Fundamental Study on the Production of Ultrapure Water VIII. Removal of Leachables from Mixed-Bed Ion Exchange Resins

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A study was made concerning the removal of leachables released from mixed-bed ion exchange resins. The key concerns were to determine the optimum mixed ratio of strong acid cation exchange resins (SACERs) and strong base anion exchange resins (SBAERs), which give the minimum value of total organic carbon (TOC) released from the resin mixtures and to investigate the effect of synthetic carbonaceous adsorbents on the adsorption of the leachables. The leaching rates of the leachables from the resin mixtures were dependent on the mixed ratios of SACERs and SBAERs. The TOC value for the leachables showed a minimum for a SACER-to-SBAER volume ratio of 9:1, far different from the mixed ratio in ordinary water treatment. The release of leachables from resin mixtures was mainly due to SBAER. The carbonaceous adsorbent having a higher hydrophobic surface adsorbed the leachables well from the resin mixtures.

There has recently been increasing demand for better quality ultrapure water, especially free from TOC, in advanced and sophisticated industries.[1,2] A mixed-bed of SACER and SBAER is essential for producing primary pure water and for refining water in an ultrapure water production system.[3] There is an annoying problem concerning trace leachables released from ion-exchange resins (IERs), known as TOC throw.[4,5] It has been an urgent problem to clarify the profile of leachables from IERs and to establish a removal method. So far, the authors have reported the leaching profile, the component and the removal of leachables from SACERs and SBAERs.[6–8] Regarding the profile and removal of leachables from mixed-bed IERs, few studies have been carried out.

In this study, using two typical mixed-beds for gel-gel type and porous-porous type resins, the leaching profile, the components, and the methods for minimizing the leaching and for removing the leachables from the mixed-beds were probed by means of similar methods described in previous papers.[6–8]

Experimental

Materials. IER: Five (each) were commercially available SACERs (A—E) and SBAERs (A′—E′) employed.[6–8] Resins A, A′ and B, B′ were porous type; the others were gel type. These are typical resins for water-treatment use, and were obtained from leading makers, such as Tokyo Organic Chemical Industries Ltd. (Amberlite), Mitsubishi Chemical Industries Co., Ltd. (Diaion), Dow Chemical Co., Ltd. (Dowex), Bayer Co., Ltd. (Lewatit), and Rohm and Haas Co., Ltd. (Duolite). Pre-treatments for the IERs used were carried out by the same method as described in our previous papers.[6–8] The general properties of the IERs were also given in previous papers.[6–8] Purified water: Pure water (TOC<100 μgC dm^{-3}, μg Carbon as TOC) was prepared by Puric R (Japan Organo Co., Ltd.). Prior to use, any dissolved oxygen in the water was purged by blowing nitrogen gas, so as to minimize the effect of oxidative decomposition on the resin matrix.[9,10] Carbonaceous adsorbent: Four synthetic carbonaceous adsorbents were used to eliminate the leachables from mixed-bed IERs. Adsorbents F, G, and H were Ambersorb XE-340, 347, and 348 of Rohm and Haas Co., Ltd. Adsorbent I was BAC-MP of Kureha Chemical Co., Ltd. Prior to use, these adsorbents were repeatedly washed with doubly distilled water under boiling state until the conductivity of the supernatant became almost the same as that of the distilled water (1.5×10^{-6} S cm^{-1}). The physical properties and pore-size distribution of the adsorbents were indicated in a previous paper.[7] Reagent: Polystyrenesulfonate, MW 1800, 8000, 38180, 114400, 400000 (Gaschro Kogyo Inc.) were used to make the MW fitting curve for Gel filtration chromatography (GFC). Anhydrous sodium sulfate and acetonitrile were used to prepare the eluent for GFC. Acetonitrile was also employed for the eluent in reverse-phase chromatography (RPC).

Procedures. Leachable solution: Twenty five milliliters (each) of SACER and SBAER were mixed well and put in a 250 cm^3 volumetric flask; the purified water was then messed up to the mark. The flask was tightly sealed and kept with gentle stirring at 50 °C. The TOC of the supernatant was periodically monitored. The contents were then filtered by a 0.22 μm membrane filter. Measurements of the leachables from the resin mixture were made by GFC and RPC. Aside from this, the mixed ratios of SACERs and SBAERs were vaired to 10/0, 9/1, 4/1, 2/1, 1/2, 1/4, 1/9, 0/10 by volume (total, 50 cm^3) and the same procedures as above were conducted. Removal of leachables from IER mixture: Adsorption of the leachables from the resin mixture on the adsorbent was carried out as follows: 1) One gram of the adsorbent was added to 25 cm^3 of the leachable solution from SACER and SBAER (mixed ratio, 1:1). The mixture was gently shaken for 48 h, during which equilibrium was confirmed at 25±0.5 °C and filtered by a G3 glass filter. The adsorbed amount on each adsorbent was determined by the difference between the TOC value in the filtrate and that of the sample blank. 2) A suitable amount (8 g) of the adsorbent was put in 50 cm^3 of SACER and SBAER (mixed ratio, 1:9). The admixture was added to 250 cm^3 of a volumetric flask; the purified water was then messed up to the mark. The flask was allowed to stand for five days at

50 °C with gentle stirring; the TOC of the supernatant was then measured. After cooling the flask to 25 °C, the TOC of the supernatant was then measured again. Analytical conditions and equipment: Details of the analytical conditions and equipment for GFC and RPC were described in previous papers.[6–8)]

Results and Discussion

TOC Leaching Rate: Figure 1 shows the change of TOC from resin mixtures of 1 to 1 by volume ratio of SACERs and SBAERs. The TOC increased with soaking time. The TOC leaching rate is given in Table 1. The values are considerably lower than those of SACERs and SBAERs, respectively, obtained in previous studies.[6,8)] It is postulated that considerable amounts of leachables from each SACER and SBAER were mutually removed with paired resin of opposite charge. The order of the TOC leaching rates is A-A′>C-C′>B-B′>D-D′>E-E′. This suggests that the TOC leaching rates from resin mixtures should depend on the rates from SBAERs[8)] and that a suitable mixed ratio of SACER and SBAER should offer the minimum TOC release from mixed-bed IERs in an ultrapure water production system in which the mixed-bed is incorporated.

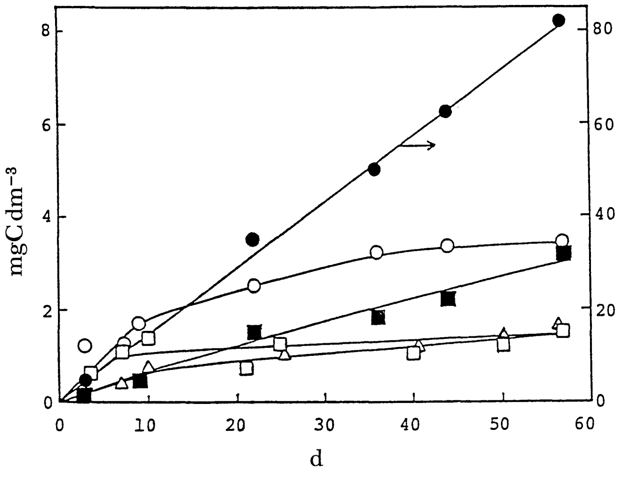

Fig. 1. Change of TOC from resin mixtures of SACER to SBAER volume ratio of 1 to 1 at 50 °C. ●: Resin A-A′, ■: Resin B-B′, ○: Resin C-C′, □: Resin D-D′, △: Resin E-E′.

Table 1. TOC Leaching Rate from Resin Mixtures of SACER to SBAER Volume Ratio of 1 to 1 at 50 °C

Resin	TOC[a)]	TOC Leaching rate
	mgC dm⁻³	mgC h⁻¹ dm⁻³-resin
A-A′	11.8	3.3×10⁻¹
B-B′	0.6	1.7×10⁻²
C-C′	1.7	4.7×10⁻²
D-D′	1.2	3.3×10⁻²
E-E′	0.5	1.4×10⁻²

a) TOC in the solution after 7 d soaking.

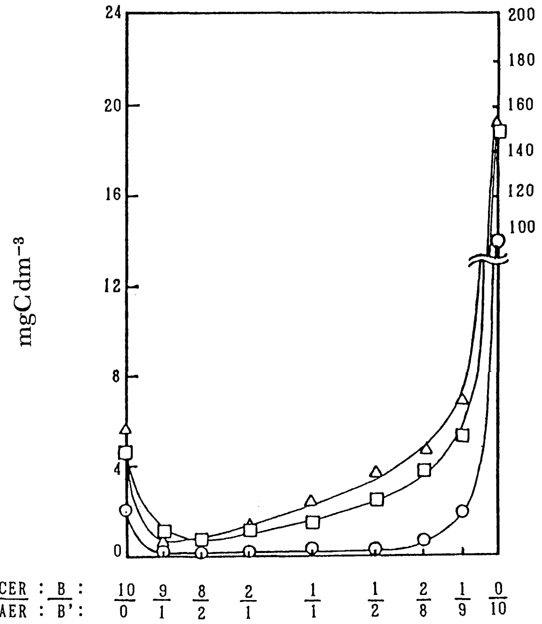

Fig. 2. Effect of mixed ratios of SACER to SBAER (B to B′) on TOC release at 50 °. ○: 10d, □: 30d, △: 60d.

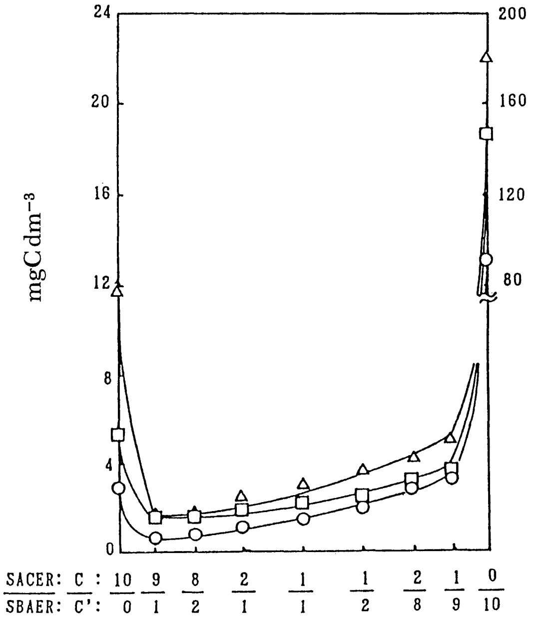

Fig. 3. Effect of mixed ratios of SACER to SBAER (C to C′) on TOC release at 50 °C. ○: 10d, □: 30d, △: 60d.

Optimum Mixed Ratio of IERs: The effect of the mixed ratios of SACERs (B, C) and SBAERs (B′, C′) on the TOC release was investigated for 60 days. The results are given in Figs. 2 and 3. The TOC leaching rates for the resin mixtures are tabulated in Tables 2 and 3. The TOC values released changed by the difference of the mixed ratios, independently with the morphologic difference of the resins. After 10 days soaking, the mixed ratios of the SACER-to-SBAER

Table 2. TOC Leaching Rate from Resin Mixtures of Different SACER and SBAER (B-B′) Ratios at 50 °C

Ratio SACER/SBAER	TOC leaching rate[a)] mgC h^{-1} dm^{-3}-resin
10/0	1.9$\times$10^{-2}
9/1	2.3$\times$10^{-3}
8/2	2.6$\times$10^{-3}
2/1	4.3$\times$10^{-3}
1/1	7.9$\times$10^{-3}
1/2	1.2$\times$10^{-2}
2/8	1.5$\times$10^{-2}
1/9	2.2$\times$10^{-2}
0/10	5.1$\times$10^{-1}

a) After 60 d soaking.

Table 3. TOC Leaching Rate from Resin Mixtures of Different SACER and SBAER (C-C′) Ratios at 50 °C

Ratio SACER/SBAER	TOC leaching rate[a)] mgC h^{-1} dm^{-3}-resin
10/0	3.8$\times$10^{-2}
9/1	5.2$\times$10^{-3}
8/2	5.8$\times$10^{-3}
2/1	7.8$\times$10^{-3}
1/1	9.7$\times$10^{-3}
1/2	1.2$\times$10^{-2}
2/8	1.4$\times$10^{-2}
1/9	1.7$\times$10^{-2}
0/10	5.9$\times$10^{-1}

a) After 60 d soaking.

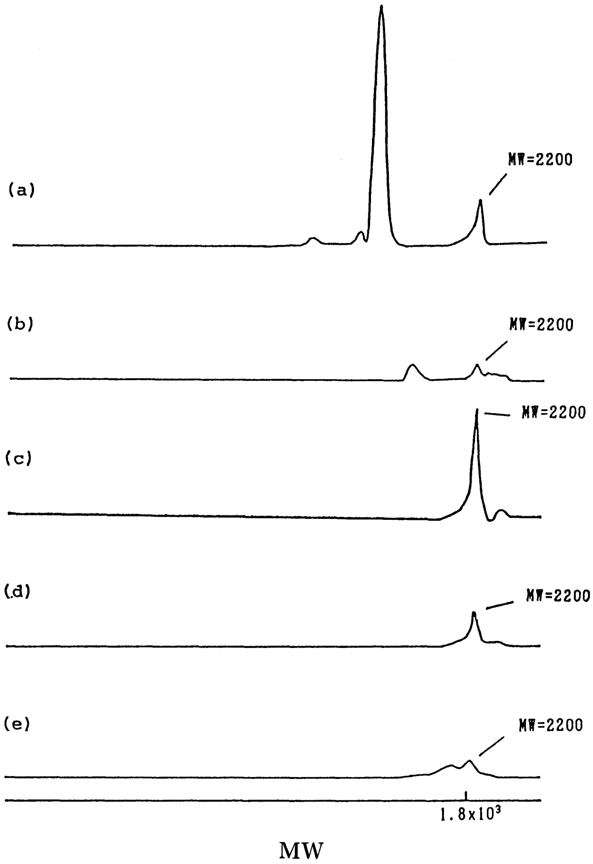

Fig. 4. GFC chromatogram of leachables from SACER to SBAER mixture of 1 to 1 after 60 d at 50 °C. (a): Leachables from resin A-A′, (b): Leachables from resin B-B′, (c): Leachables from resin C-C′, (d): Leachables from resin D-D′, (e): Leachables from resin E-E′.

volume ratio of 9 : 1 to 1 : 1 showed very low TOC values. As the soaking days and the ratios of SACERs were incresed, the minimum TOC value finally converged upon a mixed ratio of 9 : 1. This ratio is far different from the mixed ratios of the IERs in the following water treatments. A SACER-to-SBAER volume ratio of 1 to 1 is used as the mixed-bed IERs in an ultrapure water production system for semiconductor manufacturing. In the condensate water treatment at the power plant of a pressurized water reactor, a mixed-bed is operated at a SACER-to-SBAER ratio of 2 to 1 from the standpoint of preventing the pipings in the steam generator from corrosion by chloride and sulfate ions.[12)] There is usually a very low level (ppb) of ions in the condensate water at the power plant as well as the primary pure water in the ultrapure water production system. The authors therefore recommend a mixed-bed SACER-to-SBAER volume ratio of around 9 : 1, which seems to have sufficient capacity to remove ions from water; such a method should be used especially for mixed-bed IERs in an ultrapure water production system and for a condensate demineralizer from the viewpoint of minimizing TOC throw from mixed-bed resins. Not only do TOCs in water decrease the wafer yield in semiconductor manufacturing, but they foul the IER's surface and degrade the kinetics of ion exchange, while causing unexpected leakage, of corrosive ions to treated condensate water.[13–15)] Regarding field applications, a mixed-bed of 9 : 1 of the SACER-to-SBAER volume ratio may be dangerous in terms of the kinetic response of mixed-bed IERs. It may therefore be suggested that the volume ratio of SBAER to SACER in mixed-bed IERs be increased a little: for example, to 1 : 4 from 1 : 9.

Identification of Leachable Components from Mixed-Bed: Figures 4 and 5 illustrate GFC and RPC chromatograms for leachables in solutions obtained from mixtures of a SACER and SBAER volume ratio of 1 to 1. Every GFC chromatogram has a common peak at the MW 2200 position. This peak coincided with a component in the leachables from SBAERs which SACERs could not remove. RPC chromatograms show that the peak components located in the early retention time, i.e. the higher polor and low MW substances, were released out of the resin mixtures. Both components in the IER leachables would be the main contaminants for both pure and ultrapure water.

Removal of Leachables from Mixed-Bed: Table 4 shows the adsorbed amounts for leachables from resin

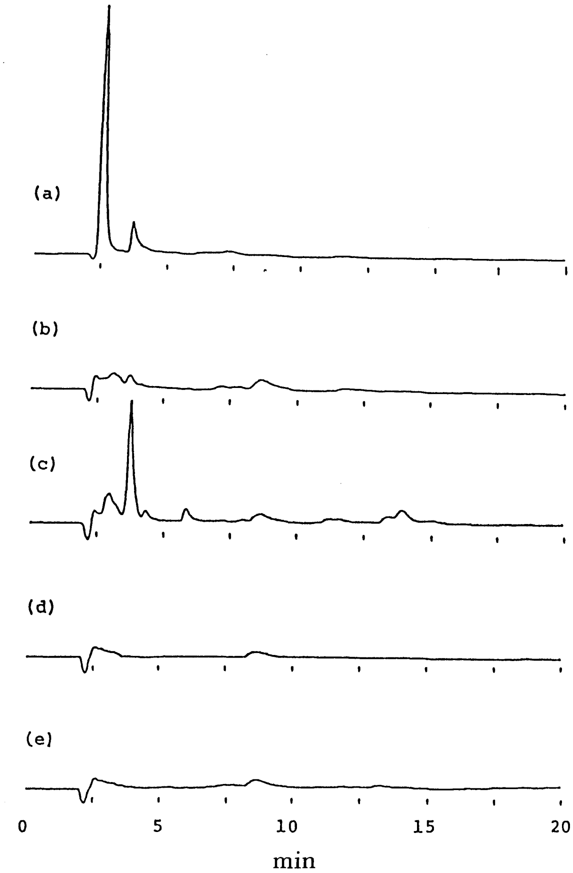

Fig. 5. RPC chromatogram of leachables from SACER to SBAER mixture of 1 to 1 after 60 d at 50 °C. (a): Leachables from resin A-A′, (b): Leachables from resin B-B′, (c): Leachables from resin C-C′, (d): Leachables from resin D-D′, (e): Leachables from resin E-E′.

Table 4. Adsorption of Leachables from SACER to SBAER Mixture of 1 to 1 with Carbonaceous Adsorbent at 25 °C

Adsorbent	*Co*[a)] mgC dm^{-3}	*Ce*[b)] mgC dm^{-3}	*Q*[c)] mgC g^{-1}
Leachables from resin B-B′			
F	2.7	0.0[d)]	6.8×10^{-2}
G	2.7	0.5	5.6×10^{-2}
H	2.7	0.7	5.2×10^{-2}
I	2.7	0.3	6.0×10^{-2}
Leachables from resin C-C′			
F	4.1	0.0[d)]	1.0×10^{-1}
G	4.1	0.0[d)]	1.0×10^{-1}
H	4.1	1.5	6.3×10^{-2}
I	4.1	3.3	4.7×10^{-2}

a) *Co*: Initial concentration, b) *Ce*: equilibrium concentration, c) Adsorbed amount, d) Less than determination limit (0.2 mgC dm^{-3}).

Table 5. Removal of Leachables from SACER and SBAER Mixture with Adsorbent F[a)]

	TOC mgC dm^{-3}
Leachables from resin B-B′	4.1
Leachables from resin B-B′ and F	2.7
Leachables from resin C-C′	5.1
Leachables from resin C-C′ and F	4.5

a) Mixed ratio of SACER : SBAER=1 : 1 by volume. After keeping for 5 d at 50 °C then for 1 d at 25 °C.

mixtures of B-B′ and C-C′, respectively, on carbonaceous adsorbents. Adsorbent F gave the largest adsorbed amount. The carbonaceous adsorbents used have very few ash and surface polarity by the functional groups, such as carbonyl and carboxyl groups. Therefore, the adsorption of the leachables on the adsorbents must be dependent on physical adsorption; there is almost no contributory role of chemical adsorption. The total surface areas and pore volumes of the adsorbents relevant to physical adsorption seem to be independent of the adsorbed amounts for leachables from resin mixtures. Organic substances which are more hydrophobic than water are preferentially adsorbed on a hydrophobic surface.[16,17)] Adsorbent F has the most hydrophobic surface, through the carbon-to-hydrogen atomic ratio's value.[18)] Consequently, it is considered that the adsorbent F showed the largest adsorbed amount because of the highest hydrophobicity. Table 5 exhibits the effect of the addition of adsorbent F on the leachables amounts from resin mixtures (SACER : SBAER=1 : 9. This mixed ratio was selected in order to obtain a sufficient leachable amount.). TOCs of 34 and 12% for resin mixtures of B-B′ and C-C′, respectively, were removed by adsorbent F. This is of importance not only in producing lower TOC (pure or ultrapure) water, but also in maintaining the long life demineralization capacity of mono-bed IERs. Haub and Foutch predicted that a SACER-to-SBAER volume ratio of 1.5 : 1 gives the lowest ion leakage in a column treatment, considering both the dissociation of water molecules and reversible ion exchange reaction.[19)] In fact, an IER mixed-bed is widely used in a mixed ratio of SACER to SBAER of 1 : 1 to 1 : 2 in ordinary water treatment, according to the ion-exchange capacity basis. It is postulated that organic contaminants, such as high MW substances and IER leachables, are well adsorbed on an IER surface. Foulants on resins hinder ions from passing smoothly through the liquid film on the resin surface.[20)] The rate-determining step for the ion-exchange reaction is the rate for liquid-film diffusion of ions in water. High MW contaminants adsorbed on IERs are difficult to wash away with ordinary regenerants.[21)] As a result, the demineralization rate and capacity for the fouled IERs decrease. Therefore, the addition of a suitable carbonaceous adsorbent to mixed-bed IERs can be expected to lighten any adverse effect, such as the deterioration of ion exchange kinetics by organic contaminants, and to maintain the long-life demineralization capacity.

Conclusions

1) The TOC leaching rates from mixed-bed IERs were far less than those from mono-bed IERs (SACERs or SBAERs).

2) The rates depended on the mixed ratios of SACERs to SBAERs and gave minimum levels in the range 9 : 1—4 : 1. (9 : 1 is the lowest.)

3) The MW 2200 component in SBAERs contributed to the leachbles released from mixed-bed IERs.

4) The leachable components released from a mixed-bed were effectively removed with a carbonaceous adsorbent with a higher hydrophobic surface.

5) An admixture of mixed-bed IERs and the carbonaceous adsorbent is considered to be suitable for preparing lower TOC (pure or ultrapure) water.

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References

1) A. C. Deborah and H. M. Theodore, *Ultrapure Water,* **1988**, 39.

2) M. Koyama and M. Nishimura, *J. Water Purification and Liauids Wastes Treatment,* **27**, 235 (1986).

3) T. Sakamoto and K. Koike, *Kogyo Yoshui,* **305**, 8 (1984).

4) H. Kuyama, Y. Takamizawa, and N. Higosaki, *Nippon Kagaku Kaishi,* **1974**, 2020.

5) S. J. Porier, 4th Semiconductor Purewater Conference Transcripts, 1985, p. 197.

6) W. Agui, M. Takeuchi, M. Abe, and K. Ogino, *J. Jpn. Oil Chem. Soc.,* **37**, 1114 (1988).

7) W. Agui, M. Takeuchi, M. Abe, and K. Ogino, *J. Jpn. Oil Chem. Soc.,* **38**, 405 (1989).

8) W. Agui, M. Takeuchi, M. Abe, and K. Ogino, *J. Jpn. Oil Chem. Soc.,* **39**, 307 (1989).

9) W. Wood, *J. Phys. Chem.,* **61**, 832 (1957).

10) J. R. Stahlbush, R. M. Strom, J. B. Henry, and N. E. Skelly, 48th International Water Conference Proceedings, 1987, p. 67.

11) W. Agui, M. Abe, and K. Ogino, *J. Jpn. Oil Chem. Soc.,* **38**, 929 (1989).

12) S. Naruto, *MOL.,* **3**, 71 (1986).

13) K. Vivien, '86 Semiconductor and Pure Water Conference Transcripts, 1986, p. 240.

14) D. I. Devore, 45th International Water Conference Proceedings, 1984, p. 253.

15) Z. Matejke and M. Jileckova, "Kinetic Investigation of Unusual Sulfate vs. Chloride Leakage in High-Flow-Rate Condensate Deionization Plants," in "Ion Exchange for Industry. SCI for the Application of Chemistry and Related Sciences," the Society of Chemical Industry, London (1988), p. 59.

16) M. Nakagaki, "Surface States and Colloid State," Tokyo Kagaku Dojin, Tokyo (1968), p. 123.

17) K. Ogino, T. Asakawa, K. Yamabe, and K. Takahashi, *J. Jpn. Oil Chem. Soc.,* **31**, 159 (1982).

18) W. Agui, M. Takeuchi, M. Abe, and K. Ogino, *J. Jpn. Oil Chem. Soc.,* **39**, 385 (1990).

19) C. E. Haub and G. L. Foutch, *Ind. Eng. Chem. Fundam.,* **381**, 25 (1986).

20) B. J. Hoffman, J. C. Konen, and J. T. McNulty, Proc. First Ultra Pure Water Jounal Conference, 1987, p. 1.

21) J. R. Stahlbush, R. M. Strom, J. B. Henry, and N. E. Skelly, "Identification, Prediction and Consequence of the Decomposition Products from Cation Exchange Resins," in "Ion Exchange for Industry. SCI for the Application of Chemistry and Related Sciences," the Society of Chemical Industry, London (1988), p. 22.