Electrotransportation of Aniline Through a Perfluorosulfonate Ion-Exchange Membrane

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ABSTRACT

Transport phenomena of aniline through Na^+-, K^+-, and Cs^+-form of a perfluorosulfonate ion-exchange membrane, Nafion® 117, under a flow of dc current, electrotransportation, were investigated. In each form, an increase in transport number of aniliniumcation was observed in the current density range from 0.3 to 1.3 mA cm^{-2}. The transport number of the anilinium cation in Cs^+-form was larger than that expected from the concentration and diffusion coefficient of the anilinium cation in Cs^+-form Nafion. These aniline transport phenomena may be attributable to a structural change of Nafion or a decrease in hydrophobic interaction between the anilinium cation and Nafion caused by the flow of dc current.

A commercially available perfluorosulfonate cation-exchange membrane, Nafion, is chemically and thermally stable, and applied to various processes such as electrolytic cells,[1,2] polymer-electrolyte-membrane fuel cells,[3] sensors,[4] batteries,[5,6] and cells for organic synthesis.[7] Results reported on its structure[8] and transport properties[1,9-11] reveal that Nafion is microscopically separated into two phases: an ionic cluster domain, which contains most of the sulfonate groups, cations, and sorbed water, and a hydrophobic backbone domain similar to that of polytetrafluoroethylene (PTFE), which surrounds the ionic cluster. This characteristic structure gives Nafion peculiar and interesting properties in swelling, ion-exchange selectivity, etc.

While organic cations reportedly interact strongly with the hydrophobic microdomain in Nafion,[12,13] few studies have been reported on the permeation of organic compounds through Nafion.[14-16] Previously, we have reported the effects of various alkali cations on permeation phenomena of aniline through Nafion in the presence of a concentration gradient across a Nafion membrane.[17] The apparent diffusion coefficients of anilinium cation and neutral aniline were determined, and it was found that they are strongly affected by the water content of the Nafion membrane. However, the permeation behavior of anilinium cation under application of dc current needs clarification. Research on the permeation behavior of organic species under current passage, electrotransportation, gives useful information on the perm selectivity of Nafion and hydrophobic interaction between organic species and Nafion. Here, our attention was focused on the electrotransportation of aniline through Nafion 117 (equivalent weight: EW = 1100).

Experimental

Membrane treatments.—A perfluorosulfonate cation-exchange membrane, Nafion 117, was used in this study. Nafion samples in H^+-form (3 cm in diameter in the dry state) were pretreated in boiling water for more than 1 h. The sample was then soaked in a source solution shown in Table I for *ca.* 24 h in the dark at 35°C. During this treatment, swelling and ion exchange between the Nafion and the source solution were brought into equilibrium.

Measuring cell.—The permeation measurements under a flow of dc current were carried out using a cell shown in Fig. 1. The cell was composed of four compartments made of PTFE. The volume of compartments A (anode compartment) and D (cathode compartment) was *ca.* 10 cm^3, and that of B and C was *ca.* 3 cm^3. Compartments B and C were separated by the Nafion membrane which had been equilibrated with the source solution. Compartments A and D were fitted with a DSA-type anode plate and an Ni cathode plate, respectively. Hydrocarbon-type anion-exchange membranes (Selemion® AMV, Asahi Glass Co.) separated compartments A and B, and compartments C and D to prevent the anilinium cation from penetrating into compartments A and D. The exposed surface area of the Nafion membrane was 3.1 cm^2.

Permeation measurements.—The compositions of the source and receiver solutions used for electrotransportation measurements are listed in Table I. The source (1000 cm^3) and receiver (50 cm^3) solutions containing a common alkali cation (M^+) were circulated separately through compartments B and C at 0.15 $cm^3\ s^{-1}$, respectively. Since the volume of the source solution was 20 times larger than that of the receiver solution, the decrease in aniline

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Table I. Composition of source and receiver solutions.

Source solution
pH 4.2 (0.06 mmol dm^{-3} H^+)
10 mmol dm^{-3} aniline
83 mmol dm^{-3} M_2HPO_4
59 mmol dm^{-3} citric acid
37 mmol dm^{-3} MCl (M = Na, K, Cs)
Receiver, anode, and cathode solutions
pH 4.2 (0.06 mmol dm^{-3} H^+)
83 mmol dm^{-3} M_2HPO_4
59 mmol dm^{-3} citric acid
42 mmol dm^{-3} MCl (M = Na, K, Cs)

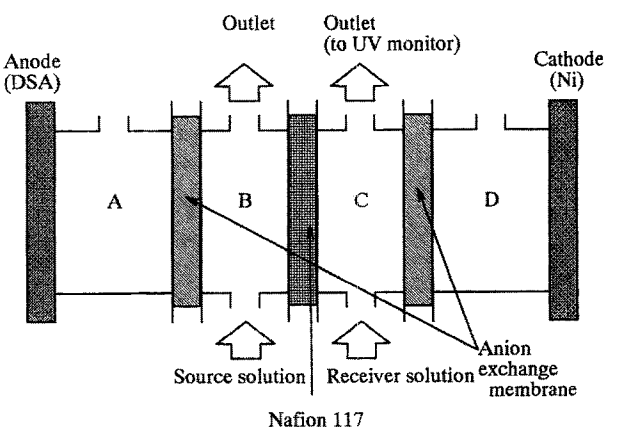

Fig. 1. Schematic diagram of the cell used for permeation measurements. A) anode compartment; B) source solution compartment; C) receiver solution compartment; and D) cathode compartment. The solutions in B and C were circulated at 0.15 $cm^3\ s^{-1}$.

concentration in the source solution was small; hence, the aniline concentration in the source solution was assumed to be constant during each permeation measurement. An external dc current was applied galvanostatically across the DSA type anode and the Ni cathode using a potentiostat/galvanostat (Hokuto Denko Model HA301). The amount of aniline transported to the receiver solution through the Nafion membrane was monitored as a change in spectroscopic absorbance at 280 nm, using a Hitachi Model 200-10 spectrometer equipped with a microflow cell, which was set in the circulating line of the receiver solution. Since the increase in aniline concentration in the cathode compartment, D, was less than 1% even after 150 C were passed, the permeation of aniline into compartment D through Selemion® AMV separator was neglected. All experiments were carried out at 35°C.

Absorbance change of aniline solution with pH.—The source solution was diluted to ten-fold volume with water, and a solution containing 1 m*M* aniline was obtained. A small volume of 1*M* HCl or 1*M* NaOH was added to the solution to change its pH. The absorbance of the resulting solutions of various pH was measured using the UV/VIS spectrometer described above.

Chemicals.—All chemicals were of reagent grade and were used without further purification. Water (>18 MΩ, nominally) was obtained from a NANO pure-water purifying system (Barnstead Co.).

Results and Discussion

Variation in spectroscopic absorbance of aniline with pH.—Spectroscopic absorbance of solutions containing aniline species of various pH was measured at 280 nm, and the variation in the absorbance with pH is shown in Fig. 2. The absorbance at 280 nm changed drastically with pH. In acidic solutions a following reaction 1 reaches equilibrium

$$\text{AN(aniline)} + H^+ \rightleftharpoons \text{AN}^+\text{(anilinium cation)} \qquad [1]$$

While neutral aniline absorbs light of 280 nm, protonated aniline (anilinium cation) does not. Hence the absorbance at 280 nm can be used as a measure of the content of neutral aniline in a solution. The dependence of the measured absorbance on the solution pH in Fig. 2 was in good agreement with the absorbance dependence calculated from the neutral aniline concentration using a pKa value of aniline, 4.7, and pH of the solutions.

Electrotransportation of aniline through Na^+-form Nafion.—The permeation of aniline was measured under a flow of dc current using Na^+-form Nafion and the solutions containing Na^+ cation (Table I). Figure 3 shows the absorbance changes at 280 nm of the receiver solution with time at various current densities. The current density means here the magnitude of a dc current per unit surface area of the separator membrane, Nafion. During each run, the pH of the receiver solution increased slightly with an increase in charge passed. The pH changes with charge passed are shown in Fig. 4. As discussed above, a pH change affects the equilibrium between neutral aniline and anilinium cation in Eq. 1. To obtain the total amount of aniline transported to the receiver solution, the amount of anilinium cation must be taken into consideration in addition to neutral aniline obtained spectroscopically. Hence the total content of aniline species in the receiver solution was calculated using the data in Fig. 2 and 4. Figure 5 shows the calculated concentration changes of the total aniline in the receiver solution at various current densities.

The slope of each curve is proportional to the aniline flux under the corresponding conditions. The flux decreased with an increase in charge passed through the Nafion. Aniline was transported by migration under a potential field across the membrane and by diffusion due to a concentration gradient between the two solutions. Since the driving

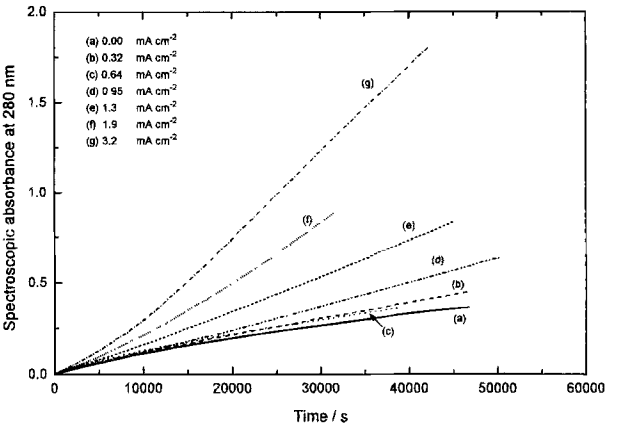

Fig. 3. Changes in absorbance of the receiver solution at 280 nm for Na^+-form Nafion at current densities of (a) 0.0, (b) 0.32, (c) 0.64, (d) 0.96, (e) 1.3, (f) 1.9, and (g) 3.2 mA cm^{-2}.

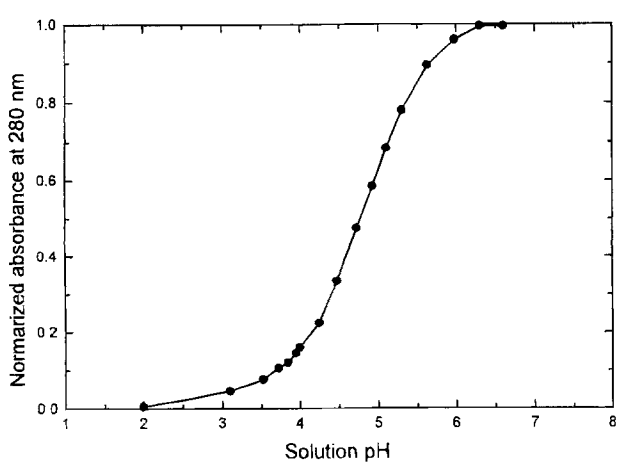

Fig. 2. Absorbance change at 280 nm of solutions containing 1 m*M* aniline with pH.

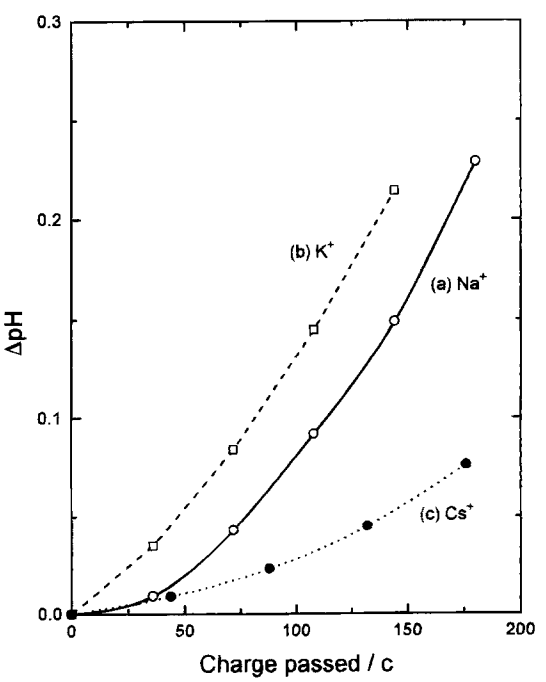

Fig. 4. Changes in pH of receiver solution for (a) Na^+-, (b) K^+-, and (c) Cs^+-forms of Nafion with charge passed.

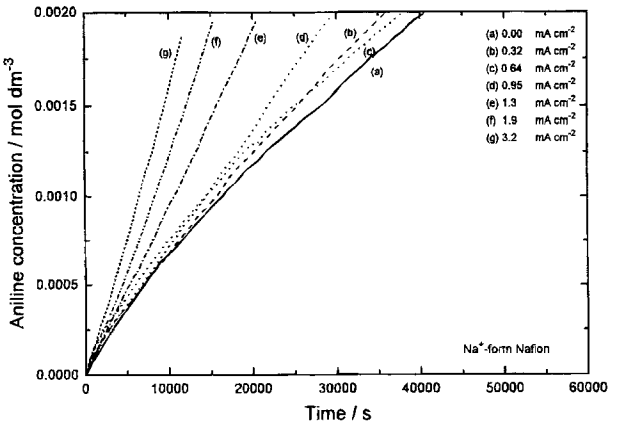

Fig. 5. Calculated concentration changes of total aniline species in the receiver solution for Na$^+$-form Nafion at current densities of (a) 0.0, (b) 0.32, (c) 0.64, (d) 0.96, (e) 1.3, (f) 1.9, and (g) 3.2 mA cm^{-2}.

force for diffusional transport decreased with the passage of time because of accumulation of aniline in the receiver solution, the decrease in aniline flux observed in Fig. 5 is attributable to a decrease in diffusional contribution at a prolonged permeation time.

Influence of co-existing alkali metal cation.—Similar permeation measurements were carried out using the K$^+$- and Cs$^+$-form Nafion and the corresponding solutions listed in Table I. Changes of total aniline concentration in the receiver solution are shown in Fig. 6 (i) and (ii) for K$^+$- and Cs$^+$-form Nafion membranes, respectively. The tendencies were similar to that for Na$^+$-form Nafion, although the aniline concentration for K$^+$- and Cs$^+$-forms increased less remarkably than that for the Na$^+$-form Nafion.

Influence of current density on aniline flux.—The dependence of aniline flux through Nafion on current density is of primary interest here. Since the aniline flux decreased with an increase in aniline concentration in the receiver solution as mentioned above, aniline fluxes at various current densities were compared using the values at a fixed aniline concentration (0.6 mM) in the receiver solutions. The pH change in the receiver solution should be negligibly small (Fig. 4). We assumed that the fluxes due to the diffusional transport at the fixed aniline concentration difference were equal to one another because the driving force for diffusional transport was independent of the current density. On the basis of this assumption, the aniline fluxes were calculated from the data in Fig. 5 and 6, and are plotted in Fig. 7. Although the values in Fig. 7 are still not free from a contribution from the diffusional transport, that diffusional contribution is assumed to be independent of current density. In each form, the slope of aniline flux increased abruptly in the current density range from 0.3 to 1.3 mA cm^{-2}. The aniline flux was highest for Na$^+$-form-Nafion. At low current densities, the aniline flux for the Cs$^+$ form was lowest. However, the increase in aniline flux for the Cs$^+$-form was slightly larger than that for the K$^+$-form.

Transport number of anilinium cation.—Since the ionic strength of the external solutions was much smaller than that inside the Nafion membrane, the Donnan exclusion works well, and the absorption of anions inside the Nafion membrane can be neglected under the present experimental conditions. Hence three species, *i.e.*, anilinium cation (AN^+), alkali metal cation (M^+), and proton (H^+), are supposed as mobile ionic species in Nafion. These three cations are the charge carriers inside Nafion. The total ionic conductivity, σ_t, of the Nafion is expressed as

$$\sigma_t = \Sigma t_i \sigma_t = \Sigma \sigma_i \qquad [2]$$

where t_i and σ_i denote the transport number and conductivity of individual charged species. The conductivity of individual charged species having a valence of unity is expressed as

$$\sigma_i = F^2 C_i u_i = F^2 C_i D_i / RT \qquad [3]$$

where C_i, D_i, and u_i denote the concentration, diffusion coefficient, and mobility of the individual charged species in Nafion, and F and R are the Faraday and gas constants. The electrotransported aniline flux was estimated by subtracting the diffusional aniline flux (the aniline flux at zero current density in Fig. 7) from the total aniline flux. The resulting transport numbers were plotted in Fig. 8 against current density. In each form, the transport number increased in the range from 0.3 to 1.3 mA cm^{-2}, and reached a constant value at higher current densities. However, these transport numbers of AN^+ were small, and most of the charge was therefore carried by the other cations in Nafion. The concentration changes of H^+ in the source and receiver solutions were small during the measurements (for example, see Fig. 4). In addition, the proton concentration inside Nafion was much lower than those of the other cations because of the low H^+ concentration in the solutions ($10^{-4}M$) and of the low H^+-selectivity coefficient of Nafion. Hence, the charge carried by proton can be neglected, and most of the charge was carried by M^+ in Nafion.

As shown in Fig. 8, the magnitudes of transport number of AN^+ in the plateau region in Na$^+$-, Cs$^+$-, and K$^+$-form Nafion membranes decreased in that order. From Eq. 3, the individual conductivity should be proportional to C_i and D_i. The diffusion coefficients and concentrations of aniline in Na$^+$-, K$^+$-, and Cs$^+$-forms of Nafion 117 in contact with a solution of the same composition as the source solution have been reported and are summarized in Table II.[17] (The diffusion coefficients of alkali metal cations are the values reported for Nafion 120.) The products of C_{AN^+} and D_{AN^+} for each form of Nafion also are shown in Table II. From the values we expect that the magnitudes of the transport number of AN^+ follow the order in Na$^+$ > in K$^+$ > in Cs$^+$ forms. However this was not the order. The transport number of AN^+ (t_{AN^+}) in the plateau region for Na$^+$-form in Fig. 8 was about three times larger than that for K$^+$-form, which is in good agreement with the ratio of the products, C_{AN^+} D_{AN^+}, for Na$^+$- and K$^+$-forms. However, t_{AN^+} in Cs$^+$-form was much larger than the value expected from the product. Hydrophobic properties of Cs$^+$ seem to cause the higher transport number in Cs$^+$- than in K$^+$-form Nafion, and this result is discussed in the following sections.

Electrotransportation of aniline without a concentration gradient.—To eliminate the contribution from the diffusional transport, permeation measurements were carried out using a buffer solution of pH 4 containing Na$^+$ and 2 mM aniline as both source and receiver solutions. The change in aniline concentration in the receiver solution was monitored for 20 min. In this experiment, a contribution from the diffusional transport can be neglected because there was almost no concentration gradient of aniline. The aniline concentration in the receiver solution increased linearly with time. The calculated aniline flux change is shown in Fig. 9. While the tendency was similar to those in Fig. 7, the flux at a given current density was much smaller than those in Fig. 7, and the transition region of aniline flux shifted somewhat to a lower current density range (from 0.3 to 1.0 mA cm^{-2}). The lower aniline concentration (2 mM) may be responsible for the smaller flux. The shift of the transition region suggests that the observed change in t_{AN^+} is dependent on the AN^+ concentration in the Nafion membrane.

Causes for the aniline flux change.—Gluga and Dindi reported that deprotonation of anilinium cation at the Nafion/water interface is the rate-determining step in the permeation of aniline from an acidic solution to pure water through H$^+$-form Nafion.[22] They concluded that the rate of the ion-exchange process at the solution/Nafion interface is faster than the rate of the deprotonation process at the Nafion/water interface. Here, pH of both receiver and source solutions was about 4, and interfacial reactions such as protonation and deprotonation seem not to have a significant influence on total aniline transportation. Hence, the phenomena observed here seem attributable to bulk properties of Nafion.

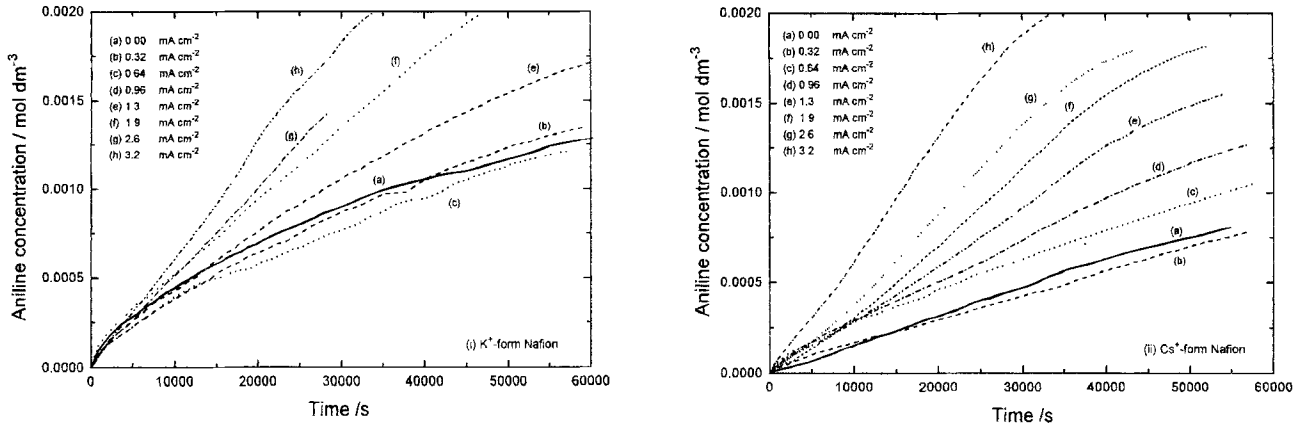

Fig. 6. Calculated concentration changes of total aniline species in the receiver solution for (i) K^+ and (ii) Cs^+ forms of Nafion at current densities of (a) 0.0, (b) 0.32, (c) 0.64, (d) 0.96, (e) 1.3, (f) 1.9, (g) 2.6, and (h) 3.2 mA cm^{-2}.

The phenomena may be explained in terms of the following two possibilities; (*i*) the change of the ionic cluster network structure is caused by an application of a dc current. The movement of cations and water may distort the microscopically phase-separated structure of Nafion and make the channels connecting the ionic clusters wider; (*ii*) the hydrophobic interaction between aniline and Nafion may be decreased due to the mass transport caused by a flow of dc current.

It is difficult to separate *i* and *ii*. The transport number of anilinium cation in Cs^+ form in Fig. 8 was larger than that expected from the product of C_{AN^+} and D_{AN^+}. Cesium ion is known to be located in the interfacial region between the ion cluster region and the PTFE-like backbone region inside Nafion.[10] Since anilinium cation interacts strongly with the hydrophobic region in Nafion,[17] the anilinium cation may be located in and permeate through the interfacial region as Cs^+ does. When Cs^+ moves in Nafion, it disturbs and decreases the hydrophobic interaction between anilinium cation and Nafion. Then, the mobility of the anilinium cation may increase, leading to an increase in t_{AN^+}. In addition, the movement of Cs^+ through the interfacial region of Nafion may cause friction in the interfacial region of Nafion, and this friction also leads to a distortion of the ionic cluster structure, *i.e.*, the channels of Nafion, which may affect the mass transport in Nafion,[23] are broadened. This broadening enhances the mobility of the anilinium cation, which moves most slowly among the cations examined here, and then the transport number of anilinium cation may be increased.

Sandeaux *et al.* reported that an externally applied voltage accelerated the permeation of acetate ion through the anion-exchange membrane, Selemion AMV, more than that of chloride ion.[22] They suggested that this acceleration was caused by a higher value of the so-called transfer coefficient (a measure of the permeation rate through the interface between a membrane surface and the adjacent solution) of acetate ion. They proposed the hydrophobic character of acetate ion as one possible reason why the acetate ion movement was enhanced by the application of external current. Although the situation is different from our system, this type of influence should be taken into consideration in our system for further discussion because the interaction between the anilinium cation and Nafion is much stronger than that between acetate ion and Selemion AMV.

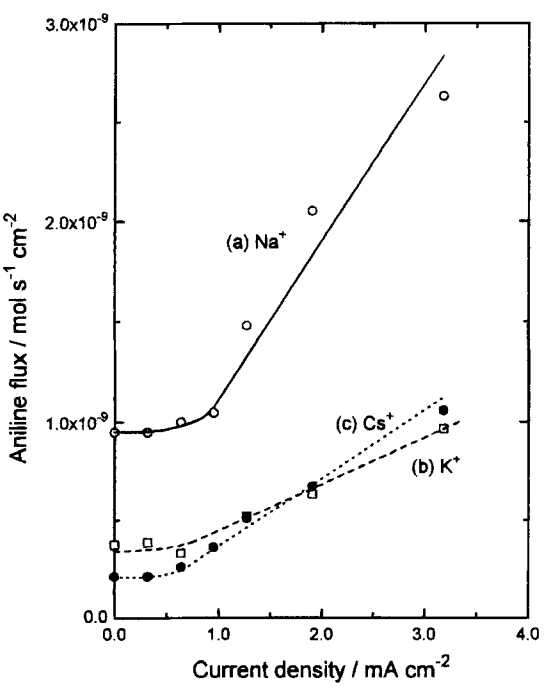

Fig. 7. Aniline fluxes at an aniline concentration of 0.6 mM in the receiver solution against current density for (a) Na^+-, (b) K^+-, and (c) Cs^+-forms of Nafion.

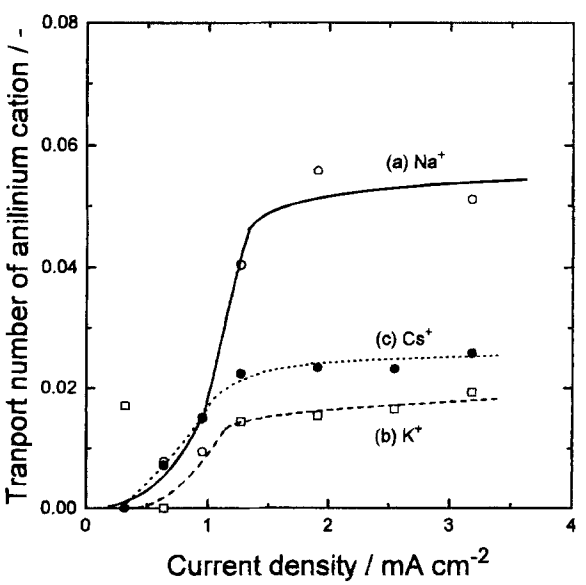

Fig. 8. Changes in transport number of anilinium cation in Nafion with current density for (a) Na^+-, (b) K^+-, and (c) Cs^+-forms of Nafion.

Table II. Diffusion coefficients and concentrations of aniline in Nafion.

Ionic form	$D_{M^+}^{Nafion} 10^{-7}$ [a] ($cm^2\ s^{-1}$) (25°C)	($cm^2\ s^{-1}$) (40°C)	Water content[b] (mol H_2O/mol $-SO_3^-$)	$K_{H^+}^{M^+}$ [c]	$D_{AN^+}^{Nafion}/10^{-9}$ [d] ($cm^2\ s^{-1}$)	$C_{AN^+}^{Nafion}$ [d] (mol dm^{-3}) equilibrated with the source sol.	$C_{M^+}^{Nafion}$ [d] (mol dm^{-3})	$C_{AN^+}^{Nafion} D_{AN^+}^{Nafion}/10^{-12}$ (mol $cm^{-1}\ s^{-1}$)
Na^+	9.8	15.0	11.9	1.18	11.8	1.14	0.54	13.5
K^+			8.8	3.48	6.7	0.75	0.92	5.0
Cs^+	1.9	2.7	6.6	7.06	3.2	0.50	1.71	1.6

[a] From Ref. 8.
[b] From Ref. 19.
[c] From Ref. 20.
[d] From Ref. 17.

Conclusion

The transport phenomena of aniline through several ionic forms of a perfluorosulfonate ion-exchange membrane, Nafion 117, under a flow of dc current were investigated. In each form, an increase in transport number of anilinium cation was observed in the current density range from 0.3 to 1.3 mA cm^{-2}. The transport number of anilinium cation in Cs^+-form Nafion was larger than that expected from the concentration and diffusion coefficient in Cs^+-form Nafion. These phenomena may be attributed to a decrease in hydrophobic interaction between anilinium cation and Nafion or to a change in the ion cluster network structure due to the mass transport caused by the flow of dc current.

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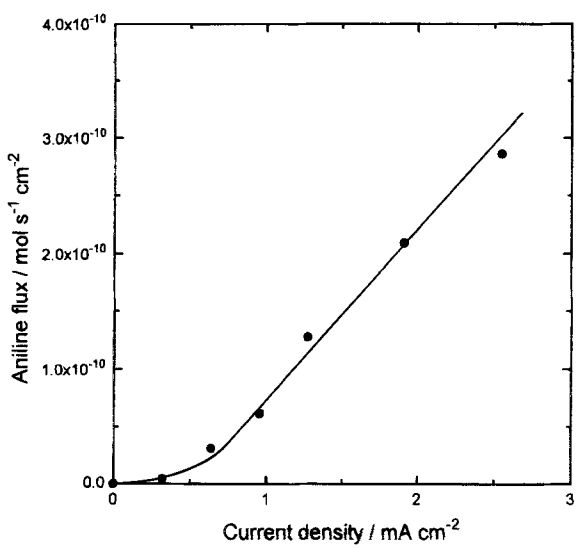

Fig. 9. Aniline fluxes at the aniline concentrations of 2 m*M* in both the source and receiver solutions against current density for Na^+-form of Nafion.

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