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# Adsorption of Nonionic Surfactants on Chemically Modified Styrene–Divinylbenzene Copolymers

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## Abstract

Two series of resins with both polar and nonpolar regions were synthesized by the introduction of α-oxoalkyl and α-hydroxyalkyl groups to a porous low cross-linked styrene–divinylbenzene (7.5% divinylbenzene). These resins showed higher adsorption capacity for polyoxyethylene-type nonionic surfactants than did the starting resin. Resins with shorter alkyl chains are particularly more effective than those with longer chains. It is suggested that the polar groups on the modified resins contribute to the increase in adsorption of the surfactants.

## INTRODUCTION

Various types of surfactants have been used for a wide range of industrial and household purposes. Contamination of wastewater with these surfactants is unavoidable, and this leads to environmental pollution. A variety of techniques have been applied to remove surfactants from wastewater. These include biodegradation (*1*), adsorption on synthetic polymers (*2*) and activated carbon (*3*). In the field of water pollution research and control, development of a more effective method to remove surfactants is desirable.

Surfactants possess both polar and nonpolar regions on the same molecule. In general, cationic/anionic surfactants containing dissociative functional groups may be easily removed by ion-exchange resins. On the other hand, nonionic surfactants with undissociated groups in their hydrophilic region have been removed with porous styrene–divinylbenzene (St-DVB) copolymers (*4*). The adsorption of nonionic surfactants onto the polymer

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is mainly based on the hydrophobic interaction between the surfactant and adsorbent. Therefore, a prerequisite for an effective adsorbent is a large surface area. However, it is also necessary to take into account the existence of factors other than hydrophobicity, such as the interaction between the adsorbent and the hydrophilic region of a nonionic surfactant. The introduction of an appropriate substituent possessing both polar and nonpolar groups to the hydrophobic resin matrix is a possible approach to obtaining an effective adsorbent for nonionic surfactants. In this paper we propose two series of new macroreticular (MR)-type St-DVB resins possessing α-oxoalkyl and α-hydroxyalkyl groups. We investigated their adsorption behavior for two kinds of nonionic surfactants. The effect of functional groups introduced into an aromatic nucleus on the adsorption of a nonionic surfactant is further discussed by considering changes in the physical properties of the resins.



## EXPERIMENTAL

### Apparatus and Reagents

The physical pore structures of resins were measured with a MONOSORB (Iwaki Co. Ltd.) and a mercury porosimeter (type 220, Carlo Erba). Infrared spectra (KBr disks) were recorded with a Hitachi 270-30 spectrophotometer. Absorption spectra in the ultraviolet region were measured with a Hitachi U-3200 spectrophotometer. Divinylbenzene (DVB 50–55%) and styrene (St) were washed with a 5% sodium hydroxide solution to remove stabilizer. The St-DVB resin (7.5% DVB, MR type, 35–60 mesh fraction), used as the starting resin, was synthesized by suspension polymerization in our laboratory as previously described (5). Heptaoxyethylene dodecyl ether (HOE) was purchased from Wako Pure Chemical Ind. Ltd. Nonylphenyl deca(oxyethylene glycol) monoether [NP-EO(10)] was obtained from Wakayama Research Laboratory KAO Co. All other chemicals were reagent grade.

### Synthesis of α-Oxoalkylated Resin

Thirty grams of the starting resin and 300 mL carbon disulfide stood at room temperature overnight in a 500-mL three-necked flask. Finely powdered anhydrous aluminum chloride was added to the flask. Acyl chloride (0.45 mol) was added dropwise at temperatures from 10 to 12°C for 1 h, and then the reaction mixture was stirred at 25°C for 6 h. The reaction mixture was poured into 10% hydrochloric acid containing cracked ice. The resulting resin was filtered, washed successively with water, acetone, benzene, and methanol, and then dried at 60°C for 24 h.

### Preparation of α-Hydroxyalkylated Resins

Ten grams of the α-oxoalkylated resin, 100 mL dioxane, 10 g sodium borohydride, and 100 mL distilled water were gently stirred in a 300-mL three-necked flask at room temperature for 24–48 h. A small portion of the resin collected at various times was analyzed by infrared spectrophotometry to confirm the disappearance of the absorption band due to the carbonyl group at 1680 $cm^{-1}$. After completion of reduction, the product was filtered, washed with water and methanol, and then dried at 60°C.

### Determination of the Acyl Group of α-Oxoalkylated Resins

One gram of the resin, 1 g hydroxylamine hydrochloride, 12 mL pyridine, and 8 mL methanol were refluxed and stirred in a 50-mL three-necked flask for 12 h. The reaction product was washed with water, 0.1 *M* hydrochloric acid, and methanol, and then dried. The nitrogen content of the resin was determined by elemental analysis.



### Measurement of Swelling Ratio

Approximately 1 g dried resin was accurately weighed and transferred to a 10-mL measuring cylinder to measure the dry volume ($V_1$) per unit weight of resin. An appropriate amount of organic solvent was added to the measuring cylinder. After deaeration, the cylinder was allowed to stand at 25°C for 24 h to measure the wet volume ($V_2$) per unit weight of resin. The swelling ratio of resin was expressed as $V_2/V_1$.

### Adsorption Studies

Fifty milligrams of dried resin was immersed in methanol in a 50-mL conical flask. The methanol was replaced with distilled water, and 20 mL nonionic surfactant solution was added. The flask was shaken at 25°C for 24 h and then the resin was filtered off. The concentration of surfactant in the filtrate was measured. The adsorption was determined from the difference between the initial and equilibrium concentrations.

HOE was determined by the cobalt thiocyanate method (*6*), and NP-EO(10) was determined by UV absorption spectrophotometry at 275 nm.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Resins

The macroporosity of MR-type St-DVB is defined in terms of pore volume or surface area in the dry state. These resins possess gel porosity formed in the swollen state. In St-DVB with a low degree of crosslinking, the gel porosity is significant in the final polymer network rather than the

macroporosity. In this study, St-DVB crosslinked with 7.5% DVB was selected as the starting resin in order to evaluate the effects of chemical modification on structural parameters and adsorption of nonionic surfactant.

An oxoalkyl group [$CO(CH_2)_nCH_3$); $n$ = 0–3, 6] was introduced into St-DVB by the Friedel-Crafts reaction by using anhydrous aluminum chloride as a catalyst. The carbonyl groups of the resulting resin were converted into oximate by treatment with hydroxylamine in the presence of pyridine. Since the characteristic absorption of carbonyl groups at 1680 $cm^{-1}$ disappeared from the infrared spectra of the resins after oximation, the content of the α-oxoalkyl groups was estimated from the nitrogen contents, as shown in Table 1. These results indicate that five kinds of resins containing different lengths of oxoalkyl groups were synthesized. Predictably, the content of oxoalkyl groups decreased with an increase in the length of the alkyl chain.

The carbonyl groups in the α-oxoalkylated resins [P-$CO(CH_2)_nCH_3$] were reduced to hydroxyl groups with sodium borohydride (7). The extent of reduction was evaluated by the decrease in absorption at the band corresponding to the carbonyl group. The infrared spectra of the reduced resins [(P-$CH(OH)(CH_2)_nCH_3$)] exhibited a substantial decrease in the characteristic absorption of carbonyl groups and gave a broad absorption band near 3400 $cm^{-1}$, assigned to a OH stretching vibration. From the change in the absorption spectrum it was found that most of the oxoalkyl group was reduced to a hydroxyalkyl group, but a small amount of the carbonyl group remained in the inner parts of the resin.



TABLE 1
Determination of Acyl Groups in Oxoalkylated Resins after Oximation

| Resin[a] | N content (mmol/g) |
|---|---|
| P-$COCH_3$ | 5.21 |
| P-$CO(CH_2)_1CH_3$ | 5.04 |
| P-$CO(CH_2)_2CH_3$ | 4.70 |
| P-$CO(CH_2)_3CH_3$ | 4.31 |
| P-$CO(CH_2)_6CH_3$ | 3.62 |

[a]P = MR-type polystyrene crosslinked with 7.5% DVB, 35–60 mesh fraction.

TABLE 2
Physical Characteristics of Resins

| Resin[a] | Specific surface area ($m^2/g$) | Pore volume (mL/g) | Average pore radius (nm) |
|---|---|---|---|
| P | 50.4 | 0.316 | 14.1 |
| P-$COCH_3$ | 60.7 | 0.457 | 21.3 |
| P-$CO(CH_2)_2CH_3$ | 40.5 | 0.526 | 27.3 |
| P-$CO(CH_2)_6CH_3$ | 13.6 | 0.370 | 41.0 |
| P-$CH(OH)CH_3$ | 35.1 | 0.344 | 14.2 |
| P-$CH(OH)(CH_2)_2CH_3$ | 33.9 | 0.443 | 17.4 |
| P-$CH(OH)(CH_2)_6CH_3$ | 20.2 | 0.277 | 18.7 |

[a]P = MR-type polystyrene crosslinked with 7.5% DVB, 35–60 mesh fraction.



Table 2 summarizes the specific surface area, pore volume, and average pore radius of the resins as determined in the dry state. The starting resin used in this experiment has a physical pore structure. The chemically modified resins also possess a characteristic physical pore structure which differed from that of the starting resin. In most of the modified resins, a decrease in specific surface area and an increase in pore volume and average pore radius were observed compared with the starting resin. Therefore, although it is difficult to explain the relationship between the functional groups introduced and the physical properties, the differences in the physical properties of the resins indicate that the polymer network has high flexibility.

Table 3 shows the volume swelling ratios in various solvents. The introduction of polar groups, such as carbonyl and hydroxy groups, to the hydrophobic starting resin caused a considerable change in the swelling property. Among the resins tested, P-$CH(OH)CH_3$ showed the highest swelling ratio in methanol and the lowest swelling ratio in benzene. Thus the swelling property of P-$CH(OH)CH_3$ is markedly different from that of the starting resin. In a low crosslinked resin, such as 7.5%, alteration in the chemical structure based on different chemical modifications was clearly reflected in the swelling property.

## Adsorption of Nonionic Surfactants

Figures 1 and 2 show the adsorption isotherms of HOE and NP-EO(10) on P-$CO(CH_2)_nCH_3$ and P-$CH(OH)(CH_2)_nCH_3$, respectively. HOE and

TABLE 3
Volume Swelling Ratio[a] of Chemically Modified Resins in Organic Solvents

| Resin[b] | Methanol | *n*-Propanol | Acetonitrile | Benzene | Dioxane | Tetra-hydrofuran |
|---|---|---|---|---|---|---|
| P | 1.09 | 1.14 | 1.31 | 1.66 | 1.66 | 1.73 |
| P-$COCH_3$ | 1.20 | 1.28 | 1.37 | 1.48 | 1.62 | 1.68 |
| P-$CO(CH_2)_2CH_3$ | 1.15 | 1.24 | 1.29 | 1.52 | 1.47 | 1.59 |
| P-$CO(CH_2)_6CH_3$ | 1.26 | 1.18 | 1.38 | 1.84 | 1.65 | 1.77 |
| P-$CH(OH)CH_3$ | 1.93 | 1.97 | 1.48 | 1.36 | 1.98 | 2.01 |
| P-$CH(OH)(CH_2)_2CH_3$ | 1.66 | 1.68 | 1.38 | 1.51 | 1.70 | 1.78 |
| P-$CH(OH)(CH_2)_6CH_3$ | 1.53 | 1.59 | 1.29 | 1.60 | 1.50 | 1.68 |

[a]Swelling ratio is expressed in the ratio of dry volume of resin per weight (mL/g) to wet volume of resin per weight (mL/g).
[b]P = MR-type polystyrene crosslinked with 7.5% DVB, 35–60 mesh fraction.



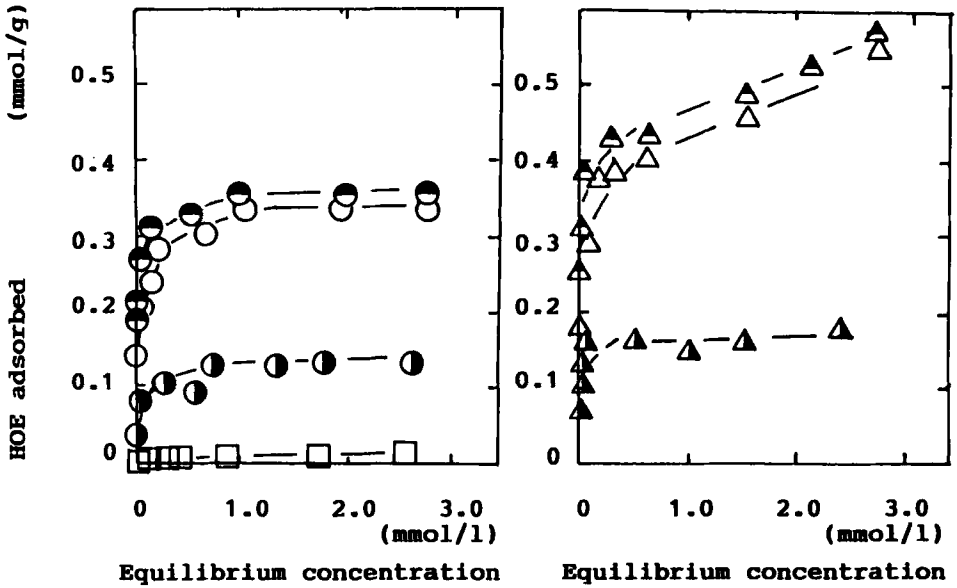


FIG. 1. Adsorption isotherms of HOE on the resins at 25°C. (□) P; (◓) P-$COCH_3$; (○) P-$CO(CH_2)_2CH_3$; (◑) P-$CO(CH_2)_6CH_3$; (▲) P-$CH(OH)CH_3$; (△) P-$CH(OH)(CH_2)_2CH_3$; (▲) P-$CH(OH)(CH_2)_6CH_3$. P = MR-type polystyrene crosslinked with 7.5% DVB, 35–60 mesh fraction.

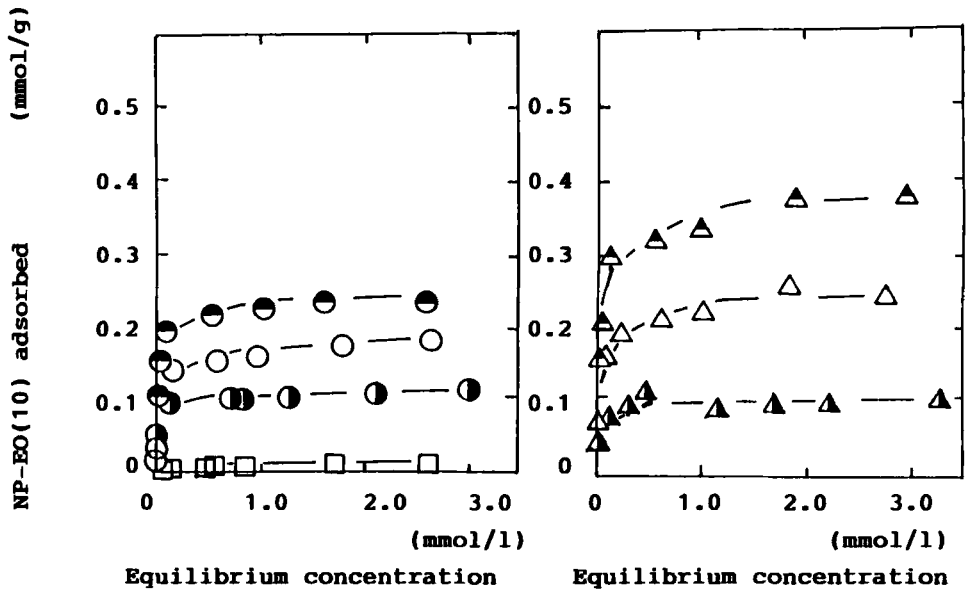


FIG. 2. Adsorption isotherms of NP-EO(10) on the resins at 25°C. Symbols are the same as in Fig. 1.

NP-EO(10) are typical polyoxyethylene series nonionic surfactants and contain hydrophilic ether linkages and undissociated hydroxyl groups. HOE contains an alkyl chain, while NP-EO(10) has an alkylbenzene hydrophobic group.

As seen in Fig. 1, the adsorption of HOE is markedly affected by the introduction of an α-oxoalkyl or an α-hydroxyalkyl group on St-DVB. The modified resins effectively adsorbed more HOE than the starting resin, and this feature was marked in P-$CO(CH_2)_{n=0,2}CH_3$ and P-$CH(OH)(CH_2)_{n=0,2}CH_3$. In the case of P-$CO(CH_2)_6CH_3$ and P-$CH(OH)(CH_2)_6CH_3$, which have longer alkyl chains, the adsorption of HOE was decreased compared with those resins with shorter alkyl chains, i.e., the adsorption of HOE tends to decrease with an increase in the length of the α-oxoalkyl or α-hydroxyalkyl chains introduced. In the case of NP-EO(10), a similar tendency in adsorption was also observed, although NP-EO(10) adsorbed less than HOE. The favorable effects of the modification of the starting resin were ascertained.

A large surface area is one of the important factors for effective adsorption, especially in highly crosslinked polystyrene. The surface areas of the modified resins are not as large due to the low crosslinkage of the starting resin used in this experiment. Therefore, a marked increase of

adsorption by chemical modification demonstrates the contribution of other factors rather than the surface area.

Any MR network has, besides permanent porosity, a degree of swelling porosity which exists only in the swollen state (*8*). It is to be expected that the swelling porosity plays an important role in increasing the adsorption of nonionic surfactants. The swelling data in methanol shown in Table 3 may support our idea, i.e., P-CH(OH)$CH_3$ indicates that the highest swelling ratio has the highest efficiency for the adsorption of both surfactants.

The adsorption of the surfactant was also influenced by the chemical structure of the substituents. This suggests that the hydroxyl or carbonyl group in the substituent contributes to adsorption. There is more adsorption on the hydroxyalkylated than on the oxoalkylated resins with the same number of carbon atoms. A contribution by hydrogen bonding between the ethylene oxide groups in polyoxyethylene-type surfactants and hydroxyl or carbonyl groups on the modified resin must be considered. The hydrogen bondability of the hydroxyl group is stronger than that of the carbonyl group, which reflects a difference in adsorption capacity. In addition, the extent of swelling in methanol used for immersion of the hydroxyalkylated resin is larger than that of the oxoalkylated resin, and this may be another factor.

It is concluded that the introduction of an appropriate substituent with polar groups to the hydrophobic resin matrix is a useful, versatile approach in the development of an effective adsorbent for nonionic surfactants.



## REFERENCES


1. R. D. Swisher, *Surfactant Biodegradation*, 2nd ed., Dekker, New York, 1987. K. Oba and K. Miura, *Yukagaku, 34,* 10 (1985); *Chem. Abstr., 102,* 137141r (1985). R. M. Sykes, A. J. Rublin, S. A. Rath, and M. C. Chang, *J. Water Pollut. Control Fed., 51,* 71 (1979).
2. P. Anand and B. Dasare, *Indian J. Technol., 22,* 225 (1984). R. L. Hinrichs and V. L. Snoeyink, *Water Res., 10,* 79 (1976). I. M. Abrams, *Am. Chem. Soc., Div. Wastewater Chem. Prepr.*, p. 68 (1963); *Chem. Abstr., 61,* 11737e (1964). I. M. Abrams and S. M. Lewon, *J. Am. Water Works Assoc., 54,* 537 (1962).
3. M. Allali-Hassani, O. Dusart, and M. Mazet, *Water Res., 24,* 699 (1990). C. E. Renn, *J. Am. Water Works Assoc., 53,* 129 (1961).
4. T. Saito, K. Higashi, Y. Murakami, and K. Hagiwara, *Mizu Shori Gijutsu, 19,* 825 (1978); *Chem. Abstr., 90,* 39832f (1979).
5. A. Sugii, N. Ogawa, and H. Hashizume, *Talanta, 27,* 627 (1980).
6. R. A. Greff, E. A. Setzkorn, and W. D. Leslie, *J. Am. Oil Chem Soc., 42,* 180 (1965).
7. M. Haratake, N. Ogawa, and A. Sugii, *Anal. Sci., 4,* 591 (1988).
8. P. P. Wieczorek, B. N. Kolarz, and H. Galina, *Angew. Makromol. Chem., 126,* 39 (1984).


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