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Studies on Ion Exchange Membranes. VIII. On the Anion Exchange Membranes Using Dimethyl (2-oxybenzyl) Amine*

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1. Introduction

There are many reports¹⁾ about the anion exchange membranes and resins prepared by polycondensation. In these exchangers amine groups are usually used as the ion exchange sites in the form of polymer chain unit but not in the form of side chain. For example, the preparation of the anion exchange membranes using tetraethylene pentamine was already reported^{2), 3)}.

Usually, amine groups are sensitive to oxidation. So, if amine groups were used in the form of polymer chain unit, not only the losses of ion exchange sites, but also the scissions of the polymer chains could be induced by the oxidative attack. On the other hand, if amine groups were used in the form of side chain, the losses of ion exchange sites could be occurred, but the scissions of polymer chains could be hardly induced under the same conditions. It would be anticipated that the latter should be more stable than the former for the oxidative attack.

From the viewpoints described above, the anion exchange membranes using dimethyl (2-oxybenzyl) amine were prepared and their electrochemical properties and stabilities were measured.

2. Experimental

(1) **Dimethyl (2-oxybenzyl) Amine [DMBA]** Dimethyl (2-oxybenzyl) amine was prepared by Mannich's reaction.

(2) **Preparation of Membranes** The materials (DMBA, phenol, 37% formaline and H_2SO_4 - CH_3COOH) with the appropriate molar ratio were mixed under cooling and stirring, and the mixtures of the materials were stirred for 1 hour at 50-60°C. Thus, the viscous resinous solutions were obtained. These solutions were laminated with glass clothes and cured at 60-70°C for 8 hours.

The ion exchange sites of the prepared membranes were tertiary amine groups (TA membranes). TA membranes were quaternized with CH_3I - CH_3OH (1 : 1 in volume) at room temperature (QA membranes).

(3) **Measurement** Water content, exchange capacity, specific conductivity and membrane potential were measured by the preceding methods²⁾. Specific conductivities were measured in 0.5 N NaCl at 25°C. Transport numbers were calculated from the membrane potential by Nernst's equation, which was measured with 0.5 N NaCl and 2.5 N NaCl at 25°C.

* The original written in Japanese can be seen in *Denki-Kagaku* **29**, 653 (1961).

(4) **Degradation Test** TA membranes ($5 \times 5 \text{ cm}^2$) were treated with the bleaching solutions (bleaching powder 5 g/water 1000 cc) at room temperature. The bleaching solutions were renewed every 24 hours. Dry resin weights before treatment were compared with dry resin weights after treatment. For comparison, teraethylene pentamine membranes (TP membranes)^{2),3)} were treated similarly.

(5) **Electrophoretic Concentration of Sea Water** Sea water was used after simple filtration. The polycondensed cation exchange membranes were used together. Experimental conditions were as follows:

current density : 0.8 A/dm^2

temperature of sea water : 25°C .

3. Results and Discussion

(1) **Properties** The electrochemical properties of TA membranes are shown in Table 1.

The properties of quarternized TA membranes, QA membranes, are shown in Table 2.

QA membranes are superior to TA membranes in specific conductivities, but not in transport numbers.

Table 1 Properties of TA membranes

DMBA/Phenol	1.0	1.5	2.0	2.5
Water content	0.22	0.27	0.43	0.49
Exchange capacity	2.14	2.41	2.55	2.60
Specific conductivity	1.2×10^{-3}	3.5×10^{-3}	4.5×10^{-3}	9.1×10^{-3}
Transport number	94	94	93	88

DMBA/Phenol : molar ratio,

Water content : $g\text{-H}_2\text{O}/g\text{-dry Cl form resin}$,

Exchange capacity : Milli equivalent/ $g\text{-dry Cl form resin}$

Specific conductivity : $\Omega^{-1}\text{cm}^{-1}$

Transport number : %

Table 2 Properties of QA Membranes with Different Treating Times

DMBA/Phenol		1.0	1.5	2.0	2.5
Properties	Treating time				
Specific conductivity	1	1.8×10^{-3}	3.2×10^{-3}	6.7×10^{-3}	10.4×10^{-3}
	2	2.3×10^{-3}	3.9×10^{-3}	—	11.1×10^{-3}
	3	1.8×10^{-3}	4.2×10^{-3}	7.0×10^{-3}	11.5×10^{-3}
	16	2.0×10^{-3}	4.2×10^{-3}	6.8×10^{-3}	—
Transport number	1	93	93	90	85
	2	93	93	90	85
	3	93	92	88	85
	16	91	92	89	85

DMBA/Phenol : Molar ratio

Treating time : hours

Specific conductivity : $\Omega^{-1}\text{cm}^{-1}$

Transport number : %

Table 3 Degradation by Bleaching Solution

Treating time		1 day	3 days	5 days
Degree of degradation	TA membrane	0.94	0.95	0.95
	TP membrane	0.84	0.85	0.76

TA membrane : DMBA/Phenol(molar ratio)=1.5

TP membrane : Specific conductivity $3.1 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$

Transport number 92%

(2) **Degradation** Degree of degradation is shown as follows:

Degree of degradation=dry resin weight after treatment/dry resin weight before treatment.

TA membranes are more stable than TP membranes as shown in Table 3.

When TP membranes were treated, the bleaching solutions were coloured by the degradation of resins, but when TA membranes were treated, the bleaching solutions were not coloured.

These results about the stabilities of the membranes would not be applicable to degradation of the membranes in the industrial electrophoretic concentration of sea water, because the mechanism of degradation of the membranes in sea water should be very complicated.

(3) **Electrophoretic Concentration of Sea Water** The results are shown in Table 4.

Table 4 Ionic Compositions of Concentrated Brines

Ionic composition	DMBA/Phenol	1.75		2.0	
	Membrane	TA membrane	QA membrane	TA membrane	QA membrane
Cl		2.37	2.83	2.80	2.88
SO ₄		0.089	0.091	0.047	0.038
Pso ₄		0.30	0.26	0.14	0.13
p H		Neutral	Neutral	Neutral	Neutral

Cl, SO₄ : Normality

Pso₄ : $(C_{SO_4}/C_{Cl})_{brine}/(C_{SO_4}/C_{Cl})_{sea\ water}$

QA membrane : Prepared by treatment of TA membrane for 2.5 hours

4. Conclusion

The anion exchange membranes having the ion exchange sites in the side chains were prepared by using dimethyl (2-oxybenzyl) amine, and some of them were quarternized with CH₃I. The electrochemical properties of both membranes were measured.

From the results of the degradation tests with bleaching solutions, it is concluded that dimethyl (2-oxybenzyl) amine membranes are more stable than the tetraethylene pentamine membranes.

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Polarographic Studies on Nitrophenylhydrazine Isomers*

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In order to study the reaction of phenylhydrazine derivatives with carbonyl compounds by the polarographic method¹⁻³⁾, the polarographic behavior of *o*-, *p*-, and *m*-nitrophenylhydrazine isomers was investigated.

These compounds showed a reduction wave and an anodic wave. Characteristic values of the polarographic waves were shown in Table 1. A pre-wave is accompanied by the anodic wave in the case

* The original written in Japanese can be seen in *Denki-Kagaku* **29**, 768 (1961).