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IONIC CONDUCTIVITY OF POLYACID-POLY(VINYL ALCOHOL)-METAL ION COMPLEX MEMBRANES

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ABSTRACT

Polymeric complex membranes with high ionic conductivity have been prepared from polyacid, poly(vinyl alcohol), and metal ions. It was found that the ionic conductivity of bipolymer-metal ion complexes is higher than that of single polymer-metal ion complexes. Their ionic conductivity is discussed in relation to the acid strength of the polyacid, the size of the metal ions, the dielectric constants of the additives, and the temperature.

INTRODUCTION

Polymeric metal ion hybrid membranes with ionic conductivity are currently attracting widespread interest because they have great potential uses in electric devices and can be easily processed into thin and felxible films. In general, for obtaining such a membrane, some single polymers that are flexible and polar, such as poly(ethylene oxide), perfluoropolyelectrolytes, polyacrylonitrile, etc., are used [1-4]. Some additives with high dielectric constants are often used in order to improve the toughness and ionic conductivity of the hybrid membranes [2].

Intermacromolecular complexes can be formed by interaction between two or more kinds of macromolecules through ionic bonding, hydrogen bonding, etc. It is known that the mechanical strength of some complexes is greater than that of single polymers [5], and the composition of the complexes obviously affects the morphology and the degree of crystallinity of the complexes [6]. In order to improve conductivity and processability of the polymer-metal ion conductors, we report here a study of conductivity of some bipolymer-metal ion complex membranes, each of which was composed of two kinds of polymers with hydrogen bonds between them. It was found that the bipolymer-metal ion complexes have higher ionic conductivity than the single polymer-metal ion complexes. Moreover, the influence of various factors, such as the acid strength of polyacid, the size of the metal ions, additives, temperature, etc., on the ionic conductivity of the complex membranes has been studied.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) with degrees of polymerization and of saponification of 1 700 and 88%, respectively, was obtained from the Beijing Organic Chemical Plant. Poly(methacrylic acid) (PMAA) [7], poly(acrylic acid) (PAA) [7], and sulfonated polystyrene (PSSA) [8] were prepared by literature methods. All polymer materials were purified by passing through anion and cation exchange resin column. Molecular weights of PMAA and PAA were estimated as 390 000 and 69 000, respectively, by viscometric measurement. Molecular weight and degree of sulfonation of PSSA were 110 000 and 92%, respectively.

Preparation of the Membranes

To 3.5 mL of an aqueous solution of PVA (0.18 mol/L) and the calculated amount of metal salt, the required amounts of aqueous solutions of polyacid and liquid additive were added to obtain complexes of the desired molar ratio. After complete homogenization, the solution was evaporated until the total solution volume was about 2 mL and poured into a silicone mold 3 cm in diameter. The solution was allowed to evaporate in a dry atmosphere to leave a film about 0.1-0.3 mm thick. The membrane was peeled off from the silicone substrate and dried over P_2O_5 for 3 days.

Measurement of Ionic Conductivity

A disk of hybrid membrane of 2 cm in diameter was placed between two polished stainless-steel cylindrical electrodes in an apparatus that provided an inert atmosphere of nitrogen, a controlled temperature, and a pressure loading to ensure good contact between the sample and electrodes. The ionic conductivity of the hybrid membranes was measured by means of TR-10C Dielectric Loss Measuring Set and QF-2790 RCL Bridge.

RESULTS AND DISCUSSION

Polymeric acids can form intermacromolecular complexes with PVA by hydrogen bonding. The polymeric acids used in this paper were PSSA, PAA, and PMAA, while $LiClO_4$ and $CuCl_2$ were used as charge carriers.

Figure 1 shows the relationship between the ionic conductivity of the polyacid-PVA-$CuCl_2$ hybrid membranes and the molar ratio of polyacid to PVA. These experimental results clearly demonstrate that the polyacid-PVA-$CuCl_2$ hybrid membranes possess higher ionic conductivity than the single polymer-$CuCl_2$ membranes, such as polyacid-$CuCl_2$ or PVA-$CuCl_2$ membrane. The ionic conductivity of the hybrid membranes is greatly influenced by the molar ratio of polymeric acid to PVA, and every curve has a maximum when the molar ratio of polymeric acid to PVA is unity. The reason is probably that the polymeric complex formed from polymeric acid and PVA has the most regular structure at this point so that the ions can move more easily, for the more regular the structure is, the more easily the ions move. It is well known that polymeric acid and PVA can form an intermacromolecular complex at a 1:1 molar ratio, which leads to the most regular structure at this molar ratio.

The influence of acid strength of the polymeric acid on the ionic conductivity of the hybrid membranes with $LiClO_4$ as the charge carrier is shown in Table 1. *The ionic conductivity increases with increasing acid strength of* the polymeric acids. This may be because, when polymeric acid is stronger, the intermacromolecular complex has a more regular structure.

Generally speaking, when the ions of inorganic salts move through polymeric complexes, an increase in their radius or charge carried will decrease the ionic conductivity. This is supported by the results shown in Tables 2 and 3. From Li to K, as the radius of the cation increases, the conductivity decreases. As for Cu^{2+}, although it has a smaller ionic radius, the ionic conductivity is still lower because Cu^{2+} carries more charge than the alkali metal ions. The ionic conductivity is also related to the dissociation energy of the inorganic salts and the mobilities of the cation and anion. The lower the dissociation energy, or the greater the mobility, the higher the ionic conductivity, and the mobility decreases with increasing mass of the ions. As shown in Table 3, $LiClO_4$ with its low dissociation energy gives higher ionic conductivity, and from Cl^- to $CO_3{}^{2-}$ the ionic conductivity decreases because

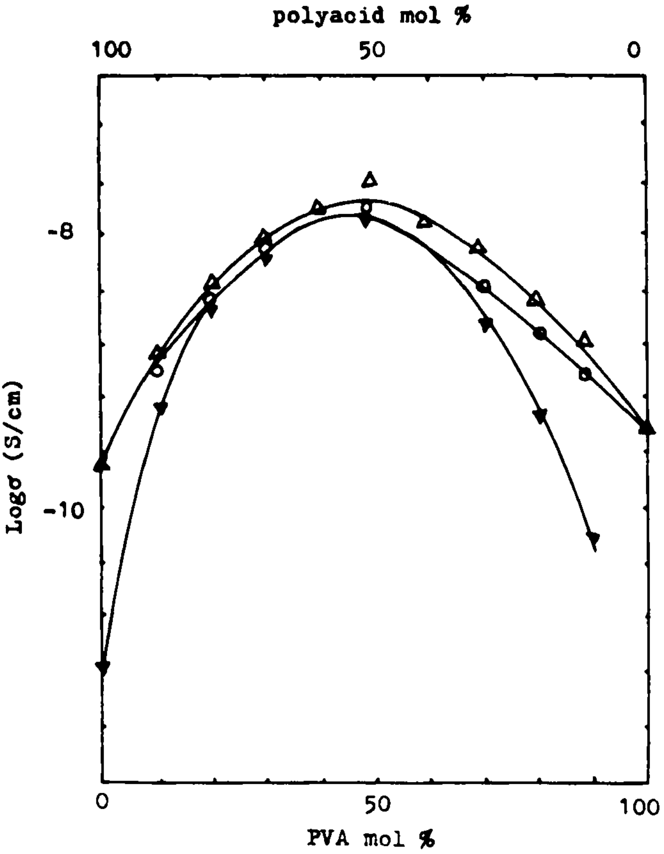


FIG. 1. Composition dependence of ionic conductivity of hybrid membranes (Cu^{2+}, 10 mol%), PSSA (△), PAA (▼), PMAA (○).

TABLE 1. Ionic Conductivity of Hybrid Membranes[a]

Composition	Conductivity $\sigma_i \times 10^8$, S/cm
PSSA-PVA-$LiClO_4$	7.63
PMAA-PVA-$LiClO_4$	4.97
PAA-PVA-$LiClO_4$	2.94

[a] Polyacid:PVA:$LiClO_4$ = 5:5:1 (mole ratio).

TABLE 2. Influence of Cations on Conductivity[a]

Cations	Conductivity $\sigma_i \times 10^8$, S/cm
$Li(Cl^-)$	5.8
$Na(Cl^-)$	1.8
$K(Cl^-)$	0.54

[a] PSSA:PVA:cation = 5:5:1 (mole ratio).

TABLE 3. Influence of Anions on Conductivity[a]

Anions	Conductivity $\sigma_i \times 10^8$, S/cm
$(Li)ClO_4^-$	7.63
$(Li)Cl^-$	5.80
$(Li)Br^-$	2.61
$(Li)I^-$	0.047
$(Li)_2CO_3^{2-}$	0.035

[a] PSSA:PVA:anion = 5:5:1 (mole ratio).

the radius of the anions increases in this order. The ionic conductivity is also influenced by the quantity of Cu^{2+} ion (Fig. 2). The highest value of the ionic conductivity is observed at about 5 mol% of Cu^{2+}.

Additives take an important part in decreasing the dissociation energy of inorganic salts, enhancing ionic conductivity and improving processability. Propylene carbonate (PC), dimethylsulfoxide (DMSO), ethylene glycol (EC), dimethylformamide (DMF), and nitrobenzene were used as additives, and the results show that the ionic conductivity increases with increasing dielectric constant of the additives (Table 4). This is mainly because the dissociation energy of $LiClO_4$ decreases with increasing dielectric constant of the additives.

The conductivity as a function of temperature is shown in Fig. 3. In the experimental temperature range, the relationship between log σ and the reciprocal of temperature is linear.

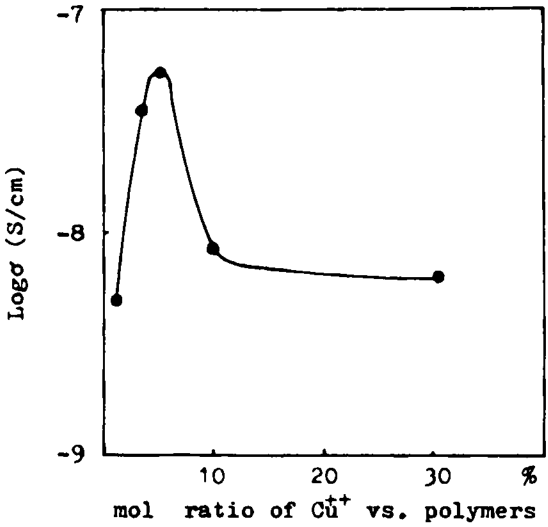
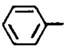


FIG. 2. Effect of the quantity of added Cu^{2+} on conductivity for the hybrid membrane PSSA-PVA-$CuCl_2$. PSSA:PVA = 1:1 (mole ratio).

TABLE 4. Effect of Additives on Conductivity[a]

Additives	Dielectric constants	Conductivity $\sigma_i \times 10^7$, S/cm
PC	64.4	8.0
DMSO	46.68	3.2
EG	38.6	2.9
DMF	36.7	2.8
—NO_2	34.8	0.66

[a] PSSA:PVA:$LiClO_4$:Additive = 5:5:1:2.5 (mole ratio).

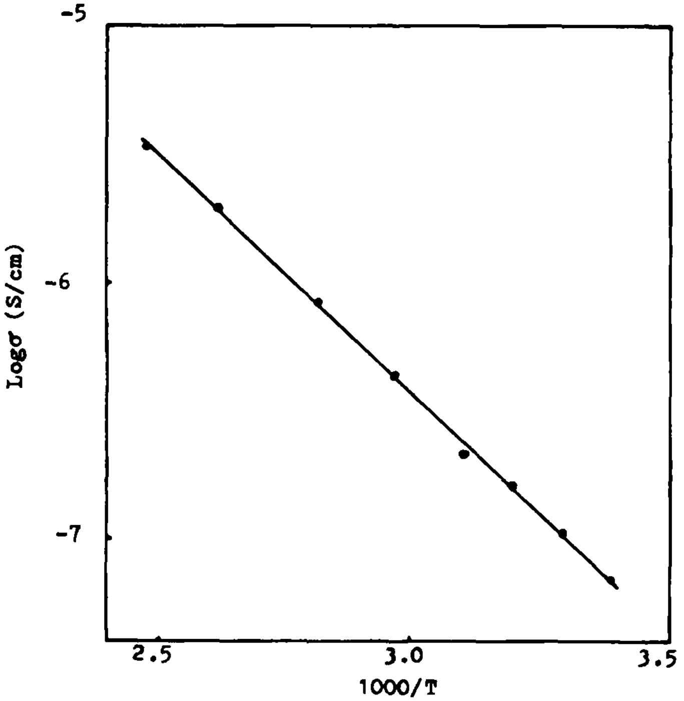


FIG. 3. Temperature dependence of the ionic conductivity of the polymeric complex membrane.

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