

# Removal of Dodecylbenzenesulfonate by a System Based on Poly(Butadiene–Maleic Anhydride)

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## Synopsis

Poly(butadiene–maleic anhydride) was aminated with methoxypropylamine. Although this reaction product (APBM) was easily soluble in water, when APBM was supported on activated alumina, APBM/alumina hybrid materials (HM) removed dodecylbenzenesulfonate (DBS) solutes in water. The effects of the supported amounts and of the initial concentrations of DBS on the removed amounts were studied.

## INTRODUCTION

Nowadays, many kinds of surfactants are used in quantity in textile dyeing and finishing industries, in manufacture of paints, agriculture chemicals, food, cosmetics, and others. The surfactants used are present in the waste water drawn off from these manufacturing factories.

From the stand points of preservation of the environment and re-use of industrial waste water, it is important to remove solutes in water. Metal ions and cationic and anionic organic substance solutes in water can be removed by ion exchange resins,<sup>1,2</sup> and also there are a number of studies on preparation of agents for removing them from aqueous solutions.<sup>3</sup> We have already reported studies on preparation of polymers which can remove polyethylene glycol mono-*p*-nonylphenyl ether, one of the nonionic surfactants, solutes in water.<sup>4-6</sup>

Although copolymers of maleic anhydride with vinyl methyl ether, butadiene, and other monomers are used in many fields, they are not done for removing surfactants from aqueous solutions. Therefore, we studied utilization as an agent for removing dodecylbenzenesulfonate (DBS), one of the anionic surfactants, from its aqueous solution.

## EXPERIMENTAL

### Materials

Reagents and materials used are as follows: Commercial poly(butadiene–maleic anhydride) (abbreviated PBM, 25% in acetone, Polyscience, Inc., Cat # 7788, Lot # 27401), methoxypropylamine (guaranteed reagent, Tokyo Kasei Co.), sodium dodecylbenzenesulfonate (BDS, extra pure, Tokyo Kasei Co.), and activated alumina (Aluminum Oxide W 200 Acid, for column chromatography, Activity grade Super 1, Pharmaceutical GmbH and Co., West Germany). The size composition of the alumina is as follows: 50–100 mesh (0.297–0.149 mm) 15.7 wt%, 100–200 mesh (0.149–0.074 mm) 65.7 wt%,

200–250 mesh (0.074–0.063 mm) 11.7 wt%, smaller than 250 mesh 6.9 wt%. These were employed without further purification.

### Reaction of PBM with Methoxypropylamine

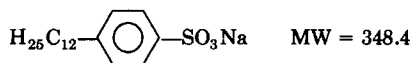
PBM (25% solid in acetone) 6.10 g, which corresponds to 1/100 of atomic group weight of the repeating unit when PBM was assumed to be 1:1 copolymer, and 10 mL of acetone were put in a three-necked flask. When methoxypropylamine 1.78 g (0.020 mol) were added in the flask with stirring at room temperature, the temperature of the reaction mixture rose rapidly. The mixture immediately became turbid and sticky block. Therefore, the reaction product separated from the solvent. After the solvent was removed by decantation, a brown sticky product like thick malt syrup was obtained. The product was dried *in vacuo* at 80°C. Yield: 2.64 g. This product was insoluble in methyl and ethyl alcohol, benzene, dioxane, and hexane, but easily soluble in water. The aminated PBM is hereafter abbreviated APBM.

### Preparation of APBM / Alumina Hybrid Materials

Support of APBM on alumina was carried out as follows: After 0.1–0.25 g of APBM were dissolved in 5 mL of distilled water, to this solution were added 5 g of activated alumina, and then this mixture was well shaken. After the APBM was allowed to impregnate onto the alumina by standing the mixture for 2 h with occasional shaking, the water was evaporated at 95–98°C. After the remained APBM/alumina hybrid material was heated for 1 h at 130°C, it was washed with distilled water by shaking in order to remove the very fine powder of APBM/alumina hybrid material and of the alumina, which were present as components of muddiness in the water, and to remove components which are easy to elute from the hybrid material. The water was removed by decantation. Although this operation was repeated four times, absorbance of the decanted water at 223 nm was still observed a very little. The washed APBM/alumina hybrid material was heated again for 1 h at 130°C. Thus APBM supported on alumina, i.e., APBM/alumina hybrid material (hereafter abbreviated HM) was obtained. The amount (%) of APBM supported on alumina was determined by gravimetric analysis.

### Removal of DBS in Water

One quarter grams of HM were put in 50 mL of Erlenmyer flasks, and then to the flasks were poured 50 mL of aqueous solution of 50–250 ppm concentration of DBS:

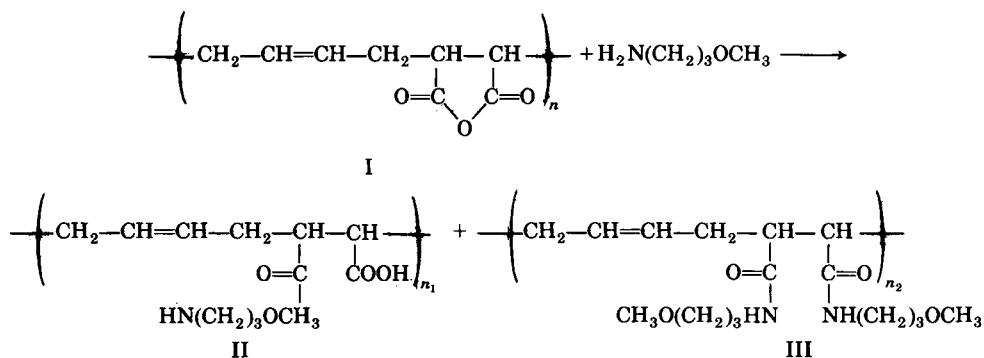


The methods for removing DBS and for determining the amount of removed DBS are similar to those described in the previous papers.<sup>4–6</sup> The absorbance of aqueous solution of DBS was measured at 223 nm using Hitachi Double Beam Spectrophotometer Type 220 A.

## RESULTS AND DISCUSSION

## Reaction of PBM with Methoxypropylamine

The reaction of PBM with methoxypropylamine seems to proceed as shown in Scheme 1:



Scheme 1.

The elementary analysis values of the reaction product as well as the calculated element contents of II and III are as follows:

	H %	C %	N %
the product	8.89	59.00	7.40
II	7.94	59.73	5.81
III	9.03	61.51	8.97

The product is assumed to be a mixture of II and III from the elementary analysis values. When the component amounts of II and III in the product are calculated from its found N %, the amounts of II and III are 56 and 44%, respectively. The calculated H and C % of this product are 8.49 and 60.60%, respectively. The found C and H % are much different from the calculated values.

## Removal Rate

One quarter grams of activated alumina and HM having a different amount of supported APBM were placed in 50 mL of the initial concentration of 100 ppm DBS. Figure 1 illustrates the decrease in the residual concentration with lapse of time. The alumina itself did not remove DBS solutes in water. Therefore, it can be said that this decrease in DBS concentration was caused by the APBM supported on alumina.

Since this removal rates of these HM were small, it took more than 4 days to arrive at the removal equilibrium. The removal rate and the removed amount at the equilibrium (10th day from the beginning of the removal) are larger in HM with larger supported amount than in smaller one. The removed amounts at the equilibrium were determined from the initial concentrations.

Table I lists the amounts per unit masses of HM (mg/g HM) and of APBM itself {mg/g APBM [= mg/g HM/supported amount (g)]}. In the

TABLE I  
Amount of DBS Removed by the Aminated Poly(butadiene-Maleic Anhydride) Supported on the Activated Alumina<sup>a</sup>

Supported amount (%)	Removal from 50 ppm solution		Removal from 100 ppm solution		Removal from 250 ppm solution	
	Equilibrium concn (ppm)	Removed amount mg/g HM	Equilibrium concn (ppm)	Removed amount mg/g HM	Equilibrium concn (ppm)	Removed amount mg/g HM
1.7	0.9	9.8	2.1	19.7	51.6	39.7
2.3	0.9	9.8	7.2	18.5	78.1	34.4
2.4	0.9	9.8	3.1	19.4	63.3	37.3
2.6	1.2	9.8	9.2	18.2	95.0	37.3
3.4	2.5	9.5	18.1	16.4	114.2	27.2
						800

<sup>a</sup>A quarter grams of the aminated poly(butadiene-maleic anhydride) supported on activated alumina (HM) was placed in 50, 100, ..., 250 ppm aqueous solutions of DBS and allowed to stand at 25° C. These values are those determined at the state which the residual concentrations of DBS decreased scarcely.

<sup>b</sup>Aminated poly(butadiene-maleic anhydride)

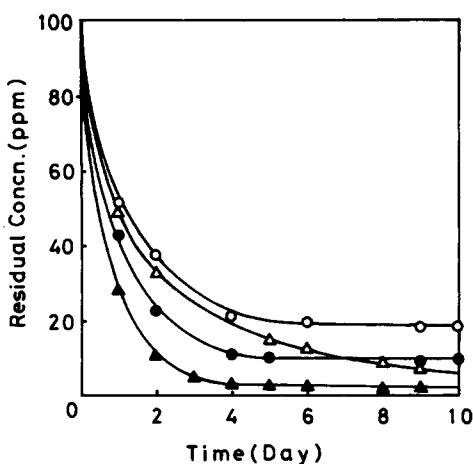
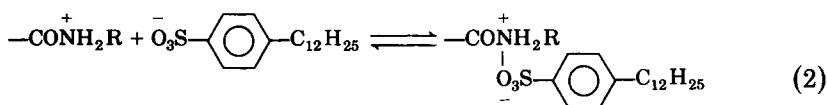
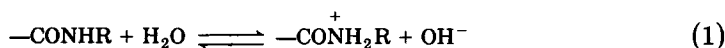


Fig. 1. Decreases of residual concentrations in the removal of DBS by SPBM/alumina hybrid materials at 25°C. Initial concentration 100 ppm-50 mL; APBM/alumina 0.25 g; supported amount: (○) 3.4%; (●) 2.6%; (△) 2.3%; (▲) 1.7%.

case of the initial concentration of 50 ppm, the removed amounts of the all HM are 9.8 mg/g HM, and the residual concentrations were 1–2 ppm. In the case of the initial concentrations of 100–250 ppm, however, the removed amounts (mg/g APBM) decrease with an increase in the amount of supported APBM in the range of 1.7–3.4% of the supported amount.

Removal of DBS by APBM seems to be carried out by the mechanism shown in Scheme 2:



Scheme 2.

The amino nitrogen atoms in APBM are protonated in water, and DBS molecules form anions in water. The DBS anions bind to the protonated amino nitrogens by electrostatic interaction. Thus, it can be considered that HM can remove DBS anions in water.

The amount of amino nitrogens contained in unit mass of HM increase with an increase in the supported amount. Accordingly, the removed amounts per unit masses of HM and of APBM ought to increase with an increase in the supported amount. In this study, however, the contrary fact was observed. This fact, which was observed in the previous study,<sup>4</sup> seems to be explained by the same causes as described in the previous paper. That is, (1) the pores of the supported alumina are clogged with APBM, and, consequently, their surface area is decreased; and (2) since the APBM layer on the alumina

becomes thicker and DBS becomes difficult to diffuse into inner of the layer, only the surface and the layer near it participate in the removal of DBS. Accordingly, it can be considered that the removed amount does not increase even if the amount of supported APBM increases.

### Effect of Initial Concentration on Removed Amount

The relationship between the residual concentration and the removed amount at the removal equilibrium were studied. Figure 2 illustrates the plots

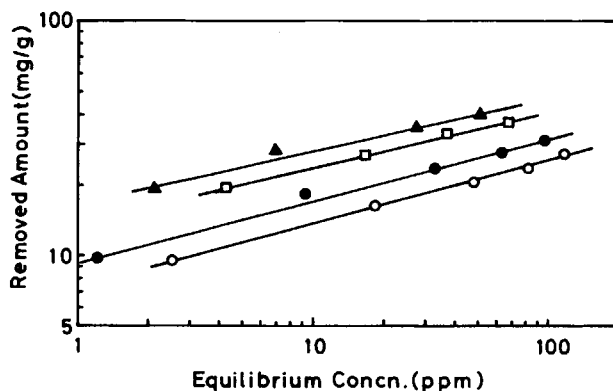


Fig. 2. Adaptability of removal behavior of DBS by APBM/alumina to Freundlich's adsorption formula, 25°C; the supported amount: (○) 3.4%; (●) 2.6%; (□) 2.4%; (▲) 1.7%.

of the removed amounts vs. the equilibrium residual concentrations in logarithmic scales. These plots give linear relationships. The removal behavior of these HM conformed to the Freundlich adsorption formula:<sup>7</sup>

$$\log Q = \frac{1}{n} \log C + \log K$$

where  $Q$  = the removed amount (mg/g HM) at the equilibrium state,  $C$  = the equilibrium concentration, and  $n$  and  $K$  are constants.

The slope ( $1/n$ ) of the lines and the logarithm of removed amounts at the equilibrium concentration of 1 ppm ( $\log K$ ) were listed in Table II. The values of  $1/n$  were 0.22–0.27, which showed some scatter. It is said that  $1/n$  is usually the values in the range of 0.2–1.0.<sup>7</sup> Judging from this experimental fact,

TABLE II  
Constants of the Freundlich Adsorption Formula (25°C)

Supported amount (%)	$1/n$	$\log K$
3.4	0.27	0.9
2.6	0.25	1.1
2.4	0.22	1.2
2.3	0.25	1.1
1.7	0.22	1.1

the values of 0.22–0.27 are small. Therefore, even a small measuring error of the residual concentration may give a relatively large effect to  $1/n$ . Accordingly, some scatter might be observed in  $1/n$ .

The fact that  $1/n$  is small means that the change in the removed amount accompanying with the change in the concentration is small. Therefore, this is desirable fact as removal reagent.

APBM is easily soluble in water. Therefore, since the loss of APBM on alumina by dissolution into the water may be caused in the removal processes, a means to prevent bleed of the supported compound has to be considered. It is to use compounds which are insoluble (or slightly soluble) in water and soluble in organic solvent, instead of APBM. Even if a compound is insoluble in water, when it is supported on alumina or other supports by dissolving in organic solvent, the supported compound can capture organic solutes<sup>4</sup> and metal ions<sup>8</sup> in water.

Although the rate for removing DBS was small under the conditions studied here (the flasks for removal were allowed to stand without shaking), it can be increased by use of more HM, and by allowing the solution to pass through a column packed with HM.

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