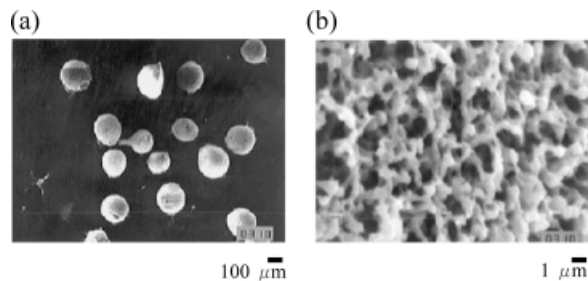


Figure 3 SEM images of chitosan gel particles, Sa08, prepared by the suspension evaporation method: (a) magnification $\times 22.5$; (b) magnification $\times 2250$.

factants was 10^{-3} M. We also prepared surfactant solutions that contained 0.1 M NaCl to investigate the effect of salt on the adsorption characteristics. The initial pH of the surfactant solutions was adjusted using 0.1 N HCl and NaOH. After the solution was separated by filtration, the pH value was measured, and the concentrations of the surfactants in the aqueous phase were analyzed using a UV-visible spectrophotometer (Hitachi U-2000A) operating at a wavelength of 254 nm. The adsorption amount was determined by the following mass balance equation:

$$q_e = \frac{V(C_0 - C_e)}{W}$$

where q_e [mol/g-drygel], V [L], C_0 [M], C_e [M], and W [g-drygel] represent the adsorption amount of the surfactant at equilibrium, the volume of the surfactant solution, the initial concentration of the surfactant solution, the concentration of the surfactant solution at equilibrium, and the weight of the chitosan gel particles, respectively.

RESULTS AND DISCUSSION

Properties of the chitosan gel particles

Figure 3(a) and 3(b) shows SEM images of the morphology and the surface of the chitosan gel particles prepared by the suspension evaporation method. The gel particles obtained were almost spherical in shape [Fig. 3(a)], and were composed of polymer networks as shown in Figure 3(b). The diameter of the gel particles was about $150 \mu\text{m}$, and the size of the macropores formed by the polymer networks was around $2 \mu\text{m}$, which was much larger than the value of the commercial chitosan beads. The properties of the gel particles developed in this study are summarized in Table I. The water content of the gel particles was high, and it decreased slightly from 78 to 74 wt % on a wet basis with increasing degree of crosslinking. The ion exchange capacity, which is equivalent to the total number of free amino groups, $\text{R}-\text{NH}_2$, in the gel

TABLE I
The Properties of Chitosan Polymer and Various Chitosan Gel Particles

	Polymer	Sa0	Sa08	Sa30	Sa100
Water content (%)	—	78	77	74	74
Ion exchange capacity (mEq/g-drygel)	—	—	3.84	1.86	1.49
pK_a (-)	6.37	— ^a	5.02	4.45	4.27

^a The ion exchange capacity and the pK_a value of Sa0 could not be determined because the gel particles were dissolved during the titration.

particles, decreased with increasing degree of crosslinking, because some amino groups were consumed with the reaction of the crosslinker (HMDI) during the preparation of the gel particles. The acidity constant, pK_a , of the amino groups was dependent on the degree of crosslinking. The pK_a values were 5.02 for lowest level crosslinked gel particles, for example, Sa08, 4.45 for highly crosslinked gels, for example, Sa30 and 4.27 for the highest crosslinked gel, Sa100. This implies that the dissociation of the amino groups can be altered according to the network structure of the gels.

Effect of the number of carbon atoms of the surfactant on adsorption

The adsorption isotherms of EBS and DBS on the chitosan gel particles, Sa08 and Sa30, at $\text{pH} = 3.0$ are shown in Figure 4. The adsorption amount of DBS on Sa08 (Sa30) was much larger than that of EBS on Sa08 (Sa30) over the whole range of the equilibrium concentration, C_e . The isotherms of the DBS/Sa08 and DBS/Sa30 systems were different from those of the EBS/Sa08 and EBS/Sa30 systems. The former systems showed very high adsorption levels at low C_e values, suggesting a strong interaction between DBS and the gel particles, whereas the latter systems showed a

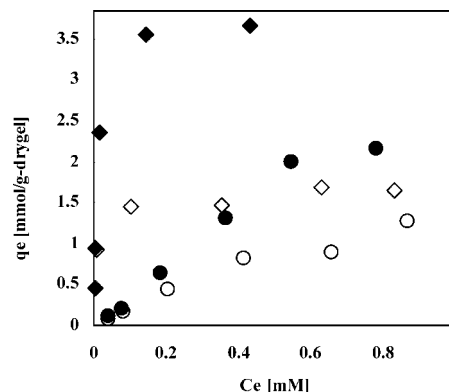


Figure 4 Adsorption isotherms of the surfactants on two types of chitosan gel particles at $\text{pH} = 3.0$: (●) EBS/Sa08; (○) EBS/Sa30; (◆) DBS/Sa08; and (◇) DBS/Sa30.

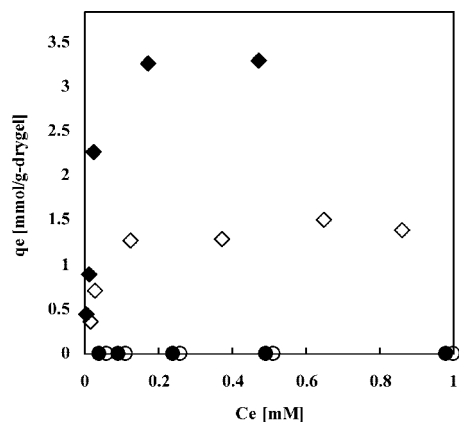


Figure 5 Adsorption isotherms of the surfactants on two types of chitosan gel particles in the presence of 0.1 M NaCl at pH = 3.0: (●) EBS/Sa08; (○) EBS/Sa30; (◆) DBS/Sa08; and (◇) DBS/Sa30.

monotonic increase in the adsorption amount with C_e . The adsorption amount of EBS (DBS) on Sa08 was much larger than that of EBS (DBS) on Sa30. To investigate such different adsorption behaviors, NaCl was added to the solutions of the surfactants. Figure 5 shows the adsorption isotherms of EBS and DBS on both gel particles (Sa08 and Sa30) in the presence of 0.1 M NaCl at pH = 3.0. It was found that very little EBS was adsorbed onto both gel particles, whereas the adsorption amount of DBS was only slightly decreased by the addition of salt.

At pH = 3.0, the amino groups in the gel particles are positively charged, because of protonation, while the sulfonic acid group within the surfactant is negatively charged. Consequently, there exists an electrostatic interaction between the anionic surfactants and the positively charged gel particles. In the absence of salt, the surfactants are likely to adsorb onto the gel particles mainly through an electrostatic interaction. As a result, Sa08 showed a higher adsorption capacity than Sa30, because the ion exchange capacity of Sa08 (3.84 mEq/g-drygel) is larger than that of Sa30 (1.86 mEq/g-drygel). Generally, in the presence of salts, an electrostatic interaction is weakened by the shielding of the electric field, and the salting out effect is caused. For these reasons, EBS was hardly adsorbed onto both gel particles when salt was added to the surfactant solution. On the contrary, the adsorption amount of DBS on the gel particles was almost the same as that in the absence of salt. This result suggests that other interactions, i.e., hydrophobic interactions, also play an important role in the adsorption of DBS, which has a much longer hydrophobic chain than EBS. Ihara measured the adsorption amount of sodium alkyl sulfate with various numbers of carbon atoms on anion exchange resins, and observed that the adsorption amount increased remarkably with an increase in the length of the hydrophobic chain of the adsorbate.¹²

Effect of pH on the adsorption of surfactants

Electrostatic and hydrophobic interactions play a major role in the adsorption of surfactants on chitosan gel particles, as mentioned above. To elucidate the role of these two interactions, the adsorption behavior of the surfactants was investigated over a wide range in pH, 3.0 to 10.0. Figure 6 shows the effect of pH on the adsorption of the three types of surfactant on Sa08 ($pK_a = 5.02$), together with the dissociation curve of the amino groups. The dissociation of an amino group ($R-NH_2$) attached to the chitosan polymer can be written as follows:



The degree of dissociation was calculated using the pK_a value obtained experimentally in this study. The dissociation curve indicates that the number of positively charged amino groups began to decrease gradually around pH = 3.0, and became almost zero at pH = 8.0. The adsorption amount of surfactant (EBS, OBS, and DBS) on the gel particles greatly depended on the pH, and decreased with increasing pH. The adsorption amount of EBS decreased monotonically with increasing pH. On the other hand, the adsorption amount of OBS and DBS on Sa08 was maintained at a high level over a wide range of pH, 3.0 to 6.0 (7.5) for OBS (DBS), and then fell abruptly beyond this pH range. The high adsorption amount around the neutral pH level, in which the amino groups are slightly dissociated, is considered to result from the predominantly hydrophobic interaction between the hydrophobic chain of the surfactants and the polymer networks of the gel particles. This implies that the hydrophobic interaction enhances with increasing pH. This interaction is dependent on the chain length (namely the hydrophobicity) of the surfactant, as shown by the larger adsorption amount of DBS vs. OBS occurring at

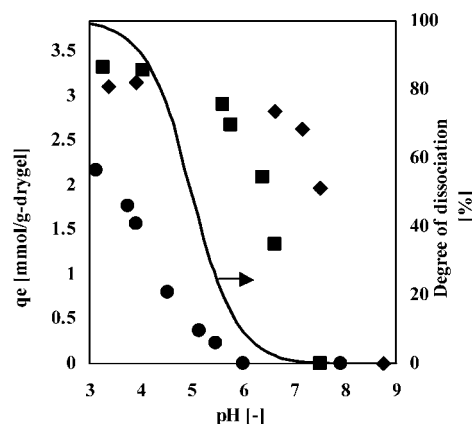


Figure 6 Effect of pH on the adsorption of the surfactants on Sa08, and the dissociation curve of the amino groups for Sa08: (●) EBS; (■) OBS; and (◆) DBS.

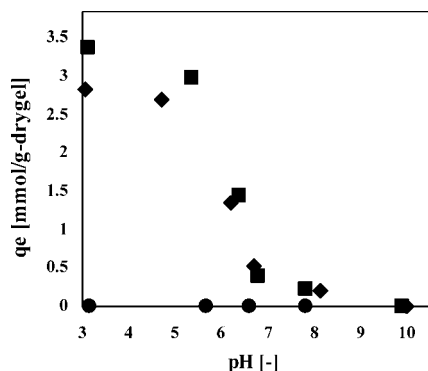


Figure 7 Effect of the addition of salt (0.1 M NaCl) on the adsorption of the surfactants on Sa08 over a wide range of pH: (●) EBS; (■) OBS; and (◆) DBS.

a rather high pH range. Both OBS and DBS were hardly adsorbed onto gel particles in the range of pH in which the dissociation of the amino groups was almost zero. This means that an electrostatic interaction is essential, even for the adsorption of OBS and DBS, which have longer hydrophobic chains than EBS.

Figure 7 shows the effect of the addition of salt (0.1 M NaCl) on the adsorption of the surfactants on Sa08 over a wide range of pH. EBS was hardly adsorbed onto Sa08 over the whole pH range examined. Compared with the results of Figures 6 and 7, different adsorption behaviors were observed for OBS and DBS. In the pH range 3.0 to 5.0, where the ratio of positively charged amino groups would be greater than 50%, the adsorption amount of OBS and DBS were almost equivalent to those values observed in the absence of salt. In the pH range 5.0 to 8.0, where the ratio of positively charged amino groups would be less than 50%, the adsorption amount decreased remarkably, compared with those observed in the absence of salt. This suggests the importance of an electrostatic interaction for adsorption, even in the presence of salt. Therefore, both OBS and DBS were hardly adsorbed in the range of pH in which dissociation did not occur. From these results, it can be said that EBS, with its short hydrophobic chain, adsorbs onto the gel particles mainly by an electrostatic interaction; whereas the adsorption of OBS and DBS, with relatively long hydrophobic chains, is able to take place through a hydrophobic interaction in the presence of an electrostatic interaction, even if the essential interaction is weakened owing to the presence of salt.

Effect of the gel structure on the adsorption of the surfactants

The dissociation curves of the amino groups attached to the chitosan polymers and its polymer gel particles (Sa08 and Sa30) are predicted in Figure 8(a), using the pK_a values of the chitosan polymers ($pK_a = 6.37$) and

the polymer gel particles ($pK_a = 5.02$ for Sa08 and $pK_a = 4.45$ for Sa30). The dissociation curve of Sa08 shifts towards much lower pH values compared with that observed for chitosan polymer. Chitosan polymer is composed of hydrophilic functionals, such as amino and hydroxyl groups, and relatively hydrophobic parts. When chitosan polymers are gelled in a hydrophobic solvent, as described earlier, the hydrophobic parts of the chitosan polymers are probably oriented outside and the hydrophilic parts are covered with the hydrophobic parts. This causes an inhibition of the dissociation of the amino groups. A slight shift of the dissociation curve takes place when the degree of crosslinking of the gel particles becomes high, as can be seen for Sa08 and Sa30. This results from the introduction of the hydrophobic HMDI (the crosslinker) to the hydrophilic amino groups. Similar phenomena have been presented by Hirayama et al. They showed that the pK_a of poly(ϵ -lysine) resins decreased slightly with the introduction of chloromethylloxirane acting as a crosslinker.¹³ From these results, it can be said that the pK_a of the gel particles, which is composed of chitosan polymers, is lowered remarkably owing to gelation in the hydrophobic solvent, when compared with that of chitosan polymer.

The effect of the gel structures on the adsorption of the surfactants was also investigated using gel particles having different degrees of crosslinking, Sa08 and Sa30, formed in the hydrophobic solvent, Decalin. Fig-

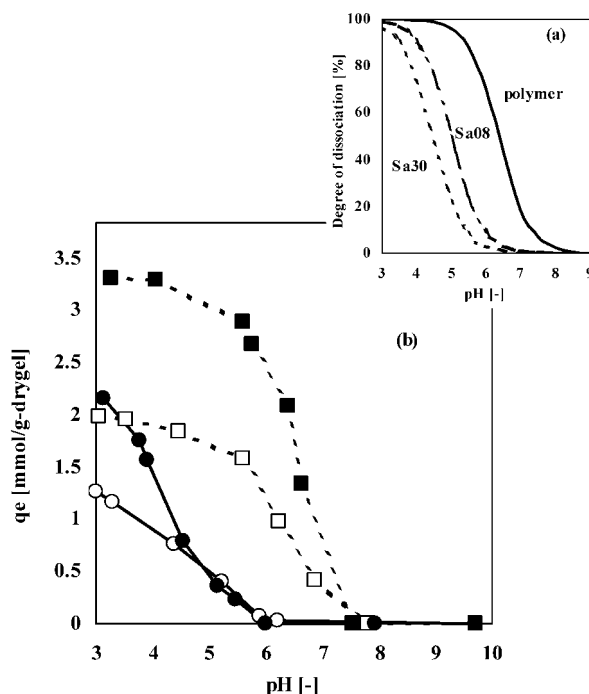


Figure 8 (a) The dissociation curves of the amino groups for chitosan polymer and the chitosan gel particles. (b) The effect of gel structures on the adsorption of the surfactants over a wide range of pH: (●) EBS/Sa08; (○) EBS/Sa30; (■) OBS/Sa08; and (□) OBS/Sa30.

ure 8(b) shows the adsorption amount of the surfactants (EBS and OBS) over a wide range of pH. At pH = 3.0, in which the dissociation of the amino groups in both Sa08 and Sa30 would be nearly 100%, the adsorption amount of both EBS and OBS on Sa08 was about twice that on Sa30. Such a difference in the adsorption amount results from a difference in the ion exchange capacity between Sa08 and Sa30, because the ion exchange capacity of Sa08 is about twice that of Sa30. The adsorption amount of the surfactants on Sa08 and Sa30 lowered to similar values with increasing pH. One reason for such an adsorption behavior seems to be that the hydrophobic network structure of Sa30 favors adsorption in the neutral pH range, where the contribution of the hydrophobic interaction on the adsorption is much larger. However, there was also no adsorption of the surfactants on Sa30 above the pH level where the dissociation of the amino groups does not occur. From the above results, it is concluded that an electrostatic interaction owing to the dissociation of the amino groups is essential for the adsorption of the surfactants, even if a strong hydrophobic interaction exists between the chitosan gel particles and the surfactants.

The chitosan gel particles developed in this study have a large potential for practical applications requiring targeted anionic amphiphilic compounds. As can be seen in Figure 6, the removal of a targeting compound under mild neutral conditions, and the separation of a multicomponent system based upon the hydrophobicity of its targets, are applicable to various industries.

Chitosan gel particles that have different pK_a values and network structures can be prepared by using various hydrophobic solvents during gelation, and a simple crosslinking procedure is applicable to further modify the network structure.

CONCLUSION

The fundamental adsorption properties of chitosan gel particles, prepared by the suspension evaporation method, were experimentally determined using three types of surfactants, ethylbenzenesulfonate (EBS), octylbenzenesulfonate (OBS), and dodecylbenzenesulfonate (DBS).

The chitosan gel particles (water content = 74 to 78 wt % on a wet basis) as prepared by the suspension evaporation method were almost spherical in shape, and were composed of polymer networks. The diam-

eter was about 150 μm , and the size of macropores formed by the polymer networks was about 2 μm .

The adsorption amount of the surfactants (EBS, OBS, and DBS) was remarkably affected by the gel structure, the chain length (the number of carbon atoms) of the surfactants, the pH value, and by the addition of salt (NaCl). The adsorption properties were evaluated from an interaction view point between the chitosan gel particles and the surfactants. The dissociation curves of the amino groups ($\text{R}-\text{NH}_2 + \text{H}^+ \leftrightarrow \text{R}-\text{NH}_3^+$) shifted toward much lower pH values, owing to gelation, compared with those of chitosan. The adsorption of EBS, with its short hydrophobic chain, mainly took place owing to an electrostatic interaction, whereas the adsorption of OBS and DBS, with their much longer hydrophobic chains, occurred via an electrostatic interaction in the low pH range ($3.0 < \text{pH} < 5.0$), and to a hydrophobic interaction as well as an electrostatic interaction in the higher pH range ($5.0 < \text{pH} < 8.0$). The electrostatic interaction, accompanied by the dissociation of the amino groups, was found to be essential for the adsorption of the surfactants having longer hydrophobic chains, even when a strong hydrophobic interaction existed between the chitosan gel particles and the surfactants.

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