BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2459—2463 (1969)

Studies of Ion Exchange Membranes. XXX. The Tetrahydrofuran Extraction of the Ion-exchange Membrane and Its Base Membrane Prepared by the "Paste Method"

Yukio MIZUTANI

Tokuyama Soda Co., Ltd., Tokuyama-shi, Yamaguchi-ken

(Received February 3, 1969)

In order to throw light on the chemical structure of the ion-exchange membrane prepared by the "Paste Method," the ion-exchange membrane and its base membrane were extracted with tetrahydrofuran. The base membrane was composed of polyvinyl chloride and the resin component of the styrene-divinyl benzene system or of the 2-methyl-5-vinyl pyridine-divinyl benzene system, the ion-exchange group was introduced into this resin component. It was established that the resin component was partially extractable through a filter paper. Although the resin component and polyvinyl chloride should be entwined with each other, and although the resin component might be grafted on polyvinyl chloride, it could be concluded that the chemical structure of the ion-exchange membrane prepared by the "Paste Method" is different from that of Amberlite IR-120, *i. e.*, the homogeneously crosslinked gel-structure.

Many procedures have been proposed for the preparation of an ion-exchange membrane.[1–8] However, in most of these procedures the base membrane, with a functional group appropriate for the introduction of an ion-exchange group, is prepared beforehand, and then an ion-exchange group is introduced. Therefore, the preparation of the base membrane has thus far been an important theme.[2–8] The present author has already reported on the "Paste Method."[5–8] Namely, a fine powder of polyvinyl chloride (PVC) and a monomer mixture, consisting mainly of styrene (St)-divinyl benzene (DVB) or 2-methyl-5-vinyl pyridine (MVP)-DVB, was mixed to prepare the paste, and then a Teviron cloth (a reinforcing material) was coated with this paste. This resultant polymer composite was heated in order to polymerize the monomers. An ion-exchange group was introduced to the base membrane by sulfonation or quarternization with methyl iodide. The ion-exchange membrane thus prepared has been used in the electrophoretic concentration[9,10] or desalination[11] of sea water.

Furthermore, this ion-exchange membrane is flexible and thermoplastic. This characteristic of ion-exchange membranes prepared by the "Paste Method" suggests that the structure of the membrane may be different from the homogeneously crosslinked gel-structure.

The base membranes for the cation-exchange membrane (base membrane-C) and for the anion-exchange membrane (base membrane-A) show quite a good transparency. For example, the base membrane-C consists mainly of PVC and the resin component of the St-DVB system. Considering that PVC is immiscible with polystyrene and that the mixture of both polymers is an opaque white, the quite good transparency of the base membrane-C has been explained by the presence

---

[1] H. Nakazawa, Y. Onoue and Y. Mizutani, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **61**, 789 (1958); Y. Onoue, Y. Mizutani and S. Akiyama, *Denki Kagaku* (*J. Electrochem. Soc. Japan*), **29**, 223 (1961); Y. Onoue, Y. Mizutani, W. Tesima, R. Yamane and S. Akiyama, *ibid.*, **29**, 468 (1961).

[2] W. K. W. Chen, R. B. Mesrobian, D. S. Ballantine, D. J. Metz and A. Glines, *J. Polym. Sci.*, **23**, 903 (1957).

[3] Y. Mizutani, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **65**, 1124 (1962).

[4] Y. Mizutani, *ibid.*, **65**, 1128 (1962).

[5] Y. Mizutani, R. Yamane, H. Ihara and H. Motomura, This Bulletin, **36**, 361 (1963).

[6] Y. Mizutani, W. Tesima and S. Akiyama, Japanese Pat., 410368.

[7] Y. Mizutani, W. Tesima, S. Akiyama, R. Yamane and H. Ihara, Japanese Pat., 481838.

[8] Y. Mizutani, R. Yamane and H. Motomura, This Bulletin, **38**, 689 (1965).

[9] R. Yamane, T. Sata and Y. Mizutani, *Nippon Kaisui Gakkai-Shi*, (*Bull. Soc. Sea Water Science Japan*), **20**, 313 (1967).

[10] R. Yamane, H. Motomura, T. Sata and Y. Mizutani, *ibid.*, **20**, 327 (1967).

[11] T. Matsuda, S. Ogawa and Y. Onoue, "Demineralization of Sea Water by Electrodialysis," Presented at the Second European Symposium on Fresh Water from the Sea, May, 9—12, 1967, Athens, Greece, European Federation of Chemical Engineering.

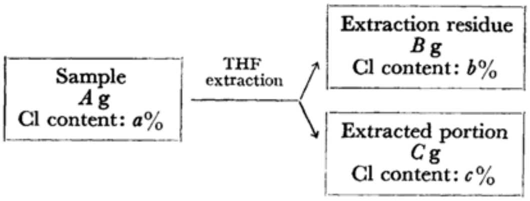
of the graft copolymer of PVC and the resin component.[5)]

In order to elucidate the correlation between PVC and the resin component (M-resin) of the St-DVB system or the MVP-DVB system, in this study the ion-exchange membrane and its base membrane were extracted with tetrahydrofuran (THF).

Experimental

The Sample. The ion-exchange membrane and its base membrane were prepared by the "Paste Method."[5–8)] Previous to the THF extraction, the sample was extracted with methanol in order to expel the unpolymerized monomer, *etc.*, by using a Soxhlet extractor.

The THF Extraction. The sample was extracted with THF for 30 hr by the use of a Soxhlet extractor.



E_p and E_R were defined as follows:

$$E_p = \frac{\text{Quantity of chlorine in the extraction residue}}{\text{Quantity of chlorine in the base membrane}}$$

$$E_R = \frac{\text{Quantity of the M-resin in the extracted portion}}{\text{Quantity of the M-resin in the base membrane}}$$

The cylindric filter paper used was Toyo Filter Paper No. 84 (Size, 25×90 mm); the particle size retainable by this filter paper is 8 μ.

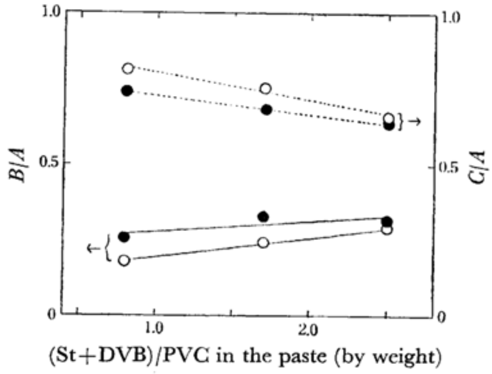


Fig. 1. The effect of the monomer content in the paste on B/A and C/A.
The composition of the paste:
DVB/(St+DVB)=0.025
Dioctylphthalate/PVC=0.31—0.4
Polymerization temperature: 110°C
-○-: Observed value
-●-: Calculated value of (St+DVB)/Base membrane-C (for B/A) or of PVC/Base membrane-C (for C/A)

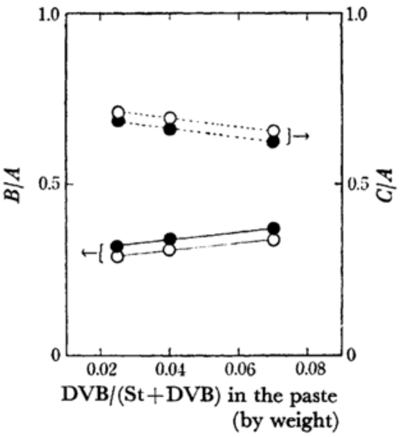


Fig. 2. The effect of the DVB content in the paste on B/A and C/A.
The composition of the paste:
(St+DVB)/PVC=2.5
Dioctylphthalate/PVC=0.31
Polymerization temperature: 110°C
-○-, -●- : Shown in Fig. 1

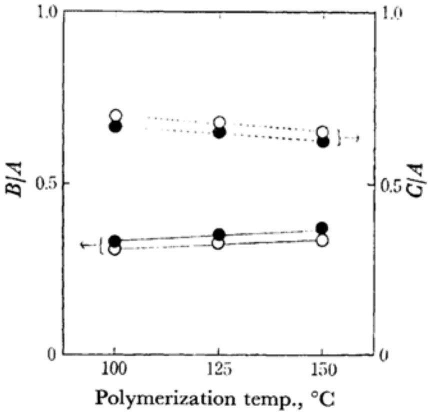


Fig. 3. The effect of the polymerization temperature on B/A and C/A.
The composition of the paste:
(St+DVB)/PVC=2.5
DVB/(St+DVB)=0.04
Dioctylphthalate/PVC=0.31
-○-, -●-: Shown in Fig. 1

Results and Discussion

The recovering ratio of the polymer after the THF extraction $[(B+C)/A]$ was larger than 0.98, and the chlorine balance $[(B\cdot b+C\cdot c)/A\cdot a]$ was 1.0±0.2.

The Base Membrane-C. Figures 1—3 show the results of the THF extraction. With the increase in the monomer content [(St+DVB)/PVC] and in the DVB content [DVB/(St+DVB)] of the paste, and with the elevation of the polymerization temperature, the quantity of the extraction residue increased linearly. The chlorine content of the extracted portion also increased linearly with the increase in the monomer content, but the DVB content in the paste and the polymerization temperature had no effect on the chlorine content in the extracted portion (Figs. 4—6). In all cases, the content of the extracted portion in the base membrane-C (*C*/*A*) was smaller than the PVC content of the base membrane-C and the chlorine content of the extracted portion was smaller than that of PVC itself (56.4%). These facts can be explained by the presence of the M-resin in the extracted portion. On the other hand, the chlorine content of the extraction residue was small (1.5—3%), but it showed the presence of PVC inextractable with THF.

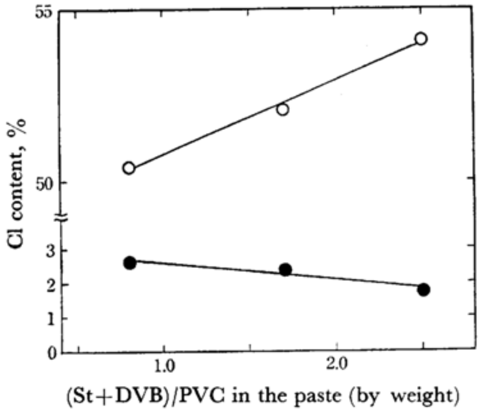


Fig. 4. The relation between the monomer content in the paste and the chlorine content of the extracted portion and the extraction residue.
The experimental condition is the same as shown in Fig. 1.
○ : Extracted portion ●: Extraction residue

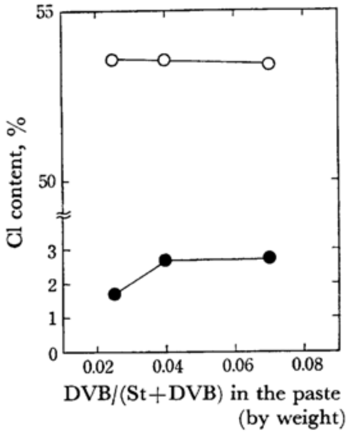


Fig. 5. The relation between the DVB content in the paste and the chlorine content of the extracted portion and the extraction residue.
The experimental condition is the same as shown in Fig. 2.
○: Extracted portion ●: Extraction residue

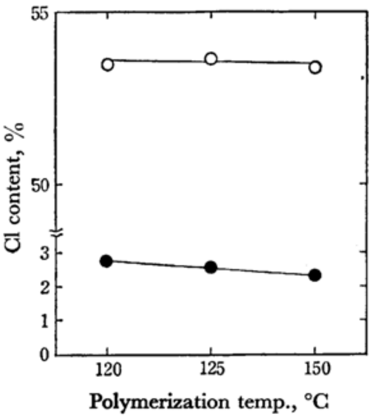


Fig. 6. The relation between the polymerization temperature and the chlorine content of the extracted portion and the extraction residue.
The experimental condition is the same as shown in Fig. 3.
○: Extracted portion ●: Extraction residue

It is very significant that a large quantity of the M-resin was found in the extracted portion. Since the M-resin should have a crosslinked structure, the presence of the M-resin in the extracted portion can be understood if the M-resin is very fine. This explanation is supported by Photo 1, which shows that the extraction residue was the aggregate of the fine particle and that its size was less than 50 mμ. When a monomer and DVB polymerize in a medium in which the monomer is soluble, while its polymer is insoluble, a fine powdery polymer with crosslinkage is obtained.[12,13] The formation of the spherical particle of the M-resin is explainable by considering PVC as a polymerization medium in which St and DVB are soluble, while polystyrene is insoluble. The network of the M-resin, formed by the polymerization of St and DVB, may be entwined with the PVC chain, and, furthermore, the M-resin may be grafted onto

Photo. 1. The electron microphotograph of the extraction residue of the base membrane-C.

---

12) Y. Mizutani, This Bulletin, **39**, 1088 (1966).
13) Y. Mizutani, *ibid.*, **40**, 1519 (1967).

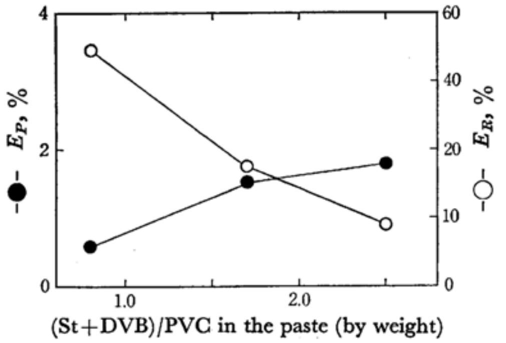


Fig. 7. The relation between the monomer content in the paste and the values of E_P and E_R.
The experimental condition is the same as shown in Fig. 1.

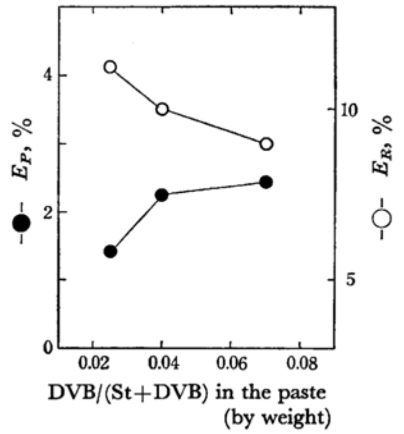


Fig. 8. The relatoin between the DVB content in the paste and the values of E_P and E_R.
The experimental condition is the same as shown in Fig. 2.

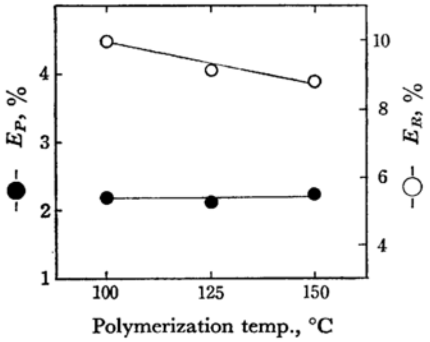


Fig. 9. The relation between the polymerization temperature and the values of E_P and E_R.
The experimental condition is the same as shown in Fig. 3.

PVC. The formation of the graft copolymer is confirmed by the graft copolymer prepared by the polymerization of St in the PVC film.[3] Thus, the presence of the M-resin in the extracted portion is explainable, but the degree of participation of the graft copolymer is still obscure, since the crosslinked M-resin was extracted through the filter paper.

Figures 7—9 show the E_R and E_P values. The E_P values show that the quantity of PVC in the extraction residue was 0.5—2% of the total PVC in the base membrane-C. With the increase in the monomer content of the paste, the E_P value increased and the E_R value decreased from 50% to 10%. These facts can be explained by the tendency for the increase in the monomer content to promote the swelling of the M-resin in the polymerization system, the entanglement of the network of the M-resin with the PVC chain, and the aggregation of the fine powdery resin. This explanation is supported by the observation that the extraction residue, although the E_R value was small, became fibrous or textural more distinct with the increase in the monomer content in the paste. With the increase in the DVB content in the paste, the E_P value increased and the E_R value decreased. These changes can be explained by the increase in the entanglement of the M-resin with the PVC chain. With the elevation of the polymerization temperature, the E_R value decreased, but this factor had no effect on the E_P value.

Table 1. The result of the THF extraction of the cation-exchange membrane

Sample	Base Membrane-C	Cation-exchange membrane	
		H^+ form	Na^+ form
B/A	0.152	0.423	0.525
E_t/E_0	—	0.731	0.878

E_t: Number of the ion-exchange site in the extraction residue.
E_0: Number of the ion-exchange site in the ion-exchange membrane.

The Cation-exchange Membrane. Table 1 shows the results of the THF extraction. By sulfonation with concentrated sulfuric acid, the ratio of the extraction residue (B/A) became larger than that of the base membrane-C. This may be explained by the reaction between PVC and the M-resin during the sulfonation and/or by the fact that the swelling of the cation-exchange membrane in THF is smaller than that of the base membrane-C. Furthermore, it was an important finding that the extracted portion had an ion-exchange capacity. This finding shows that the M-resin with the ion-exchange group was extracted; these observations are consistent with the finding concerning the base membrane-C. The presence of the fine powdery M-resin should be a reason why the cation-exchange membrane and its base

TABLE 2. THE RESULT OF THE THF EXTRACTION OF THE BASE MEMBRANE-A

	B/A	C/A	N content %	Cl content %	PVC content %	E_P %	E_R* %
Base membrane-A	—	—	2.74	39.34	69.75	—	—
Extraction residue	0.619	—	4.39	28.71	50.90	45.1	—
Extracted portion	—	0.380	0.2>	55.18	97.80	—	2.7

* Calculated from chlorine content.

TABLE 3. THE RESULT OF THE THF EXTRACTION OF THE ANION-EXCHANGE MEMBRANE (Cl^- form)

Sample	B/A	C/A	Cl content %	N content %	E_P %	E_R* %
Anion-exchange membrane	—	—	40.97	2.32	—	—
Extraction residue	0.731	—	36.68	3.04	65.6	—
Extracted portion	—	0.371	54.85	0.24	—	2.8

* Calculated from nitrogen content.

membrane have flexibility and thermoplasticity.

The Base Membrane-A. Table 2 shows the results of the THF extraction. The presence of the M-resin in the extracted portion was confirmed by the presence of nitrogen. Furthermore, the chlorine content of the extracted portion was clearly smaller (55.18%) than that of PVC itself (56.4%), and the E_R value showed that a little of the M-resin was extracted. On the other hand, much PVC was found in the extraction residue, as was shown by both the chlorine content and the E_P value, and the residue was fibrous or textural. The finding concerning the base membrane-A was considerably different from that of the base membrane-C; this difference is probably to be attributed to the difference between the affinity of St for PVC and that of MVP for PVC.

The Anion-exchange Membrane (Chloride-ion Form). Table 3 shows the results of the THF extraction. The membrane does not swell as much as the base membrane-A in Table 2. Also, the shape of the anion-exchange membrane was not destroyed by the THF extraction. The M-resin was partially extractable. This important finding can be explained by the fact, presented above, that there were fine particles of the M-resin extractable through a filter paper.

Conclusion

In order to elucidate the chemical structure of the ion-exchange membrane prepared by the "Paste Method," the ion-exchange membrane and its base membrane were extracted with tetrahydrofuran. Although the matrix of the ion-exchange resin component was complicatedly entwined with the polyvinyl chloride chain, and although the former should be grafted on the latter, the presence of fine particles of the ion-exchange resin component, extractable through a filter paper with tetrahydrofuran, was confirmed. This fact shows conclusively a characteristic of this ion-exchange membrane; it also suggests that the chemical structure of the ion-exchange membrane is different from that of Amberlite IR-120, *i.e.*, the homogeneously crosslinked gel-structure. Furthermore, this characteristic may be a reason why the ion-exchange membrane is flexible and thermoplastic.