Characterization of Na Ion-Sensitive Solvent Polymeric Membranes Based on a Neutral Carrier

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Synopsis

The states in the surface and the bulk phases of Na ion-sensitive polymeric membranes based on a synthetic carrier were investigated using SEM, IR, ^{13}C-NMR, and GC. The ^{13}C-NMR study revealed that conformation change of the carrier took place when the carrier was incorporated into the membrane phase. From SEM, IR, and ^{13}C-NMR experiments with a deteriorated membrane, the conformation change of the carrier was proposed as one of the deterioration factors other than the decrease in the diffusion coefficient of the carrier in the membrane phase.

INTRODUCTION

During the past decade, ion-sensitive solvent polymeric membranes mediated by neutral carriers have been utilized for various analytical applications because of their advantages of higher selectivity and wider variety of carriers as compared with other types of ion-sensitive membranes. For clinical applications, potentiometric analyzers for multielectrolytes have been developed and routinely used in clinical laboratories in place of flame photometric and colorimetric analyzers. Model 702 Na, K, Cl analyzer (Hitachi Ltd.), model STAT/ION Na, K, Cl analyzer (Technicon).

Besides their practical applications, there have been several fundamental studies on the elucidation of the origin of their high selectivity and their response mechanism in order to choose more systematically the membrane solvent and matrix polymer.[1-3] Thoma et al. revealed that the permselectivity of an ion-sensitive polymeric membrane based on a neutral carrier could be understood through the selective complexation of specific ions (usually cations) in the sample solution with the neutral carrier existing in the boudary region between the polymeric membrane and the sample solution, followed by transportation of these ions across the membrane phase by the carrier translocation.[1]

However, the response behavior of the ion-sensitive polymeric membranes is explained by this scheme; there still remains the problem with regard to the life time of the membrane. In clinical applications of the ion-sensitive ploymeric membrane electrodes, it has been noted that the electrode performances, i.e., sensitivity and selectivity, deteriorate after several months' contact with human serum or urine.[4] The deterioration mechanism is one of the most important problems from the practical point of view. Previously, Oesch and Simon investigated the lifetime of poly(vinyl chloride) (PVC)-

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based solvent polymeric membranes, and they demonstrated that the lifetime of the membrane could be primarily determined by the kinetics of the loss of the membrane solvent and/or the carrier from the polymeric membrane phase into the external solution.[5] When serum or urine is examined using an ion-sensitive polymeric membrane electrode, adsorption of the constituents of these body fluids, proteins and/or lipids, on the membrane surface may be another deterioration factor, for this may inhibit the extraction of ions from the sample solution into the membrane phase. In addition to the above deterioration factors, the conformation change of the carrier may deteriorate the membrane performances, for the ability of the carrier to form a complex selectively with a specific ion is affected by the conformation of the carrier.

From the point of view described above, the surface and the bulk states of the Na ion-sensitive membrane before and after the contact with human serum were compared by employing ^{13}C-NMR, Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and gas chromatography (GC).

EXPERIMENTAL

Reagents

Synthetic carrier[6] for Na ion shown in Figure 1 was graciously offered by Dr. W. Simon of the Swiss Federal Institute of Technology, Zürich, Switzerland. Dioctyl adipate (DOA) for membrane solvent, PVC (averaged degree of polymerization; nearly 1100) for membrane matrix, tetrahydrofuran (THF) for casting solvent, and NaSCN for an additive compound to increase the carrier lipophilicity in the membrane and to decrease the membrane resistance were all purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. The DOA, THF, and NaSCN were guaranteed grade chemicals.

Membrane

Using published preparation techniques,[7] Na ion-sensitive membrane, about 200 μm in thickness, was prepared. Typical compositions of the membrane slightly differed from the previously reported values,[8] but the membrane functioned as an electrode membrane. The membranes deteriorated with human serum were offered by Naka Works, Hitachi Ltd., Ibaraki, Japan.

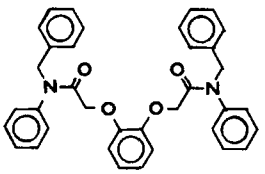

Fig. 1. Synthetic carrier used in this study.

Apparatus

The ^{13}C-NMR spectra were obtained with a Model R-900 Fourier transform nuclear magnetic resonance spectrometer operated at 22.5 MHz and 32°C (Hitachi Ltd.). The observation range was 200 ppm from TMS. Pulse width was set at 45° (22 μs), and a complete decoupling mode was employed. The NMR sample of membranes was prepared by stacking 20 membranes (7.0 mm in diameter) into a NMR sample tube (8 mm in outer diameter). The IR spectra of the membrane surface were observed with a Model FTS-15 Fourier transform infrared spectrometer with ATR attachment (Digilab Co. Ltd.). Scanning electron micrographs of the membrane surface and the cross section were taken with a Model S-500 SEM (Hitachi Ltd.). A membrane cross section was prepared by fracturing a membrane in liquid nitrogen. The concentration change in membrane solvent (DOA) was determined with a Model 163 gas chromatograph equipped with a Si-OV-101 glass capillary column in the programmed temperature mode (Hitachi Ltd.). Samples for GC experiments were prepared by dissolving the membrane in THF. The DOA content of the deteriorated membrane was determined by comparing the peak height of DOA from the deteriorated membrane with that from a new membrane.

RESULTS AND DISCUSSION

Membrane Morphology

Morphological change of the Na ion-sensitive membrane was examined with SEM. Figure 2 shows the cross-sectional SEM image of a new (i.e., not used) membrane. The membrane has a smooth cross section. However, there are some rough areas which may have occurred on fracturing [in the right half of Fig. 2(A)]. In magnified SEM image of the damaged region [Fig. 2(B)], droplike swelling with a few μm in diameter was found. This swelling may be due to the oozing of DOA, since its concentration in membrane is close to the upper retaining limit of DOA in the membrane.

The SEM image of a cross section of the deteriorated membrane is shown in Figure 3. Compared with a cross section of a new membrane, morphological changes caused by the contact with serum are apparent. When a new membrane is immersed in a methanol/CCl_4 mixed solution in order to extract the membrane solvent, the residual membrane has the same porous structure as in Figure 3.

Figure 4 shows the surface SEM image of the deteriorated membrane. Threadlike aggregations, several μm in length, are seen, which may be formed by the contact with serum constituents, proteins, and/or lipids. For this membrane, the FT–IR–ATR spectrum was observed. An amide II absorption band, a characteristic band of proteins, was found at 1670 cm^{-1} (in Fig. 5), while for a new membrane no similar peak was observed. Consequently, membrane contamination was due to proteins. Since this membrane surface was only partially covered with aggregations, the surface contamination by serum proteins would not be a major factor in deterioration.

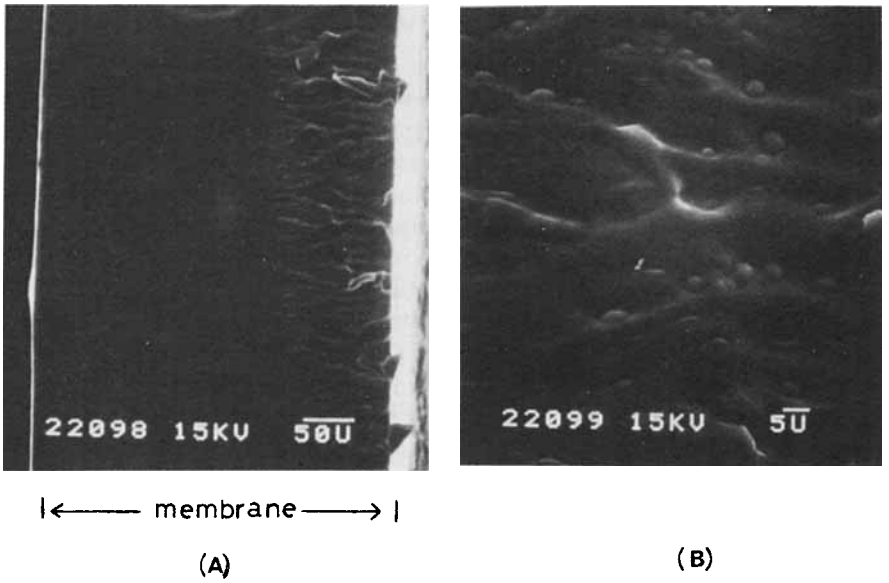

Fig. 2. Scanning electron micrograph of the cross section of a new membrane. Composition: PVC/DOA/carrier/NaSCN (wt %); 37.0/59.7/3.2/0.1. (B) is a magnified image of the right half of (A).

brane surface was only partially covered with aggregations, the surface contamination by serum proteins would not be a major factor in deterioration.

Analysis of Membrane Bulk State by ^{13}C-NMR

Preliminary ^{13}C-NMR experiments on a model casting solution were carried out to determine how many resonance lines of the carrier overlap with those of other membrane constituents. To make the spectrum clear, the

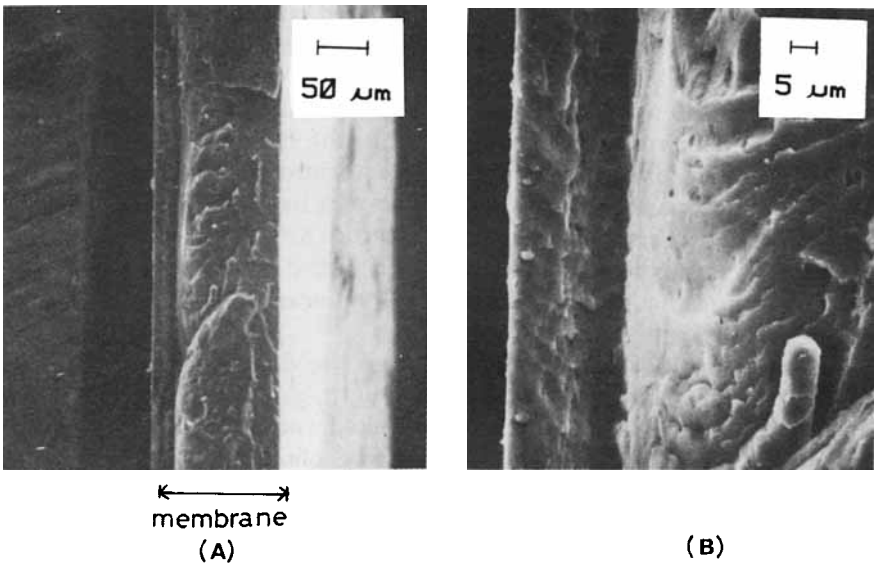

Fig. 3. Scanning electron micrograph of a cross section of a deteriorated membrane. Membrane composition (initial): as cited in Figure 2. (B) is a magnified image of (A).

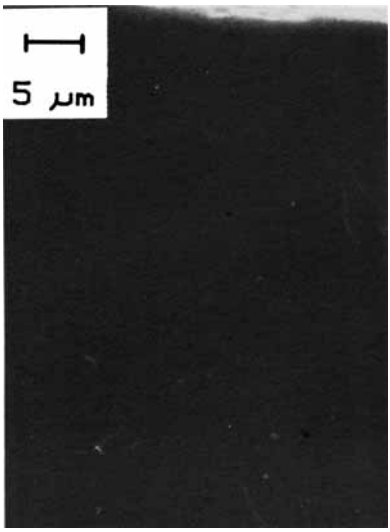

Fig. 4. Scanning electron micrograph of a deteriorated membrane surface.

amount of DOA was significantly decreased, while the amount of the carrier was increased from that in the usual membrane casting solution containing DOA at about 10 wt % and the carrier at 0.5 wt %. As shown in Figure 6, 14 peaks can be assigned to the absorption lines of the carrier because of its mirror symmetry. Although two peaks of this carrier, appearing at $\delta =$ 70 and 55, overlap with the methylene peaks of THF and DOA, the other 12 peaks do not overlap with the peaks of the membrane constituents other than the carrier. Thus ^{13}C-NMR is suitable for the investigation of the carrier in the membrane phase. Another experiment on the carrier in the liquid phase was carried out to examine the effect of NaSCN addition on the chemical shifts of the carrier carbons. A large excess of NaSCN was added so that carriers form complexes with Na ions completely. The results are shown in Figure 7. Addition of NaSCN caused several absorption lines of the carrier to shift to the higher field. A singlet carbon peak appearing

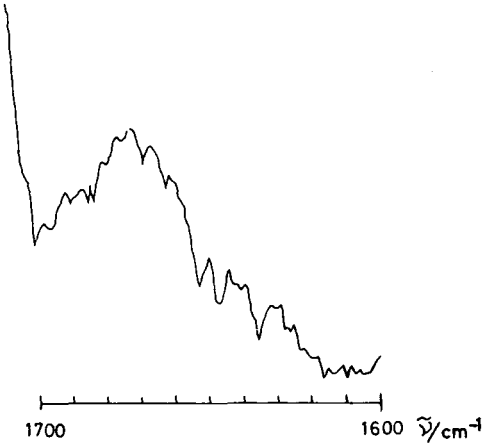

Fig. 5. FT-IR-ATR spectrum of a deteriorated membrane surface in the range from 1600 cm^{-1} to 1700 cm^{-1}.

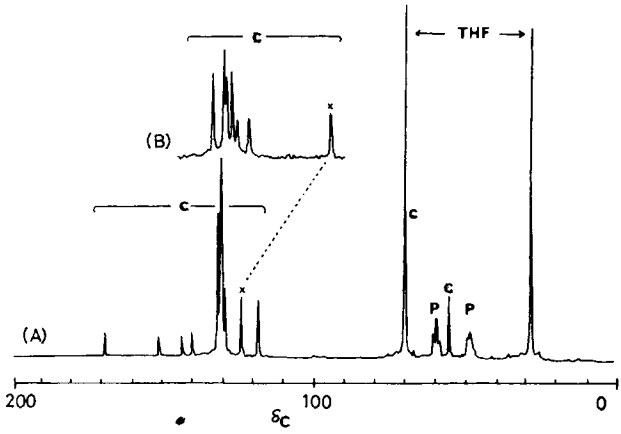

Fig. 6. ^{13}C-NMR spectrum of a model casting solution. PVC/DOA/Carrier/THF (wt %): 9.6/0.6/15/74.8 in (A). The letters C and P designate carrier and PVC, respectively. In (B), an expanded spectrum is shown.

at $\delta = 150$ and a doublet carbon peak appearing at $\delta = 118$ in Figure 7(A) were shifted by 4 ppm to the higher field as shown in Figure 7(B). Therefore, it can be estimated that changes in the chemical shift of the carrier existing in the membrane phase in contact with the Na ion containing solution are 4 ppm at most from the free state (unbounded state in solution) if other effects resulting from the introduction of the carrier into the membrane phase are to be neglected.

Figure 8(A) shows the ^{13}C-NMR spectrum of a Na ion-sensitive membrane having a composition known to function as well as an electrode membrane.[8] Though the accumulation was carried out 285,167 times, the carrier peaks were not clearly observed, for the carrier concentration was very low. Two peaks at $\delta = 130$ and 102 might be those ones. Considering the results shown in Figure 7, the origin of the peak at $\delta = 102$ is not clear because this is far distant from the absorption at $\delta = 114$ where the peak of the aromatic doublet carbon was supposed to be present if Na ions were incorporated into the carrier molecules. To clarify this point, ^{13}C-NMR spectrum

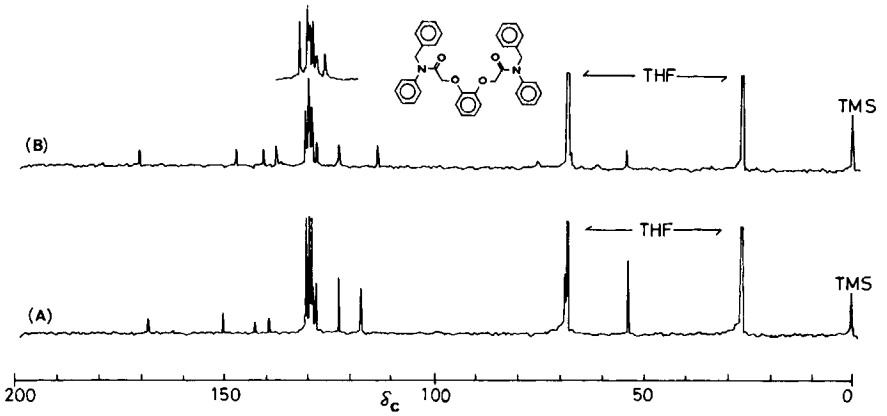

Fig. 7. Effect of NaSCN addition on ^{13}C-NMR spectrum of the carrier. Carrier/THF/NaSCN (wt %): 53/47/0 in (A) and 12.6/83.6/3.8 in (B).

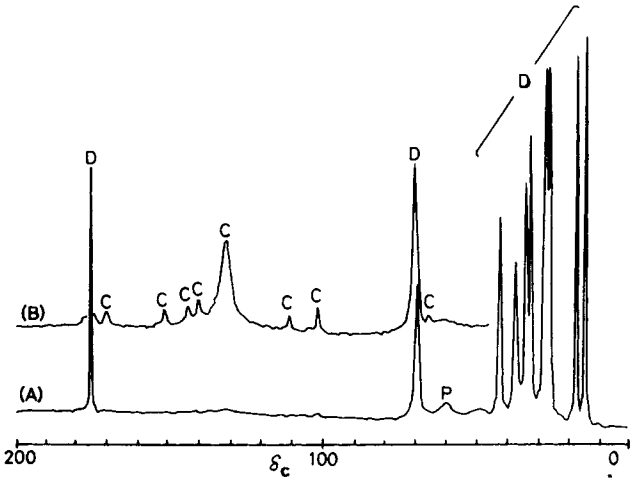

Fig. 8. ^{13}C-NMR spectrum of a Na ion-sensitive membrane. PVC/DOA/carrier/NaSCN (wt %):37.0/59.7/3.2/0.1 in (A) and 27/46/27/0 in (B). Accumulation was carried out 285,167 times for (A) and 65,833 times for (B). The letter D designates DOA.

of the model membrane whose carrier concentration was increased about nine times was observed. In order to avoid any side effects, the PVC/DOA ratio was not changed and NaSCN was not added to the model membrane. The results are shown in Figure 8(B). For this model membrane, seven carrier carbon peaks were clearly observed, while six carbon peaks centered around $\delta = 130$ in Figure 7 broadened and produced one large absorption peak. The peak which appeared at $\delta = 102$ in Figure 8(A) was also observed at the same chemical shift in this membrane [Fig. 8(B)]. Therefore, this peak was assigned to the aromatic doublet carbon peak of the carrier which appeared at $\delta = 118$ in Figure 7(A). It is reasonable to consider that this large chemical shift change, 16 ppm up field, for the aromatic doublet carbon is caused by the conformation change of the carrier incorporated into the membrane phase, because this large chemical shift change was observed for the model membrane without NaSCN. More detailed information about the conformation of the carrier in the membrane phase might be obtained if the spin-lattice relaxation times of the carrier carbons are examined at various temperatures. As line widths of DOA in the membrane phase were not so broadened compared with those in the liquid phase, it can be said that DOA molecules in the membrane phase are not significantly hindered sterically.

The bulk state of the deteriorated membrane was examined by ^{13}C-NMR. The results are shown in Figure 9. As the amount of sample was small, the *S/N* ratio of the spectrum was poor. The DOA peaks around $\delta = 30$ were broadened as compared with the results shown in Figure 8, and an additional broad peak was found at about 120 ppm. The origin of this peak is not clear because a new membrane gives no such large absorption peak in this region (cf. Fig. 8). For a deteriorated membrane, we can expect that the DOA content is decreased from the initial value. The decrease of DOA content and the accompanied increase of membrane rigidity may bring about both the peak broadening and the additional peak shift of the carrier,

PVC, and DOA. In order to determine the origin of the absorption peak appearing at about 120 ppm in Figure 9, a model membrane with a low DOA content (16.7 wt %) was examined. Figure 10 shows the ^{13}C-NMR spectrum of the membrane. A broad peak is also found at about 110 ppm in this spectrum. Considering the carrier concentration in this membrane, it is feasible to suppose that this large peak corresponds to the overlapped absorption peaks of the carrier which appeared at about 130 ppm in Figure 8(B). If this interpretation is correct, the DOA content of the deteriorated membrane should be a few tens percent.

The DOA content of the deteriorated membrane was examined by employing GC. The gas chromatographs of the deteriorated membrane and a new membrane are shown in Figure 11. Comparing with the DOA content of the new membrane, the DOA content of the deteriorated membrane was determined at 24.3 wt %. This result agrees with the estimated DOA content from the ^{13}C-NMR spectra shown in Figures 9 and 10. So the broad peak which appeared at about 120 ppm in the ^{13}C-NMR spectrum of the deteriorated membrane could be assigned to the overlapped absorption peaks of the carrier carbons. These results indicate that the conformation change of the carrier in the membrane phase becomes larger as the DOA content in the membrane phase decreases. Because the ability of the carrier to form a complex selectively with Na ion and to transport Na ion is affected by the conformation of the carrier, the conformation change accompanied by the decrease of DOA content would be a factor for membrane deterioration.

It has been claimed that the decrease of the diffusion coefficient of the carrier in the membrane phase following the decrease of DOA content slows down the translocation of Na ion.[5] As to the deteriorated membrane examined in this study, the diffusion coefficient of the carrier is estimated to be decreased more than 3 orders of magnitude from the diffusion coefficient of the new membrane.[5] This large decrease of the diffusion coefficient of the carrier has been proposed as another factor for membrane deterioration. At this moment, it is difficult to determine quantitatively the contribution

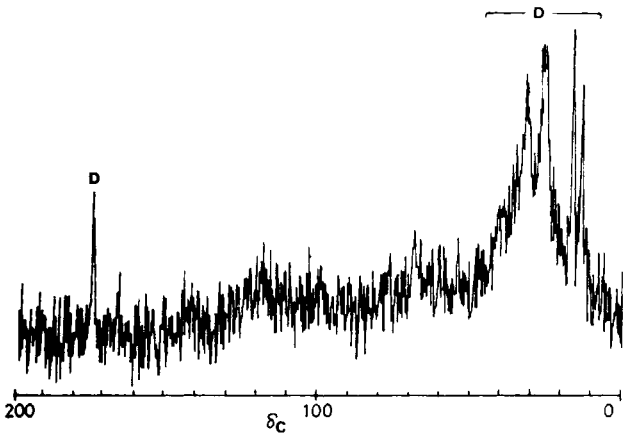

Fig. 9. ^{13}C-NMR spectrum of a deteriorated membrane. Initial membrane composition: as cited in Figure 8(A). Accumulation was carried out 100,000 times.

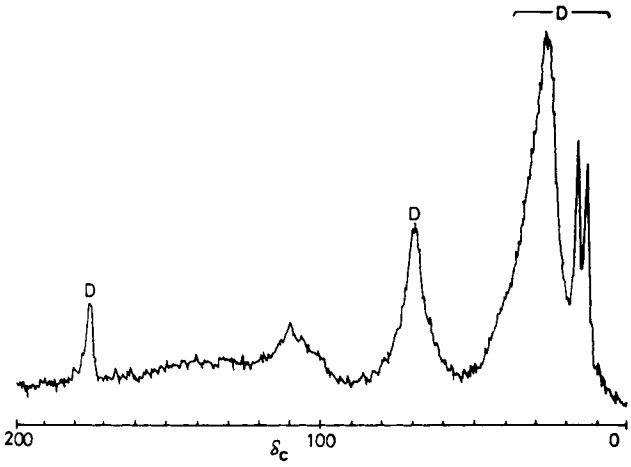

Fig. 10. ^{13}C-NMR spectrum of a membrane with low DOA content. PVC/DOA/carrier/NaSCN (wt %): 79.3/10.7/9.9/0.1. Accumulation was carried out 60,000 times.

of these two factors to membrane deterioration. Further investigation is necessary.

CONCLUSION

The ^{13}C-NMR study of Na ion-sensitive PVC membranes showed that:

(1) In a fresh membrane, the membrane state resembled a simple liquid state, and the carrier molecule was not significantly sterically hindered.

(2) The absorption line of one of the doublet carbons of the carrier in a fresh membrane shifted by 16 ppm toward up field from the line observed when the carrier was in a casting solution.

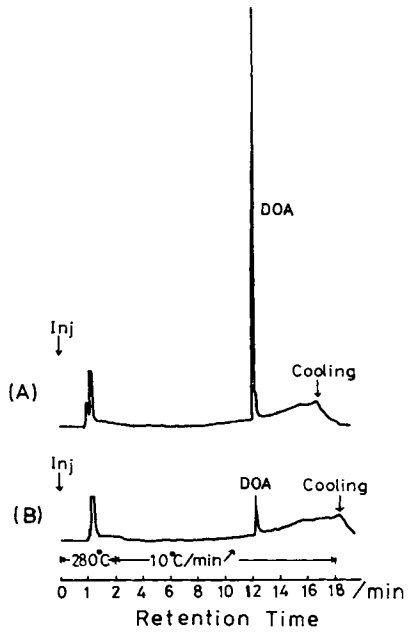

Fig. 11. Gas chromatograph of a new membrane (A) and a deteriorated membrane (B).

(3) With decreasing the DOA content in the membrane, six doublet absorption peaks of the carrier became broadened and produced one large peak appearing at about 110 ppm.

The ^{13}C-NMR, IR, and GC experiments on a deteriorated membrane contacted human serum revealed that:

(1) The membrane showed a porous structure and DOA content was decreased by one third from the initial content.

(2) Since the membrane surface was only partially covered with the aggregations of serum constituents, the surface contamination by serum proteins would not be a major deterioration factor.

(3) The significant conformation change of the carrier molecule occurred simultaneously with the oozing of DOA from the membrane phase. Besides the decrease in the diffusion coefficient of the carrier in the membrane phase, this conformation change could be a deterioration factor.

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