

## NOTES

### *Effect of Membrane Matrix on the Transport of Potassium Ions*

In a previous paper,<sup>1</sup> Wallace and Ampaya described the electromigration of hydrogen and sodium ions in a strong-acid sulfonate membrane. Ionic conductivities and mobilities were reported for this sulfonate cation exchange membrane from its virtually dry to fully water-saturated membrane conditions. These membrane measurements were conducted in the absence of an external electrolyte. In this work, the specific ionic conductances and the calculated mobilities of the potassium ion in three different cation exchange membranes, also without an external electrolyte, are presented as a function of membrane water content. The influence of several structural variables on the cation exchange membranes on the mobility of potassium ions are discussed.

### EXPERIMENTAL

#### Membrane Sample Preparation

Three common sulfonated cation exchange membranes were used<sup>2</sup>: AMF C-60 membrane (American Machine and Foundry Co., Stamford, Conn.); Asahi DK-1 membrane (Asahi Chemical, Kawasaki, Japan); and Nepton CR-61, AZL 183, Dynel-backed membrane (Ionics, Cambridge, Mass.). The AMF C-60 membrane consists of approximately 35% by weight of poly(styrenesulfonic acid), crosslinked with 2% by weight divinylbenzene and grafted to a polyethylene matrix. The Asahi DK-1 membrane is a homogeneous poly(styrenesulfonate-divinylbenzene) film without any fabric reinforcement. The Nepton CR-61 membrane is a homogeneous sulfonated polystyrene copolymer cast on a Dynel cloth backing.<sup>3</sup>

Strips of these membranes were soaked in 1*N* KCl solution and leached thoroughly with deionized water. These membranes ( $K^+$ ) were kept in desiccators prior to conductance measurements at different relative humidities by employing saturated salt solutions.

The ionexchange capacities of these membranes were determined in accordance with standard potentiometric procedures. From these titration data and membrane dry weight, the exchange capacity was calculated to be 1.66 meq/g of dried AMF C-60 membrane, 2.60 meq/g of dried Asahi DK-1 membrane, and 2.65 meq/g of dried Nepton CR-61 membrane.

#### Ionic Concentration

Ionic concentration is defined as the milliequivalents of the total concentration of free counterions per unit volume. A wet membrane ( $K^+$ ) sample about 3 cm by 5 cm was weighed and its dimensions measured. It was subsequently equilibrated at progressively decreasing humidities employing water and eight saturated salt solutions. At each humidity level, membrane ( $K^+$ ) weight and dimensions were recorded only when the membrane attained equilibrium. The membrane ( $K^+$ ) was dried under vacuum to obtain its density. The relative ionic concentration referred to the dried membrane ( $K^+$ ) is expressed in terms of  $c/c_D$ , the ratio of ionic concentration in the wet to that in the dried membrane. Figure 1 presents the relative potassium ion concentration,  $c/c_D$  in three different cation exchange membranes as a function of membrane water content at 25°C.

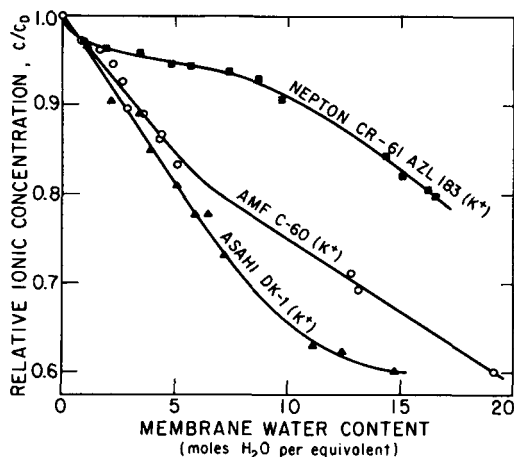


Fig. 1. Effect of water content on the relative ionic concentration of three different cation exchange membranes in potassium ion form referred to their dried state at 25°C.

#### Membrane Conductance

Preequilibrated membrane (K<sup>+</sup>) samples were cut into strips 0.50 cm wide and 4.0 cm long and then clamped tightly using electrode clamps between the platinum-plated electrodes. The electrode assembly was placed over the same saturated salt solution used in preequilibration in a brass cell enclosure. About two days were required for the membrane (K<sup>+</sup>) to attain moisture equilibrium. The same current-measuring apparatus and electrical circuit were used as was previously described.<sup>1</sup> Membrane (K<sup>+</sup>) conductivity was calculated from the relation

$$\sigma = \frac{I_s}{V_s - V_D} \left( \frac{l}{A} \right)$$

where  $V_s$  is total applied voltage,  $I_s$  is sample current,  $l$  is membrane length, and  $A$  is the cross-sectional area perpendicular to current flow. This conductivity relation makes use of the effective voltage for conduction of ion transport obtained by subtracting the membrane (K<sup>+</sup>) decomposition voltage,  $V_D$ , from the total applied voltage.

The decomposition voltage was determined by plotting membrane (K<sup>+</sup>) current as a function of applied voltage as shown in Figure 2. The intercept at zero current was taken to be the decomposition voltage of the dehydrated membranes (K<sup>+</sup>). Table I lists these membranes decomposition voltages. No systematic variation of  $V_D$  with membrane water content was noted.

TABLE I  
Decomposition Voltage of Three Dehydrated Cation Exchange Membranes in Potassium Ion Form at 25°C

Membrane (K <sup>+</sup> )	Membrane water content, moles water per equivalent	$V_D$ , volts
AMF C-60	5.57	1.2 ± 0.3
Asahi DK-1	6.67	2.0 ± 0.3
Nepton CR-61	7.57	2.0 ± 0.3

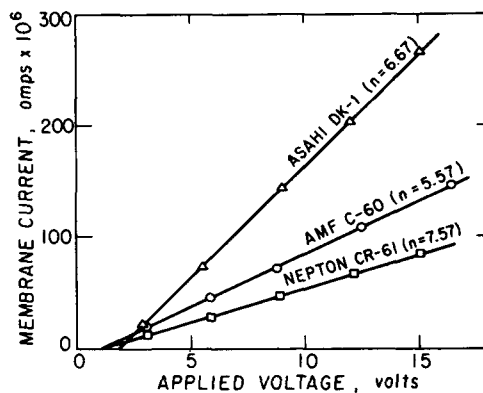


Fig. 2. Current-voltage plots for three different cation exchange membranes in potassium Ion Form at 25°C.

#### Membrane Water Content

Each membrane ( $K^+$ ) sample was weighed after its conductivity was measured using a Mettler Balance type H-6. It was next dried at 60°C under a vacuum for two days and reweighed. Moisture content in moles of water per equivalent of membrane was calculated from the two weighings and membrane exchange capacity.

#### Results and Discussion

Figures 3 and 4 present the effect of water content on the specific conductance and ion mobility of three different cation exchange membranes in their potassium ion form. Although possessing the same sulfonate exchange groups, the AMF C-60, Asahi DK-1, and

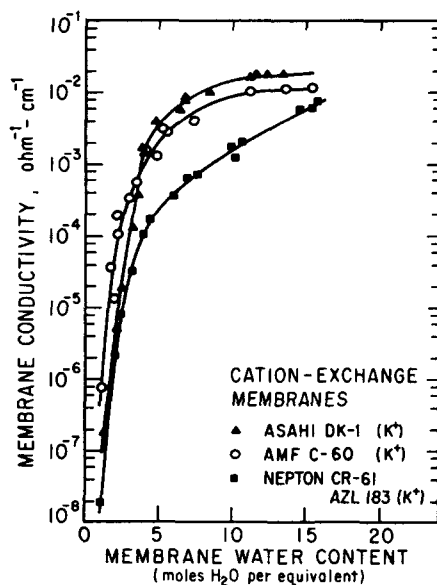


Fig. 3. Dependence of the specific conductance of three different cation exchange membranes in potassium ion form on water absorption at 25°C.

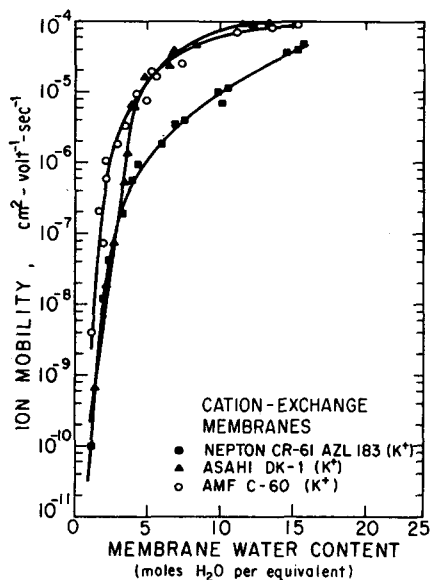


Fig. 4. Cation mobility of potassium ion in three different cation exchange membranes as a function of water content at 25°C.

Nepton CR-61 membranes have significant differences in terms of degree of crosslinking as well as the concentration and distribution of sulfonate sites. By progressively lowering the membrane water content, the influence of these structural factors on the migration of potassium ions under an applied electric field becomes accentuated.

The marked difference in transport properties of Nepton CR-61 from Asahi DK-1 and AMF C-60 membranes is pronounced in Figures 3 and 4. Aside from the lower conductance of the Nepton CR-61 membrane, we note that the conductance and mobility plots are much steeper beginning at a water content of 5 moles  $H_2O$  per equivalent. This lower conductance has been accounted for by the fact that a considerable portion of the cross-sectional area of the Nepton CR-61 membrane is occupied by the Dynel reinforcing fabric. Thereupon, the effective area for potassium ion transport is actually much smaller than the total area used in the conductivity calculations.

At the high membrane water contents above 5 moles  $H_2O$  per equivalent, the conductivity of the Asahi DK-1 membrane is about 1.5 times greater than that of the AMF C-60 membrane. This has been accounted for by the higher concentration of 1.87 meq/cc mobile counterions in the water-saturated Asahi DK-1 membrane, compared to to 1.22 meq/cc in the AMF C-60 membrane. It is apparent that the conductivities of these two membranes at high water contents are primarily determined by the concentration of ion carriers, implying that the influence of structural effects is minor. At the lower region of water absorption, Asahi DK-1 membrane becomes less conductive than the AMF C-60 membrane, despite the fact that its ionic concentration is still greater than the AMF C-60 membrane. Clearly, other variables besides ionic concentration are effectively influencing the transport of potassium ions when the membrane contains only a few moles of water per equivalent.

Of the several interactions existing in water-saturated membranes, the two most important in ion transport are the counterion-fixed site and counterion-water interactions. The membrane functions as a polyelectrolyte gel where the water-filled pores are open in all directions.<sup>6</sup> The transported counterion is influenced by the coulombic attraction of the oppositely charged fixed sites and the structure of the pore liquid.<sup>6</sup> Figure 4

shows that as water content increases, the mobility of potassium ions in the AMF C-60 and the Asahi DK-1 membranes becomes virtually the same. This suggests that the effects of the hydrophobic polymer network, crosslinked with divinylbenzene, are minimized such that the membranes are almost equivalent. Specifically, the potassium ion mobility is  $1 \times 10^{-4} \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$  in these two fully water-saturated membranes at 25°C. This mobility value compares to a potassium ion mobility of  $7.6 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$  in water solutions also at 25°C.<sup>7</sup>

At the lower membrane water contents, the mobility of potassium ion is probably influenced by additional factors due to the absence of free pore water. Thus, the transport of potassium ions involves the movement through water-free interstices. Additional interactions such as counterion-polymer chain interaction and interpolymer chain interactions may affect the mobility of potassium ion. Our conductance data indicate that these interactions are greater in the Asahi DK-1 membrane than in the AMF C-60 membrane owing to the lower potassium ion mobility in the Asahi DK-1 membrane at water absorption levels below 5 moles water per equivalent. The structural differences in the membranes are probably responsible for the observed differences in potassium ion mobilities. For instance, the sulfonate site-to-sulfonate site distance is longer in the Asahi DK-1 membrane than in the AMF C-60 membrane. The greater the ion jump distance, the more the potassium ion is subjected to the retarding effects of the polymer hydrophobic barriers in its migration path.<sup>8</sup>

#### References

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RICHARD A. WALLACE

Stanford University  
Stanford, California 94305  
and  
Oregon Graduate Center and  
University of Oregon Medical School  
Portland, Oregon 97201

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