Preparation of Resins Having Various Phosphonium Groups and Their Adsorption and Elution Behavior for Anionic Surfactants

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ABSTRACT: Resins containing phosphonium groups were prepared by reaction of chlorohydroxylated glycidylmethacrylate–divinylbenzene macroreticular resins with three trialkylphosphines. Triethylphosphine, tributylphosphine, and trioctylphosphine were used as trialkylphosphines. Adsorption and elution behavior of sodium benzenesulfonate (SBS) and sodium dodecylbenzenesulfonate (SDBS) on the resins were studied. Adsorption of SBS and SDBS increased with increasing the alkyl chain length of phosphonium groups in the resins. The adsorption of SBS decreased with increasing ionic strength of the solution, while the adsorption of SDBS increased with increasing ionic strength of the solution. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 371–378, 1999

Key words: resins; phosphonium groups; trialkylphosphines

INTRODUCTION

Recently, insolubilized agents having antibacterial activity have been developed.[1–7] Insolubilized agents having positively charged groups, such as quaternary ammonium groups and phosphonium groups, or triethylenetetramine side chains, thiol groups, and phenol derivatives are reported to exhibit high antibacterial activity.[8–12] Bacteria are well known to bear many phosphoric acid derivatives present in tissues such as the cytoplasmic membrane of bacterial cells, giving negatively charged bacteria. Therefore, the antibacterial activity of resins with positive groups such as quaternary ammonium groups is considered to be brought about by electrostatic and hydrophobic interactions between the resins and bacteria. However, very few studies have been reported on the antibacterial activities with respect to the molecular interactions between the resins and bacteria. It is difficult to clearly reveal the interaction mechanism between the resins and bacteria because of complexity of bacterial structure.

In this article, we describe the preparation of resins having various phosphonium groups and their adsorption and elution behavior of two kinds of anionic surfactants, sodium benzenesulfonate (SBS) and sodium dodecylbenzenesulfonate (SDBS), as models of the interactions between the resins and bacteria.

EXPERIMENTAL

Materials

Glycidylmethacrylate (GMA) was generously donated by Nippon Yushi Co., Ltd. Trialkylphosphine compounds were generously offered by Nippon Kagaku Kogyo Co., Ltd. Other chemicals were commercially available. GMA and 1,4-divi-

nyl benzene (DVB) were purified by a method reported earlier.[9] Others were used without further purification.

Preparation of GMA–DVB Copolymer Beads

GMA–DVB copolymer beads were prepared by the method reported earlier.[9] First, 50 cm^3 of an aqueous solution containing gelatin at a concentration of 1 wt/vol % and 6 g of anhydrous sodium sulfate were suspended in 450 cm^3 of distilled water by stirring slowly for 20 min in a glass autoclave. GMA, DVB, and isobutylacetate were added to the aqueous solution, where isobutylacetate was used as diluent. After nitrogen was introduced into the solution, 0.5 g of benzoyl peroxide as a radical initiator was added. The polymerization was carried out as follows. The suspension obtained was stirred at a rate of 270 rpm for 30 min at room temperature. The temperature of the suspension was raised to 75–80°C over a period of 1 h, and maintained at 80°C for 1 h. Then the suspension was heated up to 90°C over a period of 1.5 h, and successively maintained at that temperature for 2 h. After polymerization, the suspension was allowed to cool to room temperature. The resins obtained were collected on a funnel and washed with a large quantity of distilled water. Furthermore, the resins were washed with hot water to remove gelatin, and soaked in methanol to completely remove the diluent and the unreacted monomers. Spherical copolymer beads (RG) with a desired range of size (0.25–0.46 mm) were selected.

Preparation of Copolymer Beads Having 2-Chloro-3-hydroxypropyl Groups

Copolymer beads having 2-chloro-3-hydroxypropyl groups were prepared by the same method described previously.[9] To 20 cm^3 of a mixture of 12 mol dm^{-3} HCl (0.7 cm^3) and 1,4-dioxane (19.3 cm^3), 1 g of RG was added and swollen overnight. Afterwards, the mixture was heated at 70°C for 3 h, washed, with distilled water sufficiently and dried to give the copolymer beads having 2-chloro-3-hydroxypropyl groups (RCG).

Preparation of Resins Having Phosphonium Groups

A mixture of 1 g of RCG and a fourfold molar quantity of each trialkylphoshine relative to the amount of 2-chloro-3-hydroxypropyl groups in RCG was heated at 100°C for 10–40 h in 20 cm^3 of dimethylformamide (DMF) or no DMF. Three trialkylphosphines, triethylphosphine (TEP), tributylphosphine (TBP), and trioctylphosphine (TOP) were used in this study. The RCG resins modified with three trialkylphosphines were washed with methanol and distilled water. In addition, the resins obtained were soaked in 1 mol dm^{-3} HCl, and washed with distilled water until water became neutral. After extraction with methanol in a Soxhlet extractor over 10 h, the resin was air dried at room temperature, and was subsequently dried *in vacuo*. The Cl$^-$ -type resins, which have chloride ion as a counter anion, are abbreviated as RCG–TEP (Cl), RCG–TBP (Cl), and RCG–TOP (Cl), respectively. The structures of the resins are shown in Figure 1. Next, the Cl$^-$-type resins obtained were treated with alkaline solution to give the OH type resins that have hydroxide ion as a counter anion. The Cl$^-$-type resins were soaked in 1 mol dm^{-3} NaOH four or five times to completely replace the chloride ion to hydroxide ion in the resins. After washing with water until the water became neutral, the resins were dried to give the OH$^-$-type resins, RCG–TEP (OH), RCG–TBP (OH), and RCG–TOP (OH).

Adsorption of Anionic Surfactants on Resins

Adsorption behavior of the resins with phosphonium groups was examined by using sodium benzenesulfonate (SBS) and sodium dodecylbenzenesulfonate (SDBS) as adsorbates. In 50 cm^3 of an aqueous solution containing 1.7×10^{-3} mol dm^{-3} of SBS or SDBS, 0.1 g of resin was placed and shaken for 24 h at 30°C. The amounts of SBS and SDBS adsorbed were estimated by measuring absorbance at 263 nm for SBS and 261 nm for SDBS, respectively.

Measurement of Critical Micelle Concentration

Critical micelle concentration (cmc) of SDBS in solutions with various ionic strengths were measured by a Du Nouy tensiometer.

Elution of Anionic Surfactants from Resins

In 30 cm^3 of NaOH aqueous solutions with various ethanol contents, 0.1 g of the resin that adsorbed SBS or SDBS was placed and shaken for 24 h at 30°C. The amounts of SBS and SDBS eluted were estimated by measuring absorbance at 263 and 261 nm of the solutions, respectively.

Figure 1   Preparation of resins containing phosphonium groups.

RESULTS AND DISCUSSION

Preparation of Resins Having Phosphonium Groups

Resins containing phosphonium groups were prepared by reaction of RCG with three trialkylphosphines (TEP, TBP, TOP). The results are given in Table I. The amounts of phosphonium groups introduced into RCG in DMF decreased with increasing alkyl chain length of the trialkylphosphines. On the other hand, the reaction of RCG with TOP in the absence of DMF provided resins having higher phosphonium group content compared with the reaction in the presence of DMF. However, the amount of TOP introduced into RCG was smaller than those of other trialkylphosphines in RCG. The steric hindrance of alkyl groups in the trialkylphosphines is considered to be an important factor determining the reactivity of RCG with trialkylphosphines.

Effect of Alkyl Chain Length of the Trialkylphosphonium Groups on the Adsorption

Low molecular-weight molecules and polymers with positively charged nitrogen and phosphorus

Table I   Reaction of RCG[a] with Trialkylphosphines

Experiment No.	Resin (g)	Solvent (cm^3)	Trialkylphosphine[b] (cm^3)	Temp. (°C)	Time (h)	P Content[d] (mEq/g-R)
1	1	DMF 20	TEP[c] 9.0	100	40	0.62
2	1	DMF 20	TBP 3.5	100	40	0.52
3	1	DMF 20	TOP 7.0	100	40	0.22
4	1	—	TOP 7.0	100	40	0.34

[a] RCG; GMA:DVB = 9 : 1 (mol ratio), Cl content = 14 wt %.
[b] Trialkylphosphine: 4 mol % (/Cl).
[c] In the case of TEP, 20% toluene solution was used.
[d] P content in the resins obtained.

Figure 2 Adsorption of SBS (a) and SDBS (b) with resins (Cl type) in NaCl aqueous solutions with various ionic strength. Weight of the resins, 0.10 g; shaking at 30°C for 24 h. ($\bigcirc$, $\bullet$), RCG–TEP (0.7 mEq P^+/g); ($\triangle$, $\blacktriangle$), RCG–TBP (0.69 mEq P^+/g); ($\square$, $\blacksquare$), RCG–TOP (0.22 mEq P^+/g).

atoms such as quaternary ammonium salts, pyridinium salts, and phosphonium salts have been reported to exhibit antibacterial activity. Their antibacterial activities are interpreted in terms of strong interaction and high affinity with bacteria, because there are many phosphoric acid derivatives present in tissues such as the cytoplasmic membrane of bacterial cells. However, very few studies have been performed on the mechanism of the interaction between positively charged atoms and bacteria. We have previously reported that RCG–TOP, having the longest alkyl chains in the phosphonium groups among the three resins—RCG–TEP, RCG–TBP, and RCG–TOP—exhibited the highest antibacterial activity against *E. coli* or *S. aureus* than others.[10] It is worthwhile here to investigate the adsorption of anionic surfactants on the resins having phosphonium groups for a model of the antibacterial activity. In this study, SBS and SDBS were used as the anionic surfactants.

To explore the effect of the electrostatic and hydrophobic interactions on the adsorption behavior, the adsorption on the three Cl-type resins having different alkyl groups in the phosphonium groups—RCG–TEP, RCG–TBP, and RCG–TOP—were performed at various ionic strengths by varying concentration of sodium chloride in water. The changes in the amounts of adsorption (mol/Eq P^+) of SBS or SDBS after shaking for 24 h are shown in Figure 2. The adsorbed amounts of SBS on the resins were decreased with an increase in ionic strength, while those of SDBS were increased oppositely. SDBS is as-

sumed to be more hydrophobic than SBS, because of dodecyl group in the SDBS molecule, resulting in the higher adsorption of SDBS compared to SBS in saline. In addition, the adsorbed amounts of both SBS and SDBS were increased with an alkyl chain length of the phosphonium groups, that is, the amounts adsorbed per phosphonium group were in the order of RCG–TEP < RCG–TBP < RCG–TOP. An addition of electrolytes is known to shield the electrostatic interaction between charged species.[13] Therefore, the decrease in the adsorbed amounts of SBS by addition of the electrolyte is explained as the shielding effect of the electrolytes. On the other hand, the ionic strength dependence of the adsorption of SDBS was enhanced with the alkyl chain length, as can be seen in Figure 2(b). These results indicate that in the case of SDBS, the adsorption was significantly affected by not only electrostatic interaction but also hydrophobic interaction between the phosphonium groups in the resins and SDBS. Swelling of hydrogels in water is known to strongly depend on the concentration and kind of electrolytes in water, arising from an osmotic pressure and dehydration effect of the electrolytes.[14] The resins bear many positively charged phosphonium groups in the molecule. Thus, the shielding effect of the electrolytes is expected to affect the electrostatic repulsion between positively charged phosphonium groups in the resins. Although the reason for the significant increase in the adsorption of SDBS with the ionic strength is not clear at the present stage, it may be assumed that one factor is changes in the morphology of

Figure 3 Adsorption of SBS with RCG–TOP (OH type, 0.23 mEq P^+/g) from aqueous solutions containing no NaCl as a function of initial SBS concentration. Weight of resins, 0.10 g; shaking at 30°C for 24 h.

alkylphosphonium groups in the resins by adding the electrolyte; i.e., formation of aggregates of long alkyl chains and changes in the solvation (hydration) structure in the vicinity of the alkylphosphonium groups.

Effect of the Concentration of Anionic Surfactants on the Adsorption

The decrease in the amounts of adsorption of SBS in the presence of the electrolyte as well as the increase in those amounts with increasing alkyl chains can be interpreted in terms of the effects of the electrostatic and hydrophobic interactions. However, the origin of the significant increase in the amounts of SDBS adsorbed in the presence of the electrolyte is not yet clear. The changes in the morphology in the vicinity of the alkylphosphonium groups is one factor resulting from the peculiar electrolyte effect on the adsorption of SDBS described above. On the other hand, SDBS is known to form micelle aggregates higher than the critical micelle concentration of SDBS.[15] It is of interest here to examine the effects of morphology of adsorbates and adsorbents to reveal the effect of electrolytes on the adsorption of SDBS. Therefore, the adsorption of anionic surfactants on the resins was examined in solutions with various amounts of surfactants. Figure 3 shows the adsorbed amounts of SBS on RCG–TOP (OH) in water as a function of concentration of SBS. Although a little increase in the adsorbed amount of SBS was observed at a lower concentration of SBS, the adsorbed amounts of SBS were almost constant above 0.5×10^{-3} mol dm^{-3} of SBS. In contrast with the adsorption behavior of SBS in water, the adsorbed amounts of SDBS increased with increasing concentration of SDBS in saline,

Figure 4 Adsorption of SDBS with RCG–TOP (Cl type, 0.13 mEq P^+/g) from aqueous solutions containing NaCl as a function of initial SDBS concentration. Weight of the resin, 0.10 g; shaking at 30°C for 24 h; ionic strength, 0.15.

and that of SDBS went up to over unity of mol/Eq P^+ (Fig. 4). The data in Figures 3 and 4 exhibit the average amounts of anion surfactants adsorbed per one alkylphosponium group attached to the resin. Namely, the adsorbed amounts of SDBS were more than the stoichiometrical quantity based on the amounts of the alkylphosphonium groups introduced in the resin above 0.5×10^{-3} mol dm^{-3} of SDBS. It is known that the increase of the ionic strength brings about a decrease in the critical micelle concentration as well as the increase in the size of the micelle aggregates.[15] To study the effect of formation of aggregation on the characteristic adsorption behavior of SDBS in saline, the critical micelle concentration of SDBS was measured. Figure 5 shows the critical micelle concentration of SDBS in NaCl aqueous solutions at various ionic strengths. It is

Figure 5 Cmc of SDBS in solutions with various ionic strengths at 25°C.

Figure 6 Temperature dependence of adsorption of SBS (a) and SDBS (b) with resins from water ($\square$, $\bigcirc$) and 0.9% NaCl aqueous solutions ($\blacksquare$, $\bullet$). Weight of the resins, 0.10 g; shaking at 30°C for 24 h. ($\square$, $\blacksquare$), RCG–TBP (Cl type, 0.42 mEq P^+/g); ($\bigcirc$, $\bullet$), RCG–TOP (Cl type, 0.13 mEq P^+/g).

clearly seen that the critical micelle concentration decreases with increasing content of sodium chloride. Under the conditions for measuring adsorption of SDBS in Figure 4, the critical micelle concentration was 0.18×10^{-3} mol dm^{-3}. Consequently, SDBS was expected to form micelle aggregates above 0.18×10^{-3} mol dm^{-3}. The critical micelle concentration is roughly consistent with the concentration of SDBS, at higher concentration of which the adsorbed amount of SDBS exceeds 1 mol/Eq P^+. Therefore, the ionic strength effect on the adsorption of SDBS may also be closely related to the formation of the micelle aggregates.

Effect of Temperature on the Adsorption Behavior

The morphology change by increasing the ionic strength is attributable to the increase in the hydrophobic interaction, because the ionic strength effect is observed only for SDBS having long alkyl chain moiety in the molecule, and is enhanced with the alkyl chain length of alkylphosphonium groups introduced in the resins. The hydrophobic interaction is known to depend on temperature.[16] To explore the contribution of the hydrophobic interaction on the adsorption of the anionic surfactants, therefore, the temperature dependence of the adsorption behavior was examined. Figure 6 shows the adsorbed amounts of SBS and SDBS on both the RCG–TBP (Cl) and RCG–TOP (Cl) resins at various temperatures. The adsorbed amounts of SBS on the resins in water were larger than those on the resins in saline. Little change in the amounts of SBS adsorbed was induced by increasing temperature. There is no temperature dependence of the amounts

of adsorption. In contrast with SBS, the adsorbed amounts of SDBS on the resins were increased with increasing temperature, as shown in Figure 6(b). In addition, the amounts of SDBS adsorbed on RCG–TOP are larger than those on RCG–TBP. As clearly shown in Figure 2, the ionic strength effect became larger as the alkyl chain length became longer. The results, shown in Figures 2 and 6, emphasize that the morphology change in the vicinity of phosphonium groups contributes strongly to the adsorption behavior of SDBS in saline.

Elution of Anionic Surfactants Adsorbed on the Resins

It is worthwhile here to investigate the elution behavior of the anionic surfactants from the resins and the possibility of recycled use of the resins. Figure 7 shows the changes in the eluted amounts of the anionic surfactants from the OH type of RCG–TBP and RCG–TOP resins as a function of the normality of sodium hydroxide (NaOH). Almost quantitative amounts of SBS were eluted from both resins, while SDBS was not eluted regardless of the normality of NaOH. The adsorption of SBS on the resins with the alkylphosphonium groups is mainly attributed to the electrostatic interaction. Therefore, the elution was easily brought about through the ion exchange between SBS and OH$^-$ species.

Figure 8 shows the influence of ethanol on the elution of SDBS from the RCG–TOP (OH) resin. Although SDBS was scarcely eluted with NaOH aqueous solution of 1.0 mol dm^{-3}, as can be seen in Figure 7, the eluted amounts of SDBS increased with increasing the ethanol content in the

Figure 7 Elution of SBS ($\bigcirc$, $\square$) or SDBS ($\bullet$, $\blacksquare$) adsorbed on resins with NaOH aqueous solutions. Weight of resins, 0.10 g; shaking at 30°C for 24 h. ($\square$, $\blacksquare$), RCG–TBP (OH type, 0.47 mEq P^+/g); ($\bullet$, $\bigcirc$), RCG–TOP (OH type, 0.23 mEq P^+/g).

Figure 9 Elution of SDBS adsorbed on RCG–TOP (0.12 mEq P^+/g) with 40% ethanolic aqueous solutions containing various contents of NaOH. Weight of the resin, 0.10 g; shaking at 30°C for 24 h.

alkaline elution solution (Fig. 8). In particular, amounts of SDBS of more than 90% were eluted with NaOH solutions containing ethanol of more than 30 vol %. This acceleration of elution may be related to the interfering affect of ethanol on the hydrophobic interaction. However, a 40 vol % ethanol solution without NaOH did not bring about the elution of SDBS from the resin, as shown in Figure 9. In addition, the eluted amount of SDBS was remarkably increased by increasing NaOH content in the alcoholic solution. OH^- species are required to elute SDBS from the resins. The results imply that the adsorption and elution of SDBS are based on the cooperation of electrostatic and hydrophobic molecular interactions.

CONCLUSION

The resins containing alkylphosphonium groups were prepared by reaction of chlorohydroxylated glycidylmethacrylate–divinylbenzene macroreticular resins with three alkylphosphines.

The adsorption of SBS and SDBS increased with increasing the alkyl chain length of trialkylphosphonium groups in the resins. The adsorption of SDBS increased with increasing the ionic strength of the solution, while the adsorption of SBS decreased.

The adsorption of SDBS on the RCG–TOP increased with increasing the temperature. The elution of SDBS from the RCG–TOP was completely performed using 1 mol dm^{-3} NaOH aqueous solution containing ethanol of 40 vol %. The elution behavior demonstrates that the adsorption of SDBS is closely related to the cooperative action of the hydrophobic and electrostatic interactions.

It was thus found that RCG–TOP, showing the highest antibacterial activity, had the highest adsorption ability for anionic surfactants such as SDBS. The higher antibacterial activity of RCG–TOP is considered to be brought about by strong interaction between the resins and bacteria.

Figure 8 Elution of SDBS adsorbed on RCG–TOP (0.11 mEq P^+/g) with 1 mol dm^{-3} NaOH aqueous solutions containing various contents of ethanol. Weight of the resin, 0.10 g; shaking at 30°C for 24 h.

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