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Behavior of Silver–Thiourea Complexes in Nafion Resin

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Abstract

The behavior of silver–thiourea complexes in Nafion 117 resin was investigated with thiourea sorption and sodium–silver ion-exchange experiments. It was observed that the sorption of thiourea by the Ag-form of the ion exchanger was much higher than that obtained with the H- and Na-forms. The thiourea to silver molar ratio within the resin was found to be about 1.8. In the presence of thiourea, the fraction of silver species in the ion exchanger was about 20% greater than that in the absence of this ligand. The strong interaction between the silver–thiourea species and Nafion material may be attributed to the formation of an insoluble $Ag_2T_3(SO_3R)_2$ compound inside the ion exchanger.

INTRODUCTION

In recent work from this laboratory (*1*), the effects of complexation on ion transport selectivity in Nafion 117 membranes were investigated with the gold– and silver–thiourea–water systems. This was an extension of a previous investigation on the effects of ionic size and charge on the transport behavior of metal ions in Nafion membranes (*2*). It was found (*1*) that the formation of silver–thiourea complexes significantly decreased the membrane transport rate. At low metal concentrations ($\leq 5 \times 10^{-4}$ mol·dm^{-3}), the transport rate followed the order of Ag^+ > Au–thiourea complex > Ag–thiourea complex. More importantly, it was observed that under this low metal concentration, the overall transport of Ag^+ and Au–thiourea species was controlled by boundary layer diffusion while that of the Ag–thiourea species was dominated by membrane diffusion.

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It has been reported that silver–thiourea complexes are stable in both inorganic and organic ion exchangers (*3*, *4*). This suggests that there is a strong interaction between the Ag–thiourea complex ions and the ion-exchange materials. However, the physicochemical origins of this interaction are still not completely understood. The present work seeks to obtain further insight into the behavior of silver–thiourea complexes in Nafion membranes. Using Nafion resin (same material as the membrane), experiments were carried out involving the sorption of thiourea and the exchange of sodium and silver ions.

EXPERIMENTAL

Materials

Double-distilled water was used in all solution preparation. Thiourea (99%) was purchased from Pfaltz & Bauer, and it was recrystallized from ethanol and dried at 80°C. The reagent grade chemicals $AgNO_3$ and $NaNO_3$ were obtained from Fisher and were used without further purification. 1-Octanesulfonic acid, sodium form, was from Aldrich. Silver–thiourea complexes were prepared as reported previously (*1*).

Thiourea Sorption and Sodium–Silver Ion Exchange in Nafion Resin

Nafion 117 resin (60–100 mesh), which is the same material as Nafion 117 membrane, was obtained from Aldrich. The resin was initially immersed into 0.5 $mol \cdot dm^{-3}$ of the relevant nitrate solutions separately to form the desired H-form, Na-form, and Ag-form resins, then washed with distilled water several times and air-dried for 48 h.

Sorption of thiourea was investigated by introducing 200 mg treated resin (i.e., H-, Na-, or Ag-form) into 10 cm^3 solutions of thiourea of known concentration, then shaking for 48 h at room temperature. The initial and equilibrium solutions of thiourea were measured by potentiometric titration as described in detail later.

Sodium–silver ion exchange was conducted as described by Maes and Cremers (*3*). Na-form Nafion resin (200 mg) was contacted with 20 cm^3 solutions of $AgNO_3$ in the absence and presence of thiourea. In the case of silver–thiourea solution, the molar ratio of thiourea/Ag was controlled as 10:1. After 48 h shaking, the Ag and Na concentrations in the solutions were analyzed by atomic adsorption spectrophotometer (Perkin-Elmer Model 703).

Potentiometric Titration of Thiourea with Potassium Dichromate

Thiourea concentration in aqueous solution was determined by potentiometric titration with potassium dichromate in acid medium (*5*). A 5-cm^3 sample of thiourea solution was first diluted to 200 cm^3. About 40 g concentrated H_2SO_4 was added to obtain a final H_2SO_4 concentration of about 3.5 to 4.0 N (1.75 to 2.0 $mol{\cdot}dm^{-3}$). Then 100 cm^3 of the diluted solution was titrated with 0.05 N (8.33×10^{-3} $mol{\cdot}dm^{-3}$) $K_2Cr_2O_7$.

The potentiometric titration was carried out by an automatic titrator, which consists of a PHM84 pH meter, an ABU80 autoburette, and a TTT80 titrator. The potential was measured by a platinum electrode (P101, Radiometer) and a calomel reference electrode (401, Radiometer). The reaction during titration is

$$Cr_2O_7^{2-} + 6TH^+ + 8H^+ = 3FDH_2^{2+} + 2Cr^{3+} + 7H_2O \qquad (1)$$

where TH^+ and FDH_2^{2+} represent the protonated thiourea and formamidine disulfide ($NH_2CNH_2SSNH_2CNH_2^{2+}$), respectively. When the pH in the solutions is less than 1.44, thiourea is protonated (*6*). A typical titration curve is shown in Fig. 1. It can be seen that there is a sharp jump around the equivalent point (about 450 mV). As a result, the end point during automatic titration was chosen as 450 mV.

XRD Investigations

X-ray diffraction investigations were carried out in a Rigaku Geigerflex diffractometer. The accelerating potential was 40 kV and the current was 20 mA. The samples (i.e., bulk precipitate, membrane, or resin) were dried in air for 48 h before the x-ray diffraction investigation.

RESULTS AND DISCUSSION

Sorption of Thiourea in Nafion Resin

Figure 2 represents the sorption isotherms of thiourea on Nafion resin; initial thiourea concentrations are indicated. It was observed from solution analyses that the amount of leached sodium or silver ions was less than 1% of the total absorbed ions in the resin. It can be seen that the hydrogen- and sodium-forms of Nafion resin have little sorption capacity for thiourea over the concentration range of 0.01 to 0.1 $mol{\cdot}dm^{-3}$. On the other hand, a strong sorption of thiourea on the Ag-form resin can be observed. This indicates that in the absence of complex-forming metals, the molecular sorption of thiourea is relatively low. On the other hand, sorption of thiourea is greatly enhanced in the presence of relevant metals, and the

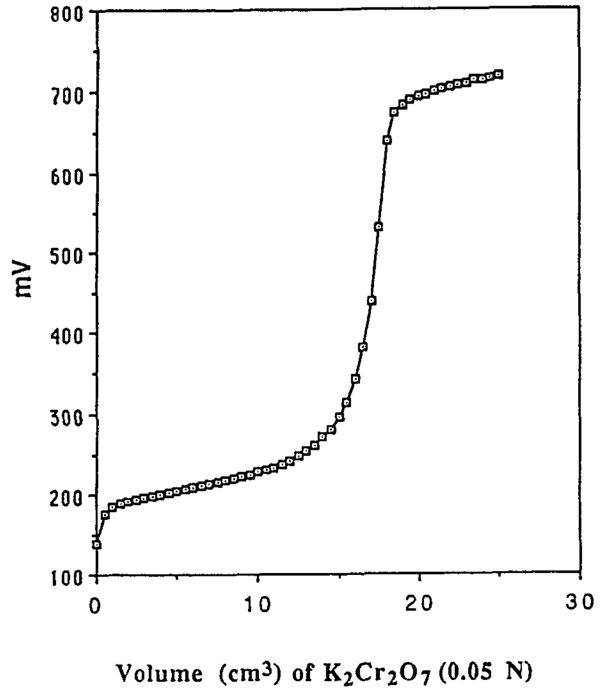

FIG. 1. Potentiometric titration curve of thiourea reaction with potassium dichromate (0.05 N).

resulting metal complexes are relatively stable in the resin as reported previously (*7*, *8*). The molar ratio of thiourea to silver ion in the resin was calculated as listed in Table 1. Under the given solution concentrations, the average molar ratio of T/Ag in the resin is about 1.8.

Sodium–Silver Ion Exchange

The interaction between the silver–thiourea complex and Nafion ion exchanger was examined by sodium–silver ion-exchange isotherms (*3*) as shown in Fig. 3. When the Na-form resin was contacted with Ag-containing solutions, Na^+ in the resin was replaced by silver ions or its complex species. The relevant reaction is

$$Ag^+ + \overline{Na^+} = \overline{Ag^+} + Na^+ \qquad (2)$$

Here a species with an overbar represents an ion in the resin. Based on Eq. (2), the equivalent fraction of silver in the resin could be measured

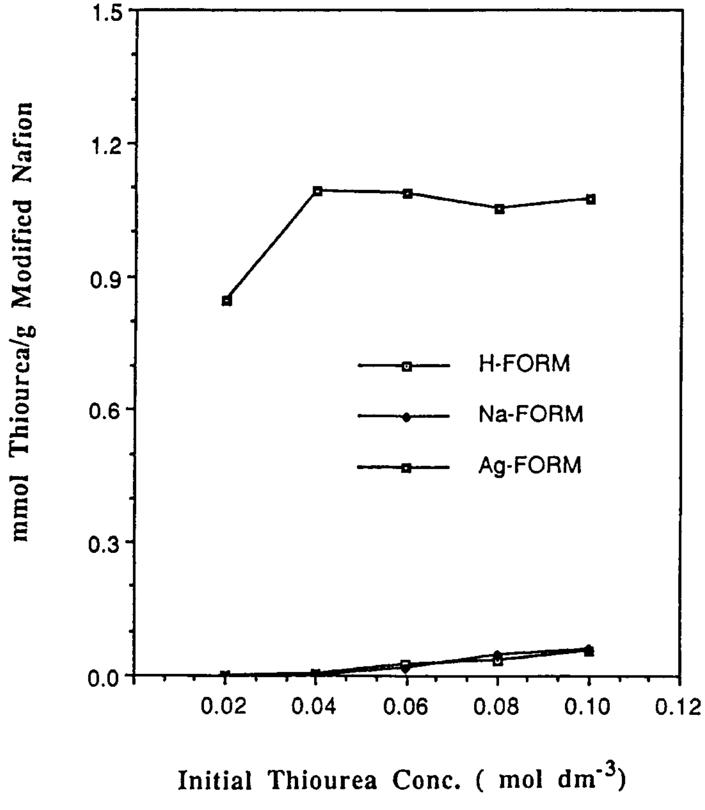

FIG. 2. Sorption isotherms of thiourea in modified Nafion resin.

TABLE 1
The Thiourea/Ag Ratio in Nafion Resin

Initial thiourea concentration in solution (mol·dm^{-3})	Thiourea absorbed in resin[a] [(mol) × 10^4]	T/Ag[b]
0.02	1.7	1.4
0.04	2.2	1.9
0.06	2.2	1.9
0.08	2.1	1.8
0.1	2.1	1.8

[a] Measured from 200 mg Nafion resin.

[b] Based on an average of 1.172 × 10^{-4} mol absorbed silver ion in 200 mg Nafion resin.

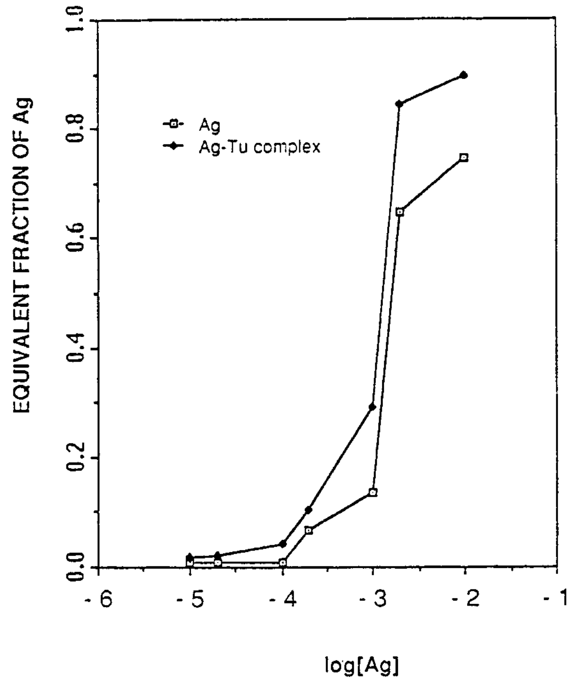

FIG. 3. Sodium–silver ion-exchange isotherms in Nafion resin in the absence and presence of thiourea; thiourea/Ag = 10:1.

through the analysis of sodium concentration in the solutions. It can be seen from Fig. 3 that in the presence of thiourea the fraction of silver in Nafion resin is about 20% higher than that in the absence of thiourea. This result demonstrates that the silver–thiourea complex ions have a higher affinity for the ion exchanger than Ag^+.

Behavior of Ag–Thiourea Complexes in Nafion Material

It is known that sulfonic acid present in Nafion membranes is a strong acid, i.e., —SO_3^- is a "hard" or "nonpolarizable" base. On the other hand, Ag^+ belongs to the "soft" or "polarizable" acid group of transition metal ions. Usually only hard acid and hard base or soft acid and soft base can form strong ion-pairs, i.e., metal ions and ligands with similar polarizabilities exhibit strong ionic interactions (*9*). Therefore, a weakly dissociated ion-pair, —$SO_3^- \cdot Ag^+$, is expected during ion-exchange processes in the absence of complexing agents as reported previously (*10*).

In the presence of complexing agents, the affinity of the silver complex for ion exchangers may be greatly enhanced. For example, it was reported that the stability of silver–ethylenediamine in the sulfonated polystyrene resin Dowex 50-W is much higher than in aqueous solutions (*11*, *12*), and a similar phenomenon was observed in the case of silver–thiourea complexes in both inorganic and organic resins (*3*, *4*). This exceptional stability of metal complexes in resins can be exploited in ligand exchange chromatography to separate chemicals such as amines (*13*).

To explain the stabilization of metal complex species in ion exchangers, Suryaraman and Walton (*12*) suggested that this behavior is due to the formation of polynuclear complexes or polymer chains in the ion exchanger. In the present work, it was observed that when 0.05 mol·dm^{-3} 1-octanesulfonic acid, sodium form ($CH_3(CH_2)_7SO_3Na$), solution (pH 5.3) was slowly dropped into a solution which contained 0.025 mol·dm^{-3} $AgNO_3$ and 0.25 mol·dm^{-3} thiourea, a white precipitate appeared gradually. X-ray diffraction investigation revealed that this precipitate is amorphous. It is known that at high silver concentrations, silver–thiourea complex species in H_2SO_4 medium can form stable solid species such as $(Ag_2T_3)SO_4$ and/or $(Ag_2T_6)SO_4$ (*14*, *16*). Therefore, it is possible that in the presence of $—SO_3^-$ groups of the membrane, solid species such as $Ag_2T_3(SO_3R)_2$ or $Ag_2T_6(SO_3R)_2$ (where R represents the organic matrix) can be formed. In the case of the Nafion ion-exchange resin used in the present investigation, the presence of a precipitate could not be verified with the naked eye. However, a piece of Nafion 117 membrane (4 × 2 cm^2), immersed in a solution containing 0.025 mol·dm^{-3} $AgNO_3$ and 0.25 mol·dm^{-3} thiourea for 48 h, developed a visible precipitate. X-ray diffraction investigation indicated that the precipitate inside the membrane was also in an amorphous state. Based on the Ag/thiourea ratio obtained from Table 1, this white precipitate is probably mainly due to the formation of the polynuclear species $Ag_2T_3(SO_3R)_2$. As a result, both the strong thiourea sorption on the Ag-form resin (Fig. 2) as well as the slow transport rate through the membrane (*1*) may be attributed to strong interaction between silver–thiourea complexes and the sulfonate groups in the ionic clusters of the membrane, with possible formation of insoluble silver–thiourea–sulfonate complexes. Thus when ion exchangers containing $—SO_3^-$ groups are used to recover silver ions from thiourea solutions, the elution of silver–thiourea species from the ion exchangers may be difficult.

CONCLUSIONS

Thiourea sorption and sodium–silver ion-exchange experiments reveal that Ag–thiourea complexes are relatively stable in Nafion materials. This stabilization is attributable to the formation of the polynuclear complex species $Ag_2T_3(SO_3R)_2$ in the resin. The slow transport rate of silver–thiourea complexes through a Nafion membrane is most likely due to the formation of this insoluble compound.

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