Removal of Nonionic Surfactant by Systems Based on Chloromethylated Polystyrene–Poly(ethylene Glycol)

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Synopsis

For the purpose of obtaining compounds which can remove nonionic surfactants in water, chloromethylated polystyrene (CMPS) was allowed to react with triethylene glycol monomethyl ether (3EGMME), tetraethylene glycol (4EG), poly(ethylene glycol) (PEG) 200, 400, 600, 1000, and 1500. The amount of PEG groups combined with CMPS decreased with an increase in the molecular weight of PEG. The ability of the product to remove polyethylene glycol mono-*p*-nonyl phenyl ether (NP, $n = 10$), a nonionic surfactant, solutes in water was greater in the product with PEG of greater MW than that with PEG of smaller MW, and in the product with more PEG groups (mol/g prod.) than in that with less PEG groups. The removal behavior of the products conformed to Freundlich's adsorption formula. Constants of the formula, the effect of temperature on the constants, the effect of combined PEG groups on the removed amount, and the removal manner were studied.

INTRODUCTION

The author and co-worker have reported in a previous paper that polystyrene–polyoxyethylene block copolymers supported on activated alumina remove polyethylene glycol mono-*p*-nonyl phenyl ether (NP, $n = 10$), a nonionic surfactant, solutes in water.[1] Generally, some polymers, which have hydrophilic and hydrophobic parts, can bind some organic compounds having hydrophobic and hydrophilic segments. The binding of the compounds to the polymers take place by the interactions between the hydrophobic segments of the polymers and those of the organic compounds.[2,3]

Although polystyrene is a hydrophobic polymer and does not bind organic compounds, when hydrophilic groups (sugar or crown ether group) were allowed to combine with polystyrene, the polymers bound methyl orange, 1-anilino-8-naphthalene sulfonate, and picrate anions.[4-8]

When polystyrene had polyethylene glycol groups on the benzene rings, it was found that the polystyrene derivatives bound NP solutes in water.

This study deals with the reactions of chloromethylated divinylbenzene crosslinked polystyrene (CMPS) with polyethylene glycols (PEGs) and with the removal behavior of NP solutes in water by the reaction products.

EXPERIMENTAL

Materials

Commercial CMPS beads (200–400 mesh) (Polyscience Inc., lot no. 11224), were used without further purification. Its chlorine and divinylbenzene contents are 2.63 meq/g (= 9.32 wt %) and 2 mol %, respectively. As for

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triethylene glycol monomethyl ether (3EGMME), tetraethylene glycol (4EG), polyehtylene glycol (PEG) 200, 400, and 600 (Nakarai Chemicals, Ltd.), first grade (= extra pure) reagents were used after drying for 5 h at 100–105°C and 1–2 mm Hg. PEG 1000 and 1500 (Nippon Soda Co. and Wako Pure Chemicals Ind., Ltd.), and NP (Tokyo Chemical Ind., Ltd.), which were first grade reagents, were used without further purification. Dioxane (Wako Pure Chemicals Ind., Ltd.) best grade (= guaranteed) reagent was purified by distillation after drying.

Reactions of CMPS with PEG

In a round-bottomed flask were placed 0.016 mol of 3EGMME, 4EG, or PEG, and 0.37 g (0.016 mol) of sodium metal. The mixture was heated at about 100°C under nitrogen atmosphere for 12–48 h till all the sodium metal reacted. After this prepared sodium polyethylene glycolate (PEG–Na) was cooled to room temperature, 3.00 g of CMPS (containing 0.0079 mol of —CH_2Cl groups) and 20 mL of dioxane were added. This mixture stood for a night to allow it to swell CMPS, and was then stirred at about 100°C for 15–72 h. After the reaction was finished, an appropriate amount of hot water was added to the mixture and boiled; then the solid matter was filtered and washed with boiling water, hot ethyl alcohol, and acetone. Furthermore, after the product was extracted with tetrahydrofuran for 72 h, it was dried at 80°C *in vacuo*.

Removal of NP

A solution of 50 mL of prescribed NP concentration was poured into a flask containing 0.250 g of each reaction product. Other operations, measurements of absorbances of sample solutions, determinations of residual concentrations of NP, and those of the amounts of NP removed were carried out by using the techniques described in the earlier paper.[1]

RESULTS AND DISCUSSION

Reactions of CMPS with PEG–Na

In the reaction of CMPS with PEG–Na, the PEG–Na reacts with —CH_2Cl groups in CMPS to give a polymer in which the chloromethylstyrene part was converted into vinylbenzyl polyethylene glycol ether:
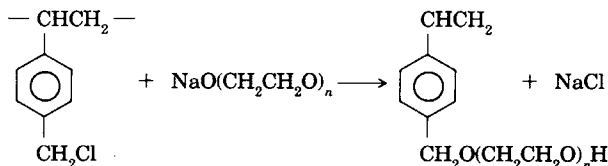

Table I lists reaction time, yields, the amount of reacted —CH_2Cl groups, molar numbers of combined PEG, and elementary analysis values. In the cases of the reactions of CMPS with 3EG–MME, 4EG, PEG 200, 400, and

TABLE I
The Elementary Analysis Values and the Removal Abilities of the Reaction Products of CMPS with PEGs

	Reaction time (h)[a]	Yield[a] (g)	Reacted[b] CH₂Cl groups (mol %)	Combined[c] PEG (mmol/g CMPS)	C (%) Found	C (%) Cald[d]	H (%) Found	H (%) Cald[d]	N (%) found	Cl[e] (%) found	Removal ability[f] Residual concn (ppm)	Removal amount (mg/g prod.)
CMPS[g]	—	—	—	—	83.64	83.66	7.02	7.02	0.02	9.32	45.0	1.0
CMPS–3EGMME(1)	9	3.90	31.54	2.63	78.56	79.17	8.69	8.23	0.20	—	19.1	6.2
CMPS–3EGMME(2)	30	4.02	31.54	2.63	78.62	79.17	8.65	8.23	0.16	—		
CMPS–4EG(1)[h]	16	3.98	31.54	2.63	77.40	77.00	8.28	8.15	0.00	—	11.0	7.8
CMPS–PEG 200(1)	18	4.08	31.54	2.63	76.42	76.91	8.36	8.16	0.29	—	9.9	8.0
CMPS–PEG 400(1)	16	4.65	22.7	1.89	73.55	73.51	8.44	8.30	0.06	—	10.0	7.9
CMPS–PEG 400(2)	24	4.41	21.0	1.75	74.05	74.00	8.47	8.27	0.13	—	7.5	8.5
CMPS–PEG 600(1)	14	5.02	15.0	1.25	73.53	73.45	8.40	8.31	0.07	—	9.9	8.0
CMPS–PEG 600(2)	24	4.82	16.2	1.35	72.76	72.82	8.15	8.34	0.08	—	8.3	8.3
CMPS–PEG 600(3)	30	5.18	16.7	1.39	72.57	72.57	8.52	8.33	0.00	—	7.7	8.5
CMPS–PEG 1000(1)	30	6.37	16.7	1.39	68.23	68.23	8.35	8.54	0.14	—	7.5	8.5
CMPS–PEG 1000(2)	24	6.28	20.5	1.71	66.64	66.61	8.86	8.61	0.15	0.00	7.5	8.5
CMPS–PEG 1000(3)	66	4.92	11.4	0.95	71.33	71.39	8.56	8.40	0.17	0.20[i]	6.6	8.7
CMPS–PEG 1500(1)	15	4.28	4.6	0.38	75.03	75.04	8.17	8.14	0.14	1.01[j]	10.8	7.8
CMPS–PEG 1500(2)	72	4.56	5.8	0.48	73.50	73.57	8.60	8.31	0.24	—	9.4	8.1
CMPS–PEG 1500(3)	48	4.41	5.5	0.43	74.08	74.02	8.27	8.28	0.05	—	10.4	7.8
CMPS–PEG 1500(4)	67	7.05	15.2	1.27	65.59	65.76	8.82	8.65	0.20	—	8.2	8.3
CMPS–PEG 1500(5)	72	5.03	16.8	1.40	65.01	65.03	8.63	8.68	0.11	0.15[i]	7.3	8.5

[a] These values are the yields in the reactions which 3.00 g of CMPS were used. In the case of CMPS–PEG 1500(5), 2.00 g were used.
[b] These, which are the amounts of the reacted —CH₂Cl groups with PEG–Na, were calculated from the elemental analysis values.
[c] These were calculated from the amounts of reacted —CH₂Cl groups.
[d] These are the calculated values of the compounds which were produced from the reactions of —CH₂Cl groups amounts of CMPS shown in the 4th column with respective PEG.
[e] The mark "—" expresses that the Beilstein test indicated negativity.
[f] These were determined on 14th day after the beginning of the removal at 25°C.
[g] This CMPS is composed of 31.54 mol % of chloromethylstyrene, 66.46 mol % of styrene, and 2.00 mol % of divinybenzene.
[h] When 27.94 mol % of —CH₂Cl groups in CMPS reacted with 4EG, the amount of combined PEG is 2.48 mmol/g CMPS, and the element contents of the product were calculated to be C 77.41% and H 8.12%.
[i] In the calculation of C and H contents, these Cl contents were neglected.
[j] This Cl content corresponds to 5.22 mol % of chloromethylstyrene unit, when 4.60 mol of it reacted with PEG 1500–Na.

600, after these PEG analogues were dried for 5 h at 1–2 mm Hg and 100–105°C, PEG–Na was prepared. When the reactions of CMPS with the PEG–Na were continued for 15 h at about 100°C, in the reactions with PEG–Na of PEG of MW below 200 all —CH_2Cl groups reacted with the PEG–Na. On the other hand, in the reactions with the PEG–Na of PEG MW above 400, only a part of —CH_2Cl groups reacted with the PEG–Na. In the reaction with PEG 1500–Na, since the amount of reacted —CH_2Cl groups was only 4.6% [CMPS–PEG 1500(1)] even after the reaction was continued for 15 h other reactions were done for more hours.

In the cases of CMPS–3EGMME, –4EG, and –PEG 200, the elementary analysis values conformed approximately to the element contents of the products which were yielded when all —CH_2Cl groups reacted with PEG–Na. In the cases of CMPS–PEG 400, 600, 1000, and 1500, the elementary analysis values did not agree with the element contents of the products which were yielded when all —CH_2Cl groups reacted with PEG–Na. Since only a negligible amount of chlorine was detected in the products, —CH_2Cl groups which did not react with PEG–Na were hydrolyzed by the post-treatment of the reaction mixtures.

In Table I, the amounts of reacted —CH_2Cl groups with PEG–Na, molar numbers of combined PEG, and the calculated values of hydrogen and carbon of the products were calculated from the elementary analysis values found in the following way. The components of percentage composition of CMPS are chloromethylstyrene unit 31.54, styrene unit 66.46, and divinylbenzene unit 2.00%. When the amount of reacted chloromethylstyrene unit with PEG–Na is x mol %, since no chlorine or only a negligible amount of chlorine was detected in the products, $(31.54 - x)$ mol % was defined as the amount of hydroxymethylstyrene unit which was yielded by hydrolysis of chloromethylstyrene unit during the post-treatment of the raw product.

Hydrogen and carbon contents of a product were calculated from the unit weight of percentage composition of the product; hydrogen and carbon weights in the unit which were calculated by substituting a numeral into x. The value of x was determined so that the calculated values of the element contents approach most closely the observed values of elementary analysis [in the case of CMPS–PEG 1500(1), chlorine content was taken into account in the calculation of x].

Since the found elementary analysis values conformed approximately with the calculated ones, the calculated amounts of reacted —CH_2Cl groups with PEG–Na approach to the true values (Table I).

As seen from Table I, although a few exceptions are found, as a whole, as the molecular weight of PEG increases, the amount of —CH_2Cl groups (mol %) reacted with PEG–Na decrease.

Significant differences in the amounts of reacted —CH_2Cl groups with PEG–Na were observed amoung CMPS–PEG 1000 and among –PEG 1500, respectively (Table I). First, the reagents PEG 1000 and PEG 1500 (Nippon Soda Co.) were used for the syntheses of CMPS–PEG 1000(1), (2), and –PEG 1500(1)–(3). Since they are solids, they were employed for preparing PEG–Na without drying. The amounts of reacted —CH_2Cl groups with PEG–Na were smaller in CMPS–PEG 1500(1)–(3) than in –PEG 1000(1).

In the cases of CMPS–PEG 1500(2) and (3), although the reactions were continued for 72 and 48, respectively, the amounts of reacted —CH$_2$Cl groups with PEG–Na were 5.8 and 5.5 mol %, respectively. This was caused by moisture in PEG 1500.

Therefore, other reagents PEG 1000 and 1500 (Wako Pure Chemicals) were provided. These are solids, which were dried for 5 h at 1–2 mm Hg and 100–105°C and used for syntheses of CMPS–PEG 1000(3) and –PEG 1500(4) and (5). The amounts of reacted —CH$_2$Cl groups with PEG–Na were smaller in CMPS–PEG 1000(3) than in 1000(1) and also than in CMPS–PEG 1500(4) and (5). The moisture in the PEG 1000(Wako) still remained even after drying. The amounts of reacted —CH$_2$Cl with PEG–Na were smaller in CMPS–PEG 1500(1)–(3) than in –PEG 1500(4) and (5). The PEG 1500 (Nippon Soda) contained much moisture. The differences in the amounts of reacted —CH$_2$Cl groups with PEG–Na are due to the differences among the amounts of moisture contained in these reagents.

In the case of CMPS–PEG 1000(2), the amount of reacted —CH$_2$Cl groups were 20.5 mol %, which were larger than those of three CMPS–PEG 600. And also, although the same reagent PEG 1000 (Nippon Soda) was used for the syntheses of CMPS–PEG 1000(1) and (2), the amount of reacted —CH$_2$Cl groups with PEG–Na was 5.5 mol % larger in CMPS–PEG 1000(2) than in –PEG 1000(1). These reasons are not clear.

Fujita et al.[9] have reported that in the reactions of CMPS (Cl : 1.84 meq/g, 6.53%) with 3–10EG–Na and 3–10EGMME–Na, the —CH$_2$Cl groups of CMPS are almost completely replaced by the PEG– and PEGMME–Na below 5EG– and 3EGMME–Na, but some amounts of residual chlorine are found in the reaction products of the CMPS with 7 and 10EG–NA, and 4–10EGMME–Na. In this study, —CH$_2$Cl groups of this CMPS reacted almost completely with 3EGMME–Na, 4EG–Na, and PEG–Na of PEG having MW 200, which has about 4.1 oxyethylene unit.

Removal Rate and Removed Amount

Figure 1 illustrates decreases in residual concentrations resulting from removal of NP by CMPS–PEG products, when 0.250 g of the products were placed in aqueous solutions of 50 mL of 100 ppm concentrations of NP. The time necessary to reach the removal equilibrium was more than 2 days, when the test samples were allowed to stand at 25°C without shaking. Removal using MR type resins, XAD-2 and XAD-4, were carried out under the same conditions. The residual concentrations were 7 and 17 ppm after 1 day, respectively. The removal rates of these resins were fairly large compared with those of the CMPS-PEG.

Table I lists the residual concentrations and the removed amounts determined on the 10th day after the beginning of the removal, when the samples, which consisted of 0.25 g of the products and 50 mL of initial concentration 50 ppm, were operated. The amount removed by CMPS–3EGMME was fairly small compared with those of the other products.

As the molecular weight of PEG increases, the molar number of PEG which combined with CMPS decreases, and also the molar number of PEG
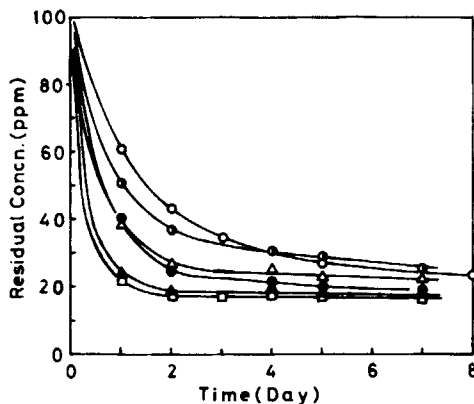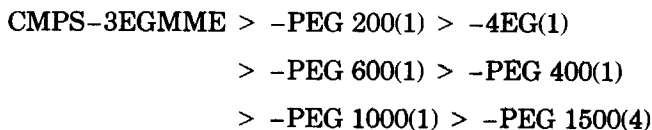
Fig. 1.   Change in the residual concentration in the removal of NP by CMPS–PEGs at 25°C: (○) CMPS–4EG; (◑) –PEG 200(1); (●) –PEG 400(1); (△) –PEG 600(1); (▲) –PEG 1000(1); (□) –PEG 1500(4).

groups contained in 1 g of the product decreases. However, the magnitude of the removal rate is in the following order:

$$CMPS-3EGMME > -PEG\ 200(1) > -4EG(1)$$
$$> -PEG\ 600(1) > -PEG\ 400(1)$$
$$> -PEG\ 1000(1) > -PEG\ 1500(4)$$

As the molecular weight of PEG increases, despite a decrease in the molar number of PEG groups contained in 1 g of a product, the residual concentration at the removal equilibrium state decreases gradually. This fact shows that the magnitude of the removed amount per unit mass of each CMPS–PEG is larger in the product with PEG groups of larger molecular weight, and also the length of PEG groups contributes greatly to the removal of NP.

In the case of CMPS–3EGMME, the residual concentration at the equilibrium is 19 ppm, which is large. In the cases of other products, however, the concentrations are 7.3–11 ppm, and the removed amounts are approximately 7.8–8.7 mg/g prod. When the PEG group is the same, the removed amount is greater in a product having many PEG groups. Consequently, since a product with large removal rate is better as removal agent, it is desirable to allow as much PEG of large molecular weight as possible to combine with CMPS.

The Effect of Initial Concentration on the Removed Amount

One fourth gram of CMPS–4EG(1), –PEG 400(1), 600(1), 1000(1), and 1500(4) were placed in 50 mL of initial concentrations of 50, 100, 150, 200, and 250 ppm. These were allowed to stand for 10–14 days in a thermostat bath until the residual concentrations were essentially constant. Figures 2 and 3 show in logarithmic scale the plots of the removed amounts vs. the residual concentrations at the equilibriums in the removals by CMPS–PEG 600(1) and –PEG 1000(1) as well as by CMPS–PEG 1000(1) and –PEG
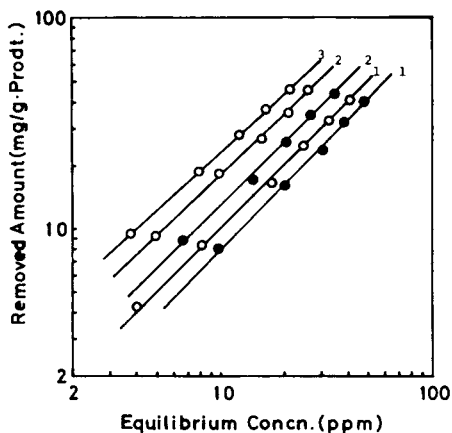
Fig. 2.   Freundlich's adsorption formula in the removal of NP by CMPS–PEG 600(1) and –PEG 1000(1): (●) CMPS–PEG 600(1); (1) 25°C, (2) 50°C; (○) CMPS–PEG 1000(1), (1) 25°C, (2) 50°C, (3) 80°C.

1500(4), respectively. [As for CMPS–PEG 1000(1) the plots are also shown (Fig. 3) in order to compare with the plots in the removals from larger initial concentrations.] These plots show linear relationships. The removal behavior of these products conform to Freundlich's adsorption formula.

The dependences of the equilibrium concentrations and the removed amounts on the initial concentrations of NP were studied on CMPS–PEG 600(1) and 1000(1) at 50 and 80°C. In the case of the removal of CMPS–PEG 1000(1) at 80°C, after the equilibrium concentrations and the removed amounts were determined at 50°C, the temperature was raised to 80°C and
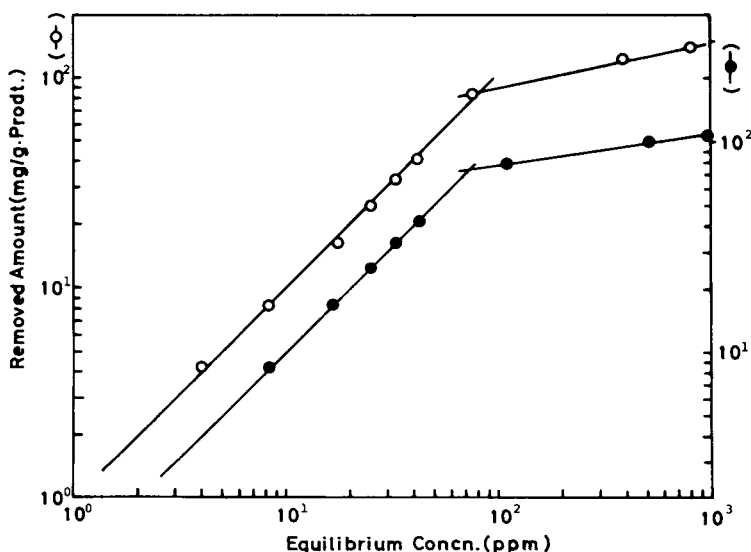

Fig. 3.   Freundlich's adsorption formula in the removal of NP by CMPS–PEG 1000(1) (○) and –PEG 1500(4) (●) at 25°C. Product: 0.250 g; initial concn: (○) 25, 50, 100, 150, 200, 250, 500, 1000, 1500 ppm, (●) 50, 100, . . . , 1500 ppm, 50 mL.

after the removal attained equilibrium, the removed amounts were determined. Plots of logarithms of the removal amounts vs. those of residual concentrations also showed fairly good linearity.

Table II lists together the slopes of these lines $(1/n)$ and logarithms of the removed amounts at the removal equilibrium concentrations 1 ppm (K). The values of $1/n$ of CMPS–4EG(1), –PEG 400(1), 600(1), 1000(1), and 1500(4) are 1.05–0.98 at 25°C, which vary little. There are few differences among the values of log K at 25°C, too. When removal temperature was raised, $1/n$ decreased slightly and log K increased slightly. As it has been said that, strictly speaking, $1/n$ and log K vary with variations of temperature and the concentration,[10] these tendencies were observed in the removal behaviors of NP by these products. The temperature dependences of $1/n$ and log K were small, but that of removal rate was very large.

Furthermore, removals from the initial concentrations of 500, 1000, and 1500 ppm were carried out under the conditions of products 0.100 g and solutions 20 mL. After the test samples were allowed to stand at 25°C for 14 days, the residual concentrations and the removed amounts were determined (Table III). The removed amounts increased with an increase in the initial concentration.

Plots of logarithms of the removal amounts vs. those of the residual concentrations showed approximately linear correlations (Fig. 3). Their $1/n$'s, however, were 0.22–0.19 in the cases of CMPS–PEG 1000(1)–(4), and 0.24 in the cases of CMPS–PEG 1500(1) and (3), which were smaller than those obtained in the initial concentrations below 250 ppm. In the case of CMPS–PEG 1000(1), the point of intersection of the two lines, which were obtained from the plots of logarithms of the removed amounts vs. those of the residual concentrations in the removals from the initial concentrations of 50–1500 ppm namely, the bend point was the residual concentration 80 (ppm) and the removed amount 84 (mg/g prod.), and in the case of CMPS–PEG 1500(4), it was 76 and 74.

The Freundlich's adsorption formula conforms to experimental results in a certain range in which concentrations of solutes are not too large or too small.[10] In the cases of CMPS–PEG 1000(1) and –PEG 1500(4), in these removal conditions the concentration ranges correspond to the residual concentrations of about 80–4 ppm or less and about 76–8 ppm or less, respectively.

In the removal (or adsorption) of organic compound solutes in water by high molecular compounds, when the removed amounts were plotted vs.

TABLE II
Freundlich Isotherm Constants

	25°C		50°C		80°C	
	$1/n$	log K	$1/n$	log K	$1/n$	log K
CMPS–4EG(1)	1.05	−0.03	—	—	—	—
CMPS–PEG 400(1)	1.02	−0.02	—	—	—	—
CMPS–PEG 600(1)	1.03	−0.12	1.02	0.08	—	—
CMPS–PEG 1000(1)	0.98	0.02	0.96	0.28	0.94	0.41
CMPS–PEG 1500(4)	0.99	0.01	0.96	0.28	0.94	0.39

TABLE III
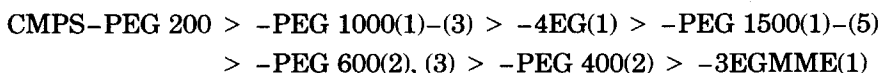The Amounts of NP Removed from the Solutions of Initial Concentrations of 500, 1000, and 1500 ppm[a]

| | Molar number of combined PEG groups (mmol/g prod.) | Amount removed | | | | | | | | |
| | | From 500 ppm soln | | | From 1000 ppm soln | | | From 1500 ppm soln | | |
		(mg/g prod.)	(mmol/g prod.)	(mmol/ mmol PEG group)	(mg/g prod.)	(mmol/g prod.)	(mmol/ mmol PEG group)	(mg/g prod.)	(mmol/g prod.)	(mmol/ mmol PEG group)
CMPS–3EGMME(1)	1.98	28	0.0424	0.0214	34	0.0515	0.0261	44	0.0666	0.0338
CMPS–4EG(1)[b]	1.96	76	0.115	0.0618	114	0.173	0.0927	151	0.228	0.121
CMPS–PEG 200(1)	1.84	87	0.132	0.0715	135	0.204	0.110	171	0.258	0.141
CMPS–PEG 400(2)	1.08	71	0.107	0.0991	94	0.142	0.131	125	0.189	0.175
CMPS–PEG 600(2)	0.808	75	0.114	0.141	97	0.147	0.182	104	0.167	0.195
CMPS–PEG 600(3)	0.790	77	0.117	0.147	100	0.151	0.192	112	0.169	0.215
CMPS–PEG 1000(1)	0.600	85	0.129	0.215	123	0.186	0.305	140	0.212	0.353
CMPS–PEG 1000(2)	0.650	86	0.130	0.200	117	0.177	0.272	126	0.191	0.293
CMPS–PEG 1000(3)	0.538	84	0.127	0.236	118	0.179	0.333	129	0.195	0.363
CMPS–PEG 1500(1)	0.251	71	0.107	0.428	94	0.142	0.567	112	0.169	0.673
CMPS–PEG 1500(2)	0.290	78	0.118	0.407	104	0.157	0.543	112	0.169	0.584
CMPS–PEG 1500(3)	0.281	76	0.115	0.409	108	0.163	0.580	122	0.185	0.658
CMPS–PEG 1500(4)	0.448	78	0.118	0.263	95	0.144	0.321	105	0.159	0.354
CMPS–PEG 1500(5)	0.463	74	0.112	0.242	101	0.153	0.330	109	0.165	0.356

[a] Temp 25°C, product 0.100 g in 20 mL of NP solution. Measured on 14th day after the beginning of the removal.
[b] When 29.74 mol % of —CH_2Cl group reacted with 4EG, the molar number of combined 4EG group is 1.80 mmol/g prod.

the residual concentrations in logarithmic scale, a few facts that the plots formed two lines with different $1/n$ had been reported by Kawabata et. al.[11-13]

The order of the removed amount (mg/g prod.) was as follows:

$$CMPS-PEG\ 200 > -PEG\ 1000(1)-(3) > -4EG(1) > -PEG\ 1500(1)-(5)$$
$$> -PEG\ 600(2), (3) > -PEG\ 400(2) > -3EGMME(1)$$

The removed amount of CMPS–PEG 200 was maximum, and that of CMPS–3EGMME(1) minimum. The numbers of oxyethylene unit of PEG 200 and 3EGMME are about 4.1 and 3, respectively, and the difference between both is about 1.1. And also, the molar numbers of combined PEG in 1 g of both products are 16.4 and 15.3, which are not so different. The difference between both removed amounts might be caused by the differences in oxyethylene unit and terminal groups between 3EGMME and PEG 200.

On the other hand, significant difference was observed between the removed amounts of CMPS–4EG and –PEG 200. Molar numbers of 4EG and PEG 200 groups contained in 1 g of both products are 15.5 and 15.3, which are approximately equal. The number of oxyethylene units of both are 4 and about 4.1. PEG 200, however, is a mixture of 4, 5, and 6EG. The difference in removal amount might be caused by difference in composition between 4EG and PEG 200.

The Effect of Combined Molar Number on the Removed Amount

The removed amount per 1 mol of the PEG group was compared. The removed amounts(mmol/g prod.) from the solutions of the initial concentrations of 500, 1000, and 1500 ppm were divided by the molar numbers of combined PEG groups, which existed in 1 g of the products. These quotients correspond to the molar numbers of NP removed by 1 mol of PEG groups. They are listed in Table III. Figure 4 illustrates the plots of removed amounts (mmol/mmol PEG group) vs. molar numbers of PEG groups which exist in 1 g of the products. As a rule, the magnitude order of the removed amounts obtained from the solutions of the three initial concentrations are as follows:

$$CMPS-PEG\ 1500 > -PEG\ 1000 > PEG\ 600 > -PEG\ 400$$
$$> -PEG\ 200 > 4EG > 3EGMME$$
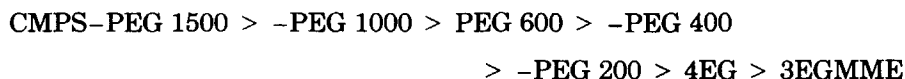
The removed amount is greater in CMPS–PEG with PEG groups of larger MW. In the cases of the three CMPS–PEG 1000, the removed amounts (mmol/mmol PEG group) are in the order of (3) > (1) > (2), and in the cases of the five CMPS–PEG 1500, they are in the order of (3) > (1) > (2) > (4) > (5). CMPS–PEG having fewer PEG groups removes a greater amount of NP than that having more. This fact seems to be attributable to the increase of steric hindrance with increasing proximity of long PEG group.

The removed amount (mg/g prod.) of CMPS–PEG 200 was greatest of all the products obtained. However, since its removal rate was second small to CMPS–3EGMME, it is not suitable as the removal agent for NP. The
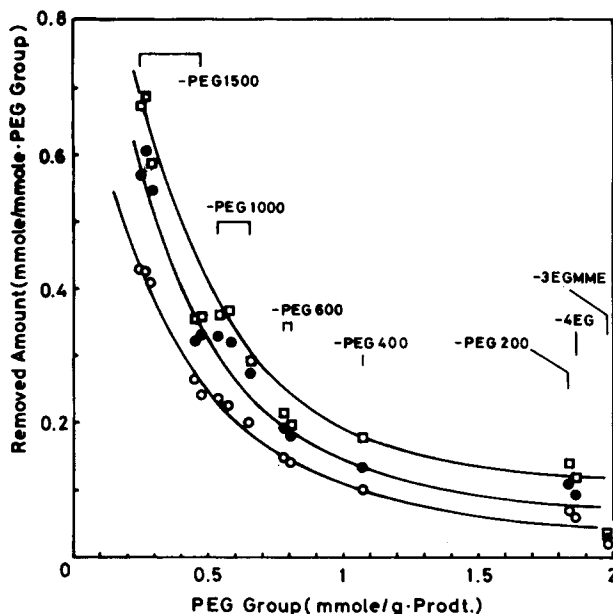
Fig. 4. Plots of molar number of PEG groups combined on CMPS vs. the amount of NP removed by CMPS–PEGs. Product: 0.10 g in 20 mL at 25°C, from (○) 500, (●) 1000, and (△) 1500 ppm solution.

removed amount (mg/g prod.) was greatest in CMPS–PEG 1000 series in the products except for CMPS–PEG 200(1) (Table III). In addition, its removal rate was next to CMPS–PEG 1500(4) (Fig. 1). Accordingly, CMPS–PEG 1000 having PEG groups above 0.54 mmol/g prod. is best as the removal agent for NP in the CMPS–PEG analogues.

Removal Manner of NP by CMPS-PEG

It has been reported that the reaction products of CMPS with 3–10EG or their MME[9] and homogeneous oligo(oxyethylene) derivatives[14,15] can form complexes with alkaline metals. However, no paper has been published on binding of organic compounds to the CMPS–PEG analogues.

The polymer of the reaction product of chloromethylstyrene with sugar [P(CMS–Sug)] can bind methyl orange (MO) or magnesium 1-anilino-8-naphthalene sulfonate (ANS) solutes in water.[6–8] One atomic group of MO anion (weight = 304) or ANS (weight = 266) is bound to the hydrophilic part of the microdomain formed by 20 repeating units in this polymer (the bound amount corresponds to 0.05 mmol/mmol sugar group). The amount of bound MO or ANS anion is 0.169 mmol/g polymer.[6–8]

The molecular weight of NP is 660.86, which is larger than twice atomic weight of MO or ANS anion. Since NP molecule, however, has alkyl and PEG groups at p-position of the phenyl ring, it is long rather than bulky.

Although CMPS–PEG are not linear polymers like P(CMS–Sug) but crosslinked polymers, since the crosslinking degree is small, movement of this polymer is not restricted. It is not clear whether they form microdomains in water or not, but their hydrophobic parts form some sites to which

NP solutes can be bound. NP solutes are bound to CMPS–PEG by the hydrophobic interaction between the sites and the hydrophobic parts of the NP solutes. According to the calculation from the amount (mmol/mmol PEG group) removed by CMPS–PEG 1500(5) from the solution of 1500 ppm concentration, one NP molecule is bound to the binding site made up by 17 vinylbenzyl groups, whose 2.8 groups have PEG groups as the pendants. This indicates that one molecule is bound to the binding site formed by fewer numbers of vinylbenzyl groups than the site of P(CMS–Sug) which binds one MO or ANS anion. This fact seems to indicate that one NP molecule is at least not more bulky than one MO or ANS anion.

SUMMARY

In the reaction of CMPS with PEG analogues, although almost all CH_2Cl groups in CMPS reacted with 3EGMME–, 4EG–, and PEG–Na having MW 200, a part of CH_2Cl groups reacted with PEG–Na above MW 400. These reaction products removed NP solutes in water, whose removal behavior conformed to Freundlich's adsorption formula. The values of $1/n$ were about 1, which decreased slightly as the removal temperature was raised. The amount (mmol/mmol PEG group) of NP removed was greater in CMPS–PEG having longer PEG groups. Judging from the removal rate and the removed amount (mg/g prod.), CMPS–PEG 1000 having PEG groups above 0.54 mmol/g prod. is best for removing NP solutes in water.

When CMPS–PEG to which NP solutes were bound in water are placed in methyl or ethyl alcohol, the NP are eluted from the products. Therefore, CMPS–PEG can be used repeatedly for removing NP solutes in water.

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