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A New Detection Method of Electromigrating Ions through a Cation-Exchange Membrane

Akihiro KAWAGUCHI,* Shin-ichi MAGAINO, Takashi SUZUKI,† and Yasushi TAKEUCHI††
Industrial Research Institute of Kanagawa Prefecture, 3173 Shouwa, Kanazawa-ku, Yokohama 236
†Department of Applied Chemistry, Yamanashi University, 4 Takeda, Koufu 400
††Department of Industrial Chemistry, Meiji University, 1-1-1 Higashi-mita, Tama-ku, Kawasaki 214
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An isotachophoretic analysis and electromigration of ions through a cation-exchange membrane have been investigated. K, Li, Na, and Cu ions were migrated at a constant current. The potential difference between fibrous ion exchanger and cathode reservoir was measured during migration of ion zone. The relative ionic mobility of K^+, Na^+, Li^+, and Cu^{2+} calculated by potential difference was 1, 0.667, 0.420, and 0.218, respectively. The concentration of mobile cations in unit volume of the membrane was calculated by the amount of migration and the migration time of each ion. The concentration of mobile Li^+ in the Li zone was about 10% lower than that of mobile K^+ in the K zone. This difference in concentration is similar to the result by the usual isotachophoresis using a capillary tube. The migration time of each ion zone through detection part was proportional to the amount of migration. K^+ and Li^+ in the concentration range from 0.6×10^{-3} to 0.2 mol dm^{-3} were quantitatively determined by the migration time with reproducible errors less than ±5 %.

The ion-exchange membrane is one of the useful electromigration media for separating ions in isotachophoresis. The ionic mobility in the membrane is different from that in aqueous solution, because ionic mobility is influenced by affinity of the membrane and hydration of the ions. Electromigration using an ion-exchange membrane was reported by Kakihana et al. for separating lithium isotope,[1,2] alkalis,[3] and alkaline earth metals.[4] They described the relationship between electromigration time and electromigration distance at a constant current. For the measurement of migration amount of ions, they used thin membranes and determined ions by means of flame spectrophotometry and mass spectrometry. In a previous paper,[5] the authors have reported a rapid detection method for migrating ions by measuring the potential gradient in the membrane without any sensing electrode on the membrane surface. A more sensitive method, however, is required for the analysis of migrating ions.

In capillary-tube isotachophoresis, platinum electrodes are usually used for potential gradient detectors. Everaerts and Verheggen,[6] and Akiyama and Mizuno[7] reported that bubbles are generated from platinum surface and that the potential gradient fluctuated at high current densities. To prevent these phenomena, they made the electrode surface smooth, and added Triton X-100 or Na_2AsO_4 to electrolyte in the capillary tube.

A redox reaction occurs on platinum surface because of high electronic conductivity. The reaction will be prevented by use of an ionic conductor electrode instead of platinum. The ionic conductivity of ion exchanger has been studied by several workers.[8,9] Although ion exchanger is widely used for electrodialysis,[10,11] fuel cells using solid polymer electrolytes,[12,13] electrolysis,[14] etc., it has not been used for potential gradient measurement in isotachophoresis.

In this study, the authors examined fibrous ion exchanger as a potential gradient detector at high current densities. The fibrous anion exchanger was contacted with cation-exchange membrane as a sensing electrode and the electromigration of K^+, Na^+, Li^+, and Cu^{2+} through membrane was examined. Firstly, the relative ionic mobility was determined in order to detect mobile cation by measuring the potential difference between fibrous anion exchanger and cathode reservoir at a constant current. Secondly, the concentration of mobile cation per unit volume of the membrane was obtained by measuring the amount of migrating ions and the migration time of each ion zone. The relationship between migration time and concentration of sample solution was discussed.

Theoretical

Qualitative Analysis of the Migration Ion. When an ion i migrates in ion-exchange membrane, migration velocity v_{mi}(cm s^{-1}) is the product of potential gradient E_{mi}(V cm^{-1}) and ionic mobility u_{mi} (cm^2 V^{-1} s^{-1}) as

$$v_{mi}=u_{mi}E_{mi}. \tag{1}$$

In isotachophoresis, v_{mi} is a constant. For example, when K^+ and Li^+ are electrically displaced by Cu^{2+} as a terminating ion, we get a formula

$$u_{mK}E_{mK}=u_{mLi}E_{mLi}=u_{mCu}E_{mCu}. \tag{2}$$

When u_{mK} and E_{mK} are defined to be unity, the relative ionic mobility of Li^+ and Cu^{2+} is obtained by the potential gradient

$$u_{mLi}=1/E_{mLi} \text{ and } u_{mCu}=1/E_{mCu}. \tag{3}$$

Migration Amount in the Membrane. When ion i migrates from aqueous solution to membrane, the amount of migration A_{mi}(mol) passing through a unit area of interfaces in a unit time is expressed by

$$A_{mi}=v_ic_i/1000, \tag{4}$$

where v_i and c_i are migration velocity in cm s^{-1} and solution concentration in mol dm^{-3}, respectively.

When v_i is proportional to mobility u_i ($\mathrm{cm^2\,V^{-1}\,s^{-1}}$) in the solution, the ratio between amounts of migration for $\mathrm{Li^+}$ and $\mathrm{K^+}$ $A_{\mathrm{mLi}}/A_{\mathrm{mK}}$ is obtained as follows:

$$A_{\mathrm{mLi}}/A_{\mathrm{mK}} = (u_{\mathrm{Li}}/u_{\mathrm{K}})(c_{\mathrm{Li}}/c_{\mathrm{K}}). \tag{5}$$

Concentration of Mobile Cation. From thickness t (cm) and width w (cm) at the detection part of membrane, the concentration of mobile cation c_{mi} (mol $\mathrm{dm^{-3}}$) per unit volume is defined by using migration amount A_{mi} and migration velocity v_{m} ($\mathrm{cm\,s^{-1}}$) by

$$c_{\mathrm{mi}} = 1000\,A_{\mathrm{mi}}/s_i v_{\mathrm{m}} t w, \tag{6}$$

where s_i (s) is the migration time of i ion zone passed through the center of detection part. The ratio of migration time of $\mathrm{K^+}$ to that of $\mathrm{Li^+}$ is obtained by Eq. 6 as

$$s_{\mathrm{Li}}/s_{\mathrm{K}} = (A_{\mathrm{mLi}}/A_{\mathrm{mK}})/(c_{\mathrm{mLi}}/c_{\mathrm{mK}}). \tag{7}$$

If $A_{\mathrm{mLi}}/A_{\mathrm{mK}}$ is unchanged during the migration, $s_{\mathrm{Li}}/s_{\mathrm{K}}$ will be constant, because $c_{\mathrm{mLi}}/c_{\mathrm{mK}}$ is constant in isotachophoresis. Substituting Eq. 5 by Eq. 7, we obtain

$$c_{\mathrm{Li}}/c_{\mathrm{K}} = (s_{\mathrm{Li}}/s_{\mathrm{K}})(c_{\mathrm{mLi}}/c_{\mathrm{mK}})(u_{\mathrm{K}}/u_{\mathrm{Li}}). \tag{8}$$

If $c_{\mathrm{mLi}}/c_{\mathrm{mK}}$ and $u_{\mathrm{K}}/u_{\mathrm{Li}}$ remain constant, $c_{\mathrm{Li}}/c_{\mathrm{K}}$ will be estimated by measuring $s_{\mathrm{Li}}/s_{\mathrm{K}}$.

Experimental

Electromigration Cell. The symbol c in Fig. 1 indicates the narrowed part of cation-exchange membrane (Selemion CMV). When potential gradient is measured at the narrowed part of membrane, a small amount of migrating ions will be detected. The membrane was washed with 1 mol $\mathrm{dm^{-3}}$ NaOH, 1 mol $\mathrm{dm^{-3}}$ HCl, and distilled water. The $\mathrm{H^+}$-form membrane was stored in distilled water. Before each run, the membrane was taken out and wiped with filter paper to remove surface water. The membrane was placed on a clean glass plate coated with a small amount of grease. Both ends of the membrane were connected to the bottom edge of each anode and cathode reservoir. A fibrous anion exchanger (Selemion AMV, $\mathrm{OH^-}$-form) of 0.02 mm in diameter and 10 mm in length was placed on the membrane at a distance of 1 mm from the cathode reservoir. The membrane was tightly covered with a glass plate coated with grease. The apparatus is shown in Fig. 1.

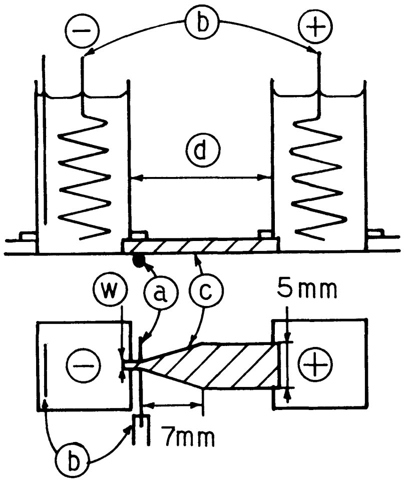

Fig. 1. Cell assemblies.
a; Anion exchange fiber, b; Pt electrode, c; cation-exchange membrane, d; distance of electromigration, w; outlet width (0.60 mm).

Isotachophoretic Separation. Ionic migration was generated by a constant current power source (Toyo PS-1510), which connects to platinum electrodes in cathode and anode reservoirs. The cathode reservoir was filled with 0.5 mol $\mathrm{dm^{-3}}$ $\mathrm{H_2SO_4}$ and the anode reservoir with a mixture of KOH and LiOH in the range from 0.6×10^{-3} to 0.2 mol $\mathrm{dm^{-3}}$. In the experiment for separating $\mathrm{K^+}$ and $\mathrm{Li^+}$, the anode reservoir was filled with KOH–LiOH mixture and a constant current of 0.8 mA was applied for 3 min. Then the reservoir solution was replaced by 0.5 mol $\mathrm{dm^{-3}}$ $\mathrm{CuSO_4}$ to continue the experiment under the same current at room temperature.

Migration Time and Amount of Ion. The fibrous ion exchanger was contacted in series with thin platinum foil and the potential difference between fibrous ion exchanger and cathode reservoir was measured by a high impedance potentiometer (Nichia NP-PM-1). The migration time and potential difference between the fibrous ion exchanger and cathode reservoir were measured. $\mathrm{K^+}$ and $\mathrm{Li^+}$ were allowed to migrate for 3 min under the same current. The membrane was then taken out of the apparatus and $\mathrm{K^+}$ and $\mathrm{Li^+}$ were eluted with 2 mol $\mathrm{dm^{-3}}$ HCl. Concentrations of $\mathrm{K^+}$ and $\mathrm{Li^+}$ in HCl were measured by means of flame spectrophotometry.

Results and Discussion

Sensing Electrode. First, a platinum wire of 0.05

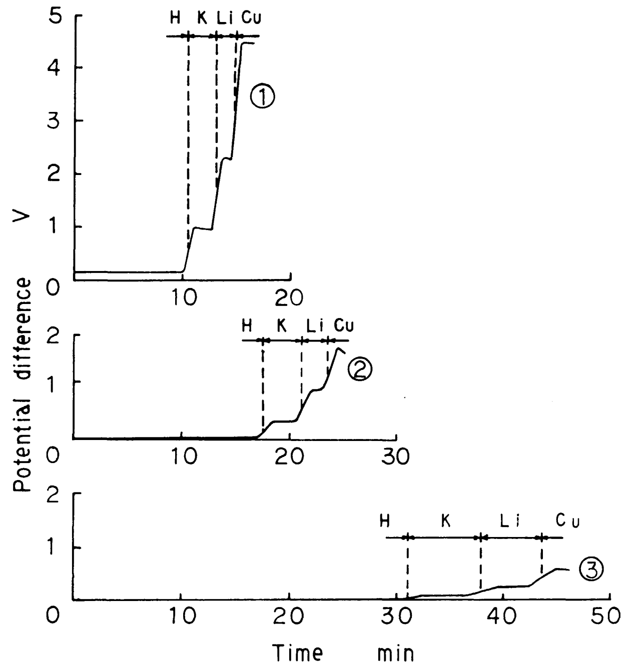

Fig. 2. Electropherograms of $\mathrm{K^+}$ and $\mathrm{Li^+}$. Sample: 0.2 mol $\mathrm{dm^{-3}}$ KOH and 0.2 mol $\mathrm{dm^{-3}}$ LiOH. Terminal solution: 0.5 mol $\mathrm{dm^{-3}}$ $\mathrm{CuSO_4}$.

	Current (mA)
①	0.8
②	0.5
③	0.3

Table 1. Relative Mobility of Ions to That of K$^+$

Ion	K$^+$	Na$^+$	Li$^+$	Cu^{2+}
Ion-exchange membrane[a)]	1.00	0.667	0.420	0.218
Ion-exchange membrane by Hosoe's data[3)]	1.00	0.675	0.431	—
Water soln. infinite dilution[b)]	1.00	0.682	0.526	0.762

a) Obtained in this study. b) From limiting equivalent conductivity at 25 °C.

mm in diameter was used as sensing electrode instead of fibrous anion exchanger. When the potential difference between platinum wire and cathode reservoir was measured, fluctuations were observed in potential curve. Bubbles were simultaneously generated from platinum wire. Moreover, Cu^{2+} passing through the membrane was reduced to black metallic copper on platinum, and black portion grew toward the anode reservoir. This phenomenon shows that a redox reaction occurred on the surface of platinum wire.

On the other hand, when the fibrous anion exchanger was used as a sensing electrode, no redox reaction was observed in the migration. Figure 2 shows typical electropherograms for K$^+$, Li$^+$, and Cu^{2+} using fibrous anion exchanger. The first moving boundary between the first zone of H$^+$ and the second zone of alkali metal ions, the second moving boundary between the second zone of alkali metal ions, and the third zone of Cu^{2+} are sharply recognized during the migration. As shown in Fig. 2, the potential difference between fibrous ion exchanger and cathode reservoir is approximately constant in each zone. When each boundary passed through the detection part, an increase in potential difference was clearly observed. These results are similar to the case of capillary-tube isotachophoresis. It seems that fibrous ion exchanger is a useful medium for detecting potential gradient at high current densities.

Qualitative Analysis. When K$^+$, Li$^+$, and Cu^{2+} zones pass through the detection part, the potential difference between fibrous ion exchanger and cathode reservoir is 0.97, 2.31, and 4.44 V, respectively, as shown in① of Fig. 2. The relative value of the potential difference for Na$^+$, Li$^+$, and Cu^{2+} to that for K$^+$ was calculated to be 1.50, 2.38, and 4.58, respectively. Equation 3 indicates that the relative mobility for an ion is the reciprocal of potential value. The calculated relative mobility is given in Table 1. The relative mobility of alkali metals was reported by Hosoe et al.[3)] using a sulfonated cation-exchange membrane. Their values agreed with those obtained in this study within ±3%.

The mobility of Cu^{2+} is considerably lower than that in aqueous solution. It has been mentioned[3,4)] that the ionic mobility in membrane is different from that in aqueous solution, because the mobility is influenced by the affinity of ions with membrane and the hydration of ions. The affinity of membrane with ions increases with the increase in valency of ions.[15)] The relative mobility of Cu^{2+} is, therefore, smaller than that of alkali metal ions. It is plausible that migrating ion is identified by the measurement of potential difference in membrane.

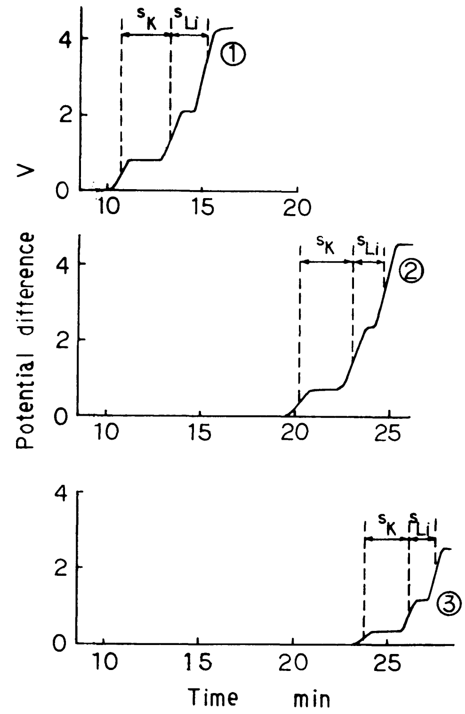

Fig. 3. Effect of the migration distance for the isotachophoretic separation. Sample: 0.2 mol dm^{-3} KOH+0.2 mol dm^{-3} LiOH; 0.8 mA for 3 min. Terminal solution: 0.5 mol dm^{-3} CuSO$_4$; 0.8 mA.

	Migration distance d (mm)
①	10
②	13
③	15

Concentration of Mobile Cation. A mixture of each 0.2 mol dm^{-3} KOH and LiOH was put into anode reservoir and a constant current of 0.8 mA was applied, then the solution in reservoir was replaced with 0.5 mol dm^{-3} CuSO$_4$ and migration continued. Figure 3 shows the effect of migration distance for isotachophoretic separation using membranes of 10, 13, and 15 mm in length. The ratio of migration time s_{Li}/s_K was determined to be 0.75, 0.61, and 0.61, respectively. The result indicates that K$^+$ and Li$^+$ migrate at a same speed by using membrane longer than 13 mm.

Table 2 gives amounts of migration A_{mK} and A_{mLi} obtained by spectrophotometry when migration current of 0.8 mA was applied for 3 min. The concentration of mobile K$^+$ and mobile Li$^+$ in unit volume of membrane was calculated using Eq. 6 and given by c_{mK}

Table 2. A_{mi}, s_i, and c_{mi} for Different Concentration of K^+ and Li^+ at $v_m = 6.94 \times 10^{-3}$ cm s^{-1}, $t = 0.0126$ cm, and $w = 0.060$ cm

c_K	A_{mK}	s_K	c_{mK}
mol dm^{-3}	μmol	s	mol dm^{-3}
0.06	0.54	105	0.98
0.10	0.92	168	1.04
0.14	1.10	198	1.06
			mean 1.03
c_{Li}	A_{mLi}	s_{Li}	c_{mLi}
mol dm^{-3}	μmol	s	mol dm^{-3}
0.06	0.28	57	0.94
0.10	0.49	102	0.92
0.14	0.70	147	0.91
			mean 0.92

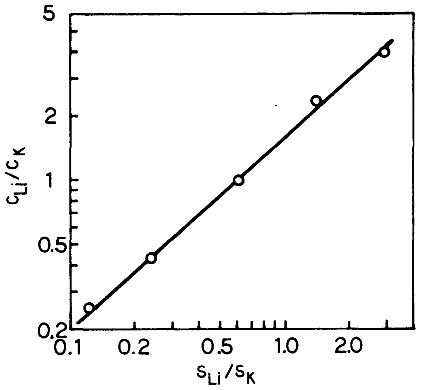

Fig. 4. Relation between c_{Li}/c_K and s_{Li}/s_K. Sample: KOH and LiOH; 0.8 mA for 3 min. Terminal solution; 0.5 mol dm^{-3} CuSO$_4$; 0.8 mA.

Table 3. Relative Values of A_{mi}, u_i, c_{mi}, and s_i for Different c_{Li}/c_K

c_{Li}/c_K	A_{mLi}/A_{mK}	u_{Li}/u_K	c_{mLi}/c_{mK}	s_{Li}/s_K
2.333	1.296	0.556	0.927	1.400
1.000	0.533	0.533	0.880	0.607
0.429	0.255	0.594	0.883	0.288
mean		0.561	0.897	

and c_{mLi} in Table 2. The mean values of c_{mK} and c_{mLi} were 1.03 and 0.92 mol dm^{-3}, respectively. These values were approximately constant in the range of migration current from 0.3 to 1.0 mA. The concentration of mobile Li^+ in Li^+ zone was about 10% lower than that of mobile K^+ in K^+ zone. This concentration difference is similar to the result in the usual isotachophoresis using a capillary tube.

Quantitative Analysis. Table 3 gives the ratios of A_{mi}, u_i, c_{mi}, and s_i to each value for K^+ for different ratios of concentration c_{Li}/c_K at the same conditions described in Table 2. Using Eq. 5, u_{Li}/u_K was obtained as an approximately constant value of 0.561, independent of A_{mLi}/A_{mK} and c_{Li}/c_K, and it was close to the value of relative ionic mobility in aqueous solution (0.526 at 25 °C). The product of c_{mK}/c_{mLi} multiplied by u_{Li}/u_K is nearly 0.61, then c_{Li}/c_K was obtained from Eq. 8 as follows:

$$c_{Li}/c_K = (s_{Li}/s_K)/0.61. \qquad (9)$$

Figure 4 shows this relation. The value of c_{Li}/c_K was estimated by use of s_{Li}/s_K in a reproducibility of ±5%. To determine the measurable concentration region of K^+ or Li^+, the migration was investigated in the concentration range of 0.6×10^{-3} to 0.2 mol dm^{-3} KOH and LiOH. In this region, it was confirmed that the concentration of K^+ or Li^+ is estimated by Eq. 9 using s_{Li}/s_K and known concentration of Li^+ or K^+. The limit of detection for K^+ was 0.11 μmol from the electropherogram in this study. The proposed method is more sensitive than the method reported previously.[5]

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