Neutrality Disturbance Phenomenon Observed in the Electrodialysis Using Ion-Exchange Resin Membranes

Tetsuya UCHINO*, Saburo NAKAOKA*, Hiroshi HANI* and Tadashi YAWATAYA*

When the electrophoretic concentration of electrolyte solution is performed by utilizing ion-exchange resin membranes, the change in hydrogen ion concentration is observed above a definite current density, which is determined by the concentration of outer solution. We call this "neutrality disturbance phenomenon."

Whereas this phenomenon seems to be generally recognized and a few reports^{1),2),3)} have been presented, no study has been reported on the different behavior of cation- and anion-exchange membranes in the subject. The purpose of this paper is to clarify the different rolls of cation- and anion-exchange membranes in this phenomenon by studying it under the various conditions, and pave the way for the fundamental understandings of the phenomenon.

The difference between the behaviors of cation- and anion-exchange membranes in neutrality disturbance phenomenon was first recognized in the following experiment. The cell as shown in Fig. 1 was constructed by the alternative combination of cation- and anion-exchange resin membranes for the continuous electrophoretic concentration of sodium chloride solution.

By the preliminary experiment it was confirmed that pH of the concentrate chambers c_1, c_2 and c_3 are not affected by the electrode reaction products. Then, the flow of the solution in the dilute chambers was halted one by one. It was found that pH in the concentrate chambers varied considerably induced by this halt of flow, while pH in c_1 was not affected by the halt of flow of solution in the chamber

Fig. 1 Multi-membranes cell.

Table 1 pH Change of the Concentrate, Induced
by Dilution of the Dilute

Exp. No.	Current density [A/dm ²]	Time (min.)	Compartment							
			d_4	c_3	d_3	c_2	d_2	c_1	d_1	
			0.5N NaCl	pH	0.5N NaCl	pH	0.5N NaCl	pH	0.5N NaCl	
1	2.0	23 hrs		5.8		5.8		5.8		
2	2.0	50		5.8		5.8		5.8	×	
3	2.0	50		5.8		0~1	×	13		
4	2.0	50		0~1	×	13		5.8		
5	2.0	50	×	13		5.8		5.8		

Dilute cell $d_1 \sim d_4$; 0.5 N NaCl feeded at 6 cc/min. rate.

The mark × means the chamber to which the feeding of 0.5 N NaCl soln. is halted.

Fig. 2 Simple-membrane cell.

* Research Laboratory, Asahi Glass Co., Ltd., Yokohama.

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d_1 , which do not have anion-exchange membrane on the anode side (Table 1.).

This result infers that there is the lesser effect of cation-exchange membrane than that of anion-exchange membrane on the neutrality disturbance phenomenon.

In order to confirm this finding, electrolysis experiments have been carried out, using the cell composed of only either cation- or anion-exchange membrane, and the change of pH was checked with the determination of limiting current density, above which membrane polarization and pH change occur (Fig. 2).

The following results were obtained with the anion-exchange membrane cell.

- L.C.D. has linear relationship with the concentration of outer sodium chloride solution.
- Vigorous stirring at the surface of the membrane causes a remarkable increase of L.C.D.
- Raise of temperature causes a little increase of L.C.D. (Fig. 3).
- The effect of the concentration of cathode side solution on L.C.D. is greatly preponderant over that of concentration of anode side solution (Table 2).
- Preliminary regulation of pH in the solution to be electrolyzed does not show appreciable effect on the neutrality disturbance phenomenon (Fig. 4).

Table 2 Relation between the L.C.D. and the Concentration of Anode Side Soln. (Concentration of Cathode Side Solution being Fixed at 0.1 N NaCl)

Concentration of anode side NaCl-soln. (N)	0.1	0.5	3.0	5.0
L.C.D. [A/dm ²]	2.8	3.0	3.2	3.3

○: room temp. under stirring } Strong basic
 ×: " " } A.M.
 ●: at 50°C } without stirring } (uniform membrane)
 □: Amberplex A-1
 △: Amberlite IRA 400+Hypalon } without stirring
 ×: Amberlite IRA 410+Hypalon } at room temp.

Fig. 3 Limiting current density *v.s.* concentration of outer sodium chloride solution (anion-exchange membranes).

⊕: Anode side soln.
 ⊖: Cathode side soln.
 C.D. 2.9 A/dm² 0.1 N NaCl-soln.
 ○: pH 5.9 × pH 3.1
 □: pH 2.5
 △: pH 10.1

Fig. 4 pH-Changes observed with soln. of varied pH.

(f) Previous treatments of anion-exchange resin membranes with acids or alkalis cause only small, non-essential change of L.C.D. (Table 3).

Table 3 L.C.D. with Anion Exchange Membranes Treated Preliminarily with Acid or Alkali. After the Treatment, the Membranes are Immersed in 1 N, HCl Soln. Rinsed with Water, and Equilibrated with 0.1 N NaCl Soln

Reagents for treatment	Temp. (°C)	Time	L.C.D. [A/dm ²]
5 N NaOH	100	1 hr	2.2
0.5 N NaOH	"	"	2.7
1 N HCl	"	"	4.0
5 N HCl	"	"	3.8
1 N H ₂ SO ₄	"	"	2.9
1 N Na ₂ SO ₄	room temp.	2 months	3.8
no treatment			2.8

(g) Anion-exchange resin membranes of various sources bring much the same L.C.D. (Fig. 5).

Fig. 5 pH-change observed with anion-exchange resin membranes of various sources.

On the contrary of these results, the following are obtained with the cation-exchange resin membrane cell.

(a) When the cell composed of two chambers as shown in Fig. 2, was used the pH change was very small, and does not depend on the current density below the value of the one used in this experiment, i.e. 4.0 A/dm².

(b) When the cell composed of several chambers as shown in Fig. 5 was used, the current density was raised up to 20 A/dm², which corresponded to about fifteen times of the L.C.D. in the case with the anion-exchange resin membrane cell. No essential change of pH (Table 4) appeared.

Fig. 6-1 Multi-cation-exchange membrane cells.

Fig. 6-2 Multi-cation-exchange membrane cells.

Table 4 pH-Change Observation with Cation-exchange Resin Membranes

(a) With three compartments cell.

No. of exp.	Voltage (Volts)	Current density (A/dm ²)	Temp. (°C)	Time (min.)	Change of pH compartment number					
					1		2		3	
					1.0 N NaCl		0.05 N NaCl		1.0 N NaCl	
					a)	b)	a)	b)	a)	b)
1	—	8.9	23~42	30	6.6	6.4	6.9	8.2	6.6	6.6
2	51~35	15.0	20~33	20	6.3	7.1	6.9	7.3	5.5	5.0
3	58~42	20.0	23~43	20	6.1	6.1	7.1	7.3	5.4	4.2
4	67~49	20.0	23~45	23	5.7	6.0	5.9	7.1	5.5	4.4

a): pH of initial solution. b): Change of pH with current.

(b) With five compartments cell.

No. of exp.	Voltage (Volts)	Current density (A/dm ²)	Temp. (°C)	Time (min.)	Change of pH compartment number									
					1		2		3		4		5	
					1.0 N NaCl		0.1 N NaCl		0.05 N NaCl		0.1 N NaCl		1.0 N NaCl	
					a)	b)	a)	b)	a)	b)	a)	b)	a)	b)
1	—	4.5	—	45	6.7	6.7	6.6	6.9	7.1	6.8	6.7	6.7	6.8	6.2
2	—	6.7	—	50	6.7	6.7	6.9	8.6	6.8	7.8	6.7	6.3	6.2	4.8
3	63~51	6.7	20~33	20	5.1	5.8	5.2	6.2	7.1	7.1	5.2	5.8	5.1	3.7

a): pH of initial solution. b): Change of pH with current.

Thus, with the cation-exchange membrane, neutrality disturbance phenomenon occurs, but is only trifle, and a definite L.C.D. can not be decided.

At present, because of the lack of perfect theory on the neutrality disturbance phenomenon, it is difficult to give satisfactory explanation as to why the rolls of cation- and anion-exchange membranes differ in such a manner. Rosenberg¹⁾ has presented a formula which determines L.C.D. It was deduced on the basis of the diffusion layer hypothesis. According to it, L.C.D. is decided by the diffusion coefficient of the electrolyte, the difference

Fig. 7 Mechanism of ion transfer at membrane interface.

between the concentration of the bulk solution at membrane surfaces, and the diffusion layer thickness. It has however, no terms which imply the essential difference between the behaviors of anion- and cation-exchange membranes (Figs. 8 and 9).

At the present step, it is only possible to make qualitative presumption that these differences may arise from the different mobility of H^+ and OH^- ion within the resin phase and the solution, or from the dissimilar affinity of H^+ and OH^- for the membrane surface. Since this investigation is still not sufficiently worked out, we shall not go into the subject in this report.

Literature :

- (1) W.N. Rosenberg, C.E. Tirrell : *Ind. Eng. Chem.*, **49**, 780 (1957).
- (2) T.R.E. Kressman, F.L. Tye : *A General Discussion of the Faraday Society*, "Membrane Phenomena", P 185, (1956).
- (3) Japan Patent No. 235335.

Fig. 8 Current loss due to polarization in relation to current density.

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