Unusual Ionic Behavior in Microemulsion-Polymerized Membranes

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Some unusual ionic conducting phenomena were observed from ion-containing microemulsion membranes. Contrary to conventional wisdom, it was found that under the same ionic concentration, large ions exhibit higher mobilities than smaller ones. They are possibly explained by the existence of hydration shells, which eventually made the lighter cations larger. This is further supported by the sharp conductivity drop when the system was cooled below the freezing point of water. In addition, conductivity drop at higher ionic concentration was also observed.

Introduction

Ion-containing membranes have attracted much attention recently, because of their potential applications in sensors, batteries, and fuel cells.[1] The polymer-based membranes can offer advantages of reduced thickness, weight, and higher ionic conductivity. In addition, the mechanical flexibility of the polymers enables solid-state cells to be designed with optimized electrode/electrolyte interface as they can be readily shaped into any desired configuration. An important example is the per-fluoro−sulfonate ionomer from DuPont, called Nafion. It contains ionic clusters of 3−5 nm size. When hydrated (water uptake to ca. 20 wt %), it can offer very high ionic conductivities, comparable to those of liquid electrolytes.[2,3] A similar example is the Dow XUS membrane, which offers even higher ionic transport abilities.[4−6] None of these conductivities is strongly dependent on the cation sizes. However, these ionic clusters tend to be rearranged during the recasting process, a necessary step in the large-scale fabrication, and result in a much reduced ionic conductivity.[7] To seek alternatives, as well as to reduce the cost, ion-containing hydrocarbon membranes were prepared via a microemulsion method.[8]

Microemulsion systems are thermodynamically stable, isotropic assemblies of oil and water, separated by an interfacial film of surfactant molecules.[9−11] The microstructues may be "oil-in-water" or "water-in-oil" depending on the compositions of oil, water, and surfactant. By determining the correct compositions, both the water and oil phase can be in continuum, forming a bicontinuous structure.[12] Thus, open-cell porous membranes can be obtained by the direct polymerization of such microemulsion systems, in which the aqueous and oil domains are interconnected randomly in the form of spongelike structures. If ionic monomers, such as 4-vinylbenzene sulfonate (SVBS), are copolymerized together, the interconnected water channels can be treated to host cations, which would then produce ionic conduction behavior.

The study of the ionic transport is important in these ion-containing membranes. Usually, this is done by radio frequency AC impedance spectroscopy**,** since ionic resistivity/conductivity cannot be directly measured by a DC ohmmeter. But it may not always be possible to obtain the full impedance spectra using such techniques from the bulk due to interfacial effects. To overcome this, impedance studies have to be carried out at higher frequencies so that the true impedance of the bulk materials can be obtained. However, a survey of previous studies leads to the conclusion that most investigations were carried out by frequencies $\leq 10^6$ Hz.[13] In other words, the complete frequency spectra for most polymer-based electrolytes were usually skipped.

To complete our impedance studies that have been reported for the low-frequency region on the microemulsion membranes,[14] we try to study in this report, the ionic conductivities in the microwave frequencies. In particular, we are going to study the conductivity dependence on the various ions, via the cation exchange, while maintaining a constant ion concentration. For some ionic species, we will also study the change in ionic conductivities against ion concentration and temperature.

Experimental Section

Materials. Acrylonitrile (AN), methyl methacrylate (MMA), and ethyleneglycol dimethacrylate (EGDMA) obtained from Aldrich were purified under reduced pressure before use; 4-vinylbenzenesulfonate, sodium salt (SVBS), and 2,2-dimethoxy-2-phenyl acetophenone (DMPA) from Aldrich and lithium chloride (LiCl) and cesium chloride (CsCl) from Merck were used as received. Polymerizable nonionic surfactant of ω-methoxy poly(ethyleneoxide)$_{40}$ undecyl-α-methacrylate (PEO-macromonomer, C_1-PEO-C_{11}-MA-40) was synthesized as reported earlier.[15] Deionized and distilled water was used for all microemulsions and dissolution of salts.

Membrane Preparation. The single-phase region of the microemulsion consisting of C_1-PEO-C_{11}-MA-40/AN/MMA/H_2O was determined systematically by titrating water to various compositions of C_1-PEO-C_{11}-MA-40, AN, and MMA in a screw-capped test tube. Each sample was vortex-mixed and allowed to equilibrate in a temperature-controlled environment

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TABLE 1: Compositions for the Microemulsion Membranes

	composition of precursor microemulsions (wt %)[a]				after polymerization
					ionic conductivity
sample	water	SVBS	C_1–PEO–C_{11}-MA-40	AN/MMA (70:30)	ionic species	(10^{-3}) at 293 K
1	35	1.8	34.2	29.0	H^+	0.136
2	35	1.8	34.2	29.0	Li^+	0.643
3	35	1.8	34.2	29.0	Na^+	5.670
4	35	1.8	34.2	29.0	Cs^+	52.90
5	35	2.7	33.3	29.0	Na^+	6.120
6	35	3.6	32.4	29.0	Na^+	6.430
7	35	4.8	31.2	29.0	Na^+	5.100
8	35	7.2	28.8	29.0	Na^+	2.860

[a] In addition, cross-linker EGDMA and photoinitiator DMPA were also added to each microemulsion. They were 5 and 0.23 wt % based on the total weight of polymerizable components, respectively. Polymerization temperature was 30 °C.

at 23 °C. The clear–turbid points were used to establish the phase boundary of the microemulsion region.[14] A rough demarcation of the bicontinuous region was further deduced from conductivity measurements using a dc conductivity meter.[8] As guided by the phase diagram,[14] various amounts of SVBS can be incorporated into some of the microemulsion compositions for the membrane preparation. The detailed compositions of the membranes were listed in Table 1.

The polymerization of the microemulsion samples was initiated by photoinitiator DMPA in the Rayonet photoreactor chamber at about 30 °C. The membranes were prepared by spreading the gel-like pre-polymerized microemulsion between two glass plates and subjected to further polymerization in the photoreactor chamber. After the completion of polymerization, the membranes were recovered and immersed in the water for about 24 h before further studies. The membranes are found to be thermally stable up to 220 °C.

The bicontinuous nature of the membrane can be checked by Scanning Electron Microscopy (SEM) of the cross section, where connected water pores are visible,[8] or simply confirmed by the membrane ultra-filtration, where water molecules are able to flow through. The quantitative measurement can be performed for the pore size distribution, which was determined from the freezing point depression of the water trapped.[14] In the present system, the pore size was found to range from 5 to 15 nm.

The amount of water uptake was found to be around 25 wt % for most of the membranes. Repeated hydration and drying process do not produce evident changes to the membranes.[14]

Ion-Exchange of Microemulsion Membranes. The sodium ions balanced by fixed sulfonic (SO_3^-) groups attached to the polymer backbone are readily exchanged at 30 °C by other monovalent cations through immersion in 2 M aqueous MCl (M = H, Li, Cs), for about 2–7 days with the larger cations taking a longer time. The samples were then allowed to equilibrate for a few days before conductivity measurements. No structural changes were found after the ion-exchange.

Ionic Conductivity Measurements. Alternating current impedance measurements over the frequency range 1 MHz to 1.8 GHz (microwave) were made with a Hewlett-Packard 4291B RF impedance/ material analyzer. Polymeric membrane samples of ca. 0.6 mm thick were sandwiched between two parallel metal electrodes and conditioned to the desired temperature. The values of the real and imaginary parts of the complex impedance Z' and Z'' were recorded for the frequency scan. The AC impedance spectra were then plotted, and the conductivities were evaluated by extrapolating the impedance arc to intercept the real axis.
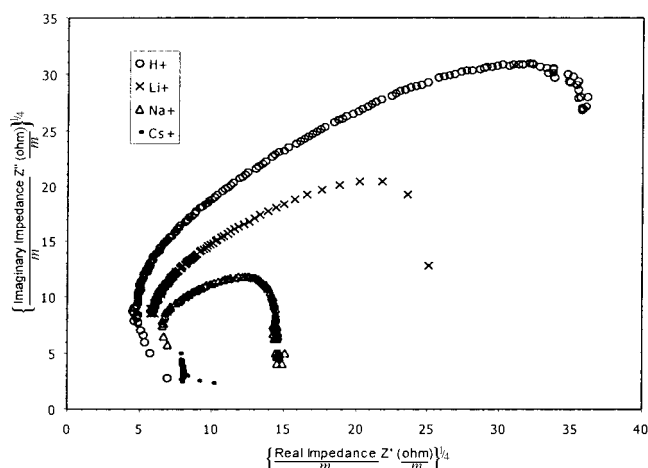
1(a) Insert 1 of Figure 1
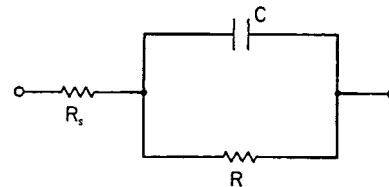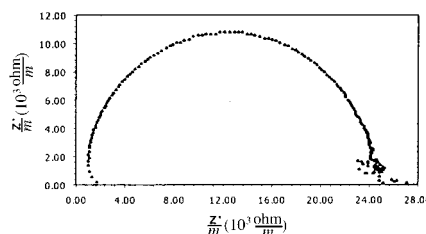

1(b) Insert 2 of Figure 1

Figure 1. Cole–Cole plot using a compressed scale of $Z^{1/4}$ for the microemulsion membranes containing various ionic species at room temperature (293 K). (a) Insert 1 of Figure 1: Equivalent circuit consisting of a parallel pair of a dc capacitor C and a dc resistor, in series with an additional dc resistor, R_s. 1(b) Insert 2 of Figure 1: Typical plot showing a semicircle plotted in linear scale for the Na^+-containing membranes.

Results

Unusual Ionic Behavior of Microemulsion Membranes. The complex impedance data for various ion-containing membranes at room temperature (293 K) are plotted in Figure 1. Each curve was formed by a series of (Z', Z'') points, with every point corresponding to a particular frequency (Cole–Cole plot). The $(Z)^{1/4}$ scale was employed to compress the data range and also to show the huge differences in the Z values from various ions. In the insert of Figure 1, the Na^+ curve was replotted in linear scale to show the semicircular shape. These semicircles are typical of those observed for ionic conductors generated by the complex impedance of the sample bulk. They can usually be simulated by a parallel pair of a capacitor C and a dc resistor R (independent of frequency)[16] in series with a dc resistor R_s, also given by the insert of Figure 1. Usually, the RC combination gives a semicircle which is centered on the real axis. The horizontal shift of the semicircles from the origin is due to the added dc resistor in series, R_s, which can be considered as a form of contact resistance between the polymer–electrode interface plus that of the connecting cables, etc. The corresponding dc resistance can then be evaluated by extrapolating the impedance semi-circular arc onto the real axis of the Cole–Cole plot. The resulting values are 1.36×10^{-4} S/cm for H^+,

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6.43×10^{-4} S/cm for Li$^+$, 5.67×10^{-3} S/cm for Na$^+$, and 5.29×10^{-2} S/cm for Cs$^+$.

From Figure 1, it is evident that the size of the semicircle decreases as the ion size increases, showing a lower bulk resistance (or higher conductance) for the sample containing the larger cations. Since, in our system, the moving particles which contribute to the ionic conductivity are the carrier ions, the ionic conductivity can be expressed as:

$$\sigma = qn\mu \tag{1}$$

where n is the ion concentration, q the elementary charge (given by $+1e$, $+2e$, etc.; $e = 1.6 \times 10^{-19}$ Coulomb) and μ the ion mobility (given by the corresponding drifting velocity over the electric field). Since the incorporation of the large sulfonate anions (SO_3^-) are bonded onto the pendant group of the polymer chains, it is ensured that the number of the counterions (n) remain constant always. In the meantime, only the univalent alkali metal ions are exchanged; therefore, the ion concentration factor n is kept unchanged. Conventional wisdom tells us that if the concentration of ions present remains constant, larger ions would possess lower mobility and hence exhibit lower conductivity at the constant temperature. However, this is not the case from the observed data, where the larger ions exhibit higher conductivity values.

Effect of Changing Cationic (Na$^+$) Concentrations. We also studied the ionic conductivity with respect to a change in ion concentration. Figure 2 displays the effect of the ion concentration on the conductivity of the Na$^+$-containing samples at 293 K. From the plot, it is obvious that as ion concentration increases, the ionic conductivity first increases and then decreases, showing an optimum conductivity at 6.46×10^{-3} S/cm. As noted previously, because the ionic conductivity is directly related to the ion concentration, a plot of σ versus weight % mobile cations should yield a straight line. This is, however, not followed here. In fact, as shown in Figure 2, when the ion concentration increases, the increase in the conductivity deviates from the linear relationship. This again provides an unusual scenario for the ionic transport.

Effect of Temperature. To study the temperature effect on the ionic conductivity, as an example, the logarithmic ionic conductivity of the Na$^+$-containing membrane was plotted against the reciprocal temperature in Figure 3. At high or low temperatures, the conductivity was found to follow the Arrhenius equation:

$$\sigma \propto \exp\left(-\frac{E_g}{RT}\right) \tag{2}$$

where E_g is the activation energy for ionic motion. Although there is no apparent change in shape and size for the membranes across the freezing point of water, it is evident that between the two regions the conductivity changes sharply at about 0 °C. The segment below the freezing temperature has an apparently steeper slope than the one above it. From Figure 3, the activation energies were found to be 0.012 and 0.38 eV for the temperature well above or below the freezing point, respectively.

Discussion

Similar to Nafion-type ionomers, where the cationic transport is mainly attributed to the cluster of water and SO_3^- groups in perfluorocarbon sulfonates (-OCF$_2$-CF$_2$-SO$_3$H),[2-7] in our microemulsion-polymerized membranes, cations are also dissolved in the $H_2O-SO_3^-$ clusters, except that the sizes of the water
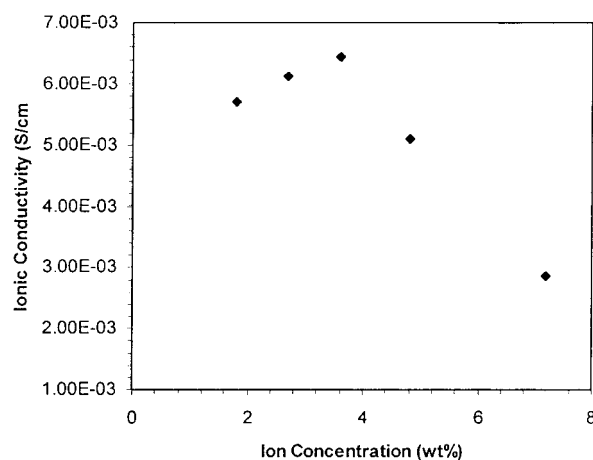

Figure 2. Conductivity versus ion concentration plot of Na$^+$-containing membranes at room temperature.
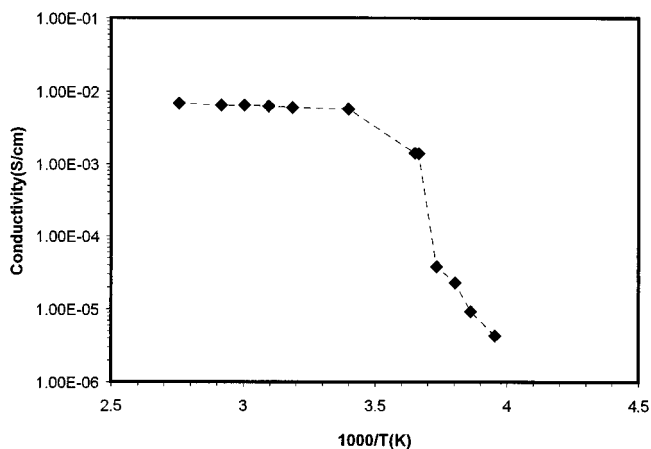

Figure 3. Logarithmic conductivities of Na$^+$-containing microemulsion membranes as a function of reciprocal temperature.

channels present in our systems are larger[14] (5−15 nm versus 3−5 nm in Nafion).

According to the free volume theory,[17] the diffusion of the carrier species is not activated but rather occurs as a result of the redistribution of free volume within the liquid phase. The molecules are assumed always confined within their "cages", except when there appears a "hole" large enough for the molecule, in our case, an ion to jump into. However, in our system, a decrease in free volume due to the increasing cation size (from H$^+$ to Li$^+$, Na$^+$, Cs$^+$) apparently does not lead to a decrease in ion mobility. This clearly indicates a discrepancy from the free-volume theory.

This apparent discrepancy can, however, be explained by the possible hydration of the cations and the clustering of the H_2O molecules.

In the case of H$^+$, a large hydration shell[18] can be formed, such that H$^+$ ions are not moving alone but in the form of H_3O^+, $H_5O_2^+$, or $H_9O_4^+$. On the other hand, large cations (e.g., Cs$^+$) are not able to carry such hydration spheres as easily,[19] due to the fact that it would then be too large to form a closed shell around the ion, to achieve a stabilized energy configuration. Therefore, the effective sizes for the lighter cations become actually larger than the heavier ones. Moreover, although the electrostatic forces operate beyond the first shell, the additional water molecules are bound in layers of decreasing firmness. The larger the cation itself, the less it binds to the outer layers. For example, the documented effective hydrated radii (in Angstroms) were found to be 3.40, 2.76, and 2.28 for Li$^+$, Na$^+$,

and Cs^{+}, respectively, which correspond to 25.3, 16.6, and 9.9 water molecules per cation.[19] In other words, as a result of cation hydration, the overall size is actually larger for smaller cations such as Li^{+}, thus leading to the lower conductivity.

The possible existence of hydration shells around the cations is further supported by the results from Figure 3, where the conductivity below the freezing point of water drops by 2 orders of magnitude. While at room temperature, the ionic transport can be assisted by the random motion of the water molecules. When the temperature falls below 0 °C, with no apparent structural changes observed, ionic transport by the aqueous phase is likely to be impeded by the frozen water. It should be noted that the Nafion-type ionomers do not exhibit such a drop across the freezing temperature, due possibly to the nanosized water clusters involved,[2−7] although similar hydration shells are observed.[18]

Another possible explanation for the unusual behavior can be due to the ionic complexes with the PEO linkages.[20] It was proposed that the ether oxygens would be coordinated to the cations, thus forming a different type of coordination shell around each cation in the "dry" environment. Hence, as the size of the cation increases, such conformations become less favorable, leading to decreasing complexing behavior with the ether oxygens. However, this is not consistent with the conductivity drop below the freezing temperature.

Although a drop in conductivity across the freezing temperature may seem undesirable, it may be useful in certain applications such as temperature sensors; when temperature goes below 0 °C, the conductivity of the membrane plunges and this reduces electric current or vice versa. Also, for potential applications in electrochemical cells requiring the stringent choice of heavy ions such as Cs^{+}, the present system can be of value in achieving higher conductivities.

As we consider the ion conductivity to be a product of both ion mobility and mobile concentration,[21] for a particular series of Na^{+}-containing membrane studied, ion mobility would remain constant as the size of the ion is unchanged. Therefore, any variation in conductivity must be related to the concentration of mobile ions present. Following this, the ionic conductivity should drop following a decrease in mobile ion concentration. As shown in Figure 2, the conductivity actually increases initially due to the increase in mobile cation concentration, but then drops as concentration increases further. This must be related to the drop of the mobility of ionic transport and in turn leads to a subsequent decrease in conductivity.

Conclusion

Some unusual ionic conducting behavior was observed in this study from the bicontinuous microemulsion membranes. Under the same ionic concentration, it is found that large ions actually exhibit higher mobilities. With the failure to account for the increase in conductivity with larger ionic sizes, the "free volume" theory cannot be applied to this system. However, the unusual phenomena can be explained by the cation hydration shells which make lighter ions bigger in size than the heavier ones. This is because the heavy ions are less binded to the outer layers of the hydration shells. The existence of the hydration has been supported by the sharp decrease in conductivity across the freezing point.

It was also observed that the ionic conductivity first increases and then falls as the ion concentration increases. Thus, there must be a corresponding decrease in the mobility of the transporting ions, which leads to an overall decrease in conductivity. These unusual observations can nevertheless be applied to situations where heavier cations are needed to achieve higher ionic conductance.

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