

# Electrodialytic properties of aromatic and aliphatic type hydrocarbon-based anion-exchange membranes with various anion-exchange groups



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## ABSTRACT

Anion-exchange membranes (AEMs) with various membrane structures were prepared by introducing various amines: trimethylamine (TMA), triethylamine (TEA), tri-*n*-propylamine (TPA) and tri-*n*-butylamine (TBA) into precursor membranes prepared from chloromethylstyrene (CMS)–divinylbenzene (DVB) and glycidyl methacrylate (GMA) – DVB. Their properties for ionic transport and anti-organic fouling were examined. Almost all of the prepared AEMs have excellent ionic transport properties: transport number of anions >0.94 and membrane resistance <4 Ωcm<sup>2</sup>. The voltage change through the AEMs during electrodialysis operation using solutions containing sodium dodecylbenzene-sulfonate as a foulant indicated that there are three cases of fouling mechanism being related to membrane structure: (a) aliphatic AEMs show lower fouling than aromatic ones; (b) the lower the water content of an AEM, the more remarkable the fouling; (c) the longer the chain length of the alkyl groups of the anion-exchange groups of an AEM, the more remarkable the fouling.

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## 1. Introduction

Nowadays, interest in desalination using membrane processes has increased with the advance of science and technology. An electrodialysis (ED) system is one of the major desalination processes. The system consists of cation-exchange membranes, anion-exchange membranes (AEMs), concentrated spacers, diluted spacers and two electrodes. In the process, ions are moved from the solution of the diluted spacers to that of the concentrated ones through the ion-exchange membranes (IEMs), driven by the electric field between the electrodes. ED processes have been applied to many industrial fields such as water treatment, the food industry, medical supplies, acid recovery from pickling solutions and wastewater treatment *etc.* [1–11]. IEMs for ED processes have excellent characteristics: high counter-ion permselectivity, low electrical resistance, a low diffusion coefficient, high mechanical strength, high chemical stability, and high dimensional stability. Membrane fouling is one of the most significant considerations in the application of ED desalination processes to industrial fields. Though super-saturation of minerals was a

serious problem in some applications of ED [12,13], organic fouling is also one of the main causes of fouling. Almost all organic foulants in multiple effluent streams have a negative charge; hence, fouling of AEMs due to deposition and/or adsorption of the foulants on/in the AEM is one of the serious problems for their application [14–16] because the fouling can lead to an unacceptably high stack resistance and replacement of membranes. Among organic foulants, natural organic matter with a large molecular weight fouls an AEM due to its accumulation on the membrane surface [17]. Also, protein foulants are known to have a fouling effect on the membrane by the formation of a gel layer on the membrane surface, leading to an additional hydraulic resistance [18,19]. A surfactant also has a fouling effect on AEMs by its accumulation on the membrane surface at high concentrations. Even at a low concentration, resistance is considerably increased by fouling due to the slow transport rate through the inner structure of an AEM [20].

Research into AEM fouling has shown that macromolecular adsorption occurs [21–23]. However, to the authors' best knowledge, the relationship between fouling mechanisms and membrane structure has not been clarified. In our previous study [24], aliphatic type and aromatic type AEMs were prepared in order to investigate fouling mechanisms on the surfaces of the AEMs. The aliphatic AEMs showed lower fouling properties than the aromatic AEMs.

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The aliphatic AEMs have a lower number of benzene rings than the aromatic AEMs; this indicates that an aromatic interaction (or  $\pi$ – $\pi$  interaction) is one of the important factors on the organic fouling between aromatic foulants and AEMs with an aromatic matrix.

Sata et al. prepared AEMs with various anion exchange groups, and measured the relative transport number of various anions compared with chloride ions [25]. In their paper, they prepared AEMs under limited conditions: a chloromethylstyrene–divinylbenzene matrix and one kind of cross-linker content (CLC). Moreover, the organic fouling behavior of these AEMs was not reported.

The aim of this study is to examine the effects of the difference in the chemical structure of AEMs: the amino groups in the anion-exchange sites, the degree of cross-linking and the two types of matrices: aromatic and aliphatic, on membrane fouling phenomena. Hence, novel AEMs with various membrane structures were prepared by introducing various amines into precursor membranes prepared from chloromethylstyrene (CMS)–divinylbenzene (DVB) and glycidyl methacrylate (GMA)–DVB, changing the degree of cross-linking. The fundamental properties of the AEMs for ED processes: ion-exchange capacity, water content and transport number were measured. The voltage change through the AEMs during electro dialysis operation using solutions containing sodium dodecylbenzene-sulfonate as a foulant was measured to investigate the effects of the membrane structure of the AEMs on membrane fouling.

## 2. Experimental

### 2.1. Sample membranes

Precursor membranes for AEMs were prepared by a paste method [26,27]. A monomer mixture consisting of chloromethylstyrene (CMS)/divinylbenzene (DVB) or glycidyl methacrylate (GMA)/DVB, and benzoyl peroxide to initiate polymerization was used to prepare the paste. The paste also contained 5 wt% of acrylonitrile–butadiene rubber (NBR) to give mechanical strength to the membrane. Fig. 1 shows a schematic diagram of the paste method. The wind-up roll 3 was the only driven roll; the others were idler rolls. A reinforcing material (woven poly (vinyl chloride) cloth), reserved on roll 1, was tensioned along its length by application of a brake on roll 1, expanded in width by the expander roll 5, and then dipped in the paste reservoir 4. A separating film such as poly(ethylene terephthalate), in which vinyl monomers were not impregnated, was fed from roll 2 and tensioned and expanded in the same way as the reinforcing material. The reinforcing material coated with the paste was wound on roll 3 in layers with the separating film. In this way, the paste (the monomer mixture) was continuously coated on the reinforcing material and covered on

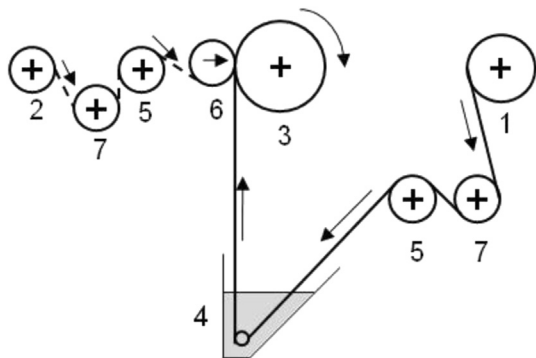


Fig. 1. Example coating method (paste method). (1) Reserve roll of reinforcing fabric; (2) reserve roll of separating film; (3) receiving role; (4) paste (mixture of vinyl monomers, inert polymers, initiator, additives, etc.) reservoir; (5) expander roll; (6) press roll; (7) guide roll.

both sides with the separating film. This resultant composite was heated at 80 °C for 10 h under a nitrogen atmosphere to polymerize the monomers. The cross-linker content (CLC) in the mixture was varied to control the network structure of the membranes. Balog et al. [28] estimated the degree of cross-linking of an ETFE-g-poly(sulfonated styrene-co-DVB) membrane with FT-IR measurements. The macromolecular structure of that membrane was homogeneous at the sub-micro meter level (<0.01–0.1  $\mu$ m). Hence, the cross-link level can be estimated by FT-IR measurements. On the contrary, as mentioned in the Appendix, our membrane has a composite structure consisting of woven poly (vinyl chloride) (PVC) cloth and polymer resin. Therefore, it is too difficult to estimate the degree of cross-linking of the AEMs with FT-IR measurements. Hence, in this study, the CLC was defined as follows:

$$CLC = \left( \frac{C_{DVB}}{C_{matrix} + C_{DVB}} \right) \quad (1)$$

where  $C_{DVB}$  and  $C_{matrix}$  are the content of DVB and matrix monomer (CMS or GMA) in the mixture.

As shown in Scheme 1, AEMs with different anion-exchange groups were prepared by reacting the precursor membrane composed of CMS-DVB or GMA-DVB with various amines: a 1.0 mol/dm<sup>3</sup> trimethylamine (TMA) aqueous solution for 20 h at 30 °C, a 1.0 mol/dm<sup>3</sup> triethylamine (TEA) methyl alcohol solution for 48 h at 50 °C, a 1.0 mol/dm<sup>3</sup> tri-*n*-propylamine (TPA) methyl alcohol solution for 48 h at 50 °C, and a 1.0 mol/dm<sup>3</sup> tri-*n*-butylamine (TBA) methyl alcohol solution for 72 h at 50 °C. After reaction, the membranes were thoroughly washed with water or methyl alcohol, and then with a 1.0 mol/dm<sup>3</sup> hydrochloric acid solution.

Fig. 2 shows the chemical structures of CMS-DVB and GMA-DVB. The figure shows that the number of benzene rings in a GMA-DVB is lower than that in a CMS-DVB. Hence, CMS-DVB and GMA-DVB AEMs are respectively referred to as aromatic and aliphatic AEMs in this paper. Table 1 shows the monomer compositions of the precursor membranes at various CLCs. The number of cross-linking points in the membrane matrices increases with increasing CLC.

Commercially-available AEMs, Neosepta AMX and ASM, prepared using CMS-DVB-based precursor membranes by the same method as described above were used as control membranes.

### 2.2. Elemental mapping of energy dispersive X-ray spectrometry (EDS)

The cross section of AEMs was observed by elemental mapping performed by energy dispersive X-ray spectrometry (EDS, Genesis2000, EDAX Inc., USA) to investigate the number and distribution of the anion-exchange groups in sample AEMs.

### 2.3. Measurement of membrane properties

Water content ( $W$ ), ion-exchange capacity ( $IEC$ ), burst strength ( $BS$ ), membrane resistance ( $R_m$ ), membrane thickness ( $d$ ), and dynamic transport number ( $t$ .) are measured by the same methods as in the previous study [24].

### 2.4. Electro dialysis measurements with NaCl solutions containing DBS

After soaking in a 5,800 mg/dm<sup>3</sup> (0.50 mol/dm<sup>3</sup>) NaCl aqueous solution for 1 h and washing with deionized water, a sample membrane was fixed between the anode and cathode chambers respectively equipped with a silver electrode and a silver chloride electrode, (Fig. 3). The anode chamber was filled with 0.1 dm<sup>3</sup> of 5,800 mg/dm<sup>3</sup> NaCl aqueous solution, and the cathode chamber with a 0.1 dm<sup>3</sup>

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