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## THE IMMOBILIZATION OF IONIC AND NEUTRAL CROWN ETHER DYES TO SPECIFIC ANIONIC POLYMER MEMBRANE USED AS A CHEMICAL SENSOR FOR THE DETERMINATION OF METAL IONS

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**Key Words:** Crown Ether Dyes, Sulfonated Block Copolymer, Polymer Swelling-Shrinking, Immobilization, Metal-Ion Complexation, Ion Determination

### ABSTRACT

In the present study, a neutral crown ether dye (NCED), [4-Nitrophenyl)(4-(4,7,10,13,16-pentaoxa-1azacyclooctadecyl)phenyl] diazen and an ionic crown ether dye (ICED), 1-Methyl-{2-[4-(4,7,10,13,16-pentaoxa-1azacyclooctadecyl)phenyl]ethenyl}pyridinium-iodide were synthesized and immobilized on sulfonated hydrocarbon-based block copolymer ionomer to determine  $Ba^{2+}$  and  $Cu^{2+}$  ions in aqueous solution.  $5.0 \times 10^{-2}$  M ion solutions were used since the best absorbance increase was obtained with this concentration. The increases in absorbances after treating the NCED-immobilized thick polymer membranes (0.20 mm thickness) with  $Ba^{2+}$  and  $Cu^{2+}$  solutions were 0.1488 and 0.2446 in 120 minutes, respectively. The absorbance increases were 0.1664 and 0.3710 during the same time-interval with ICED-immobilized membranes.

The response time decreased and absorbance values increased when thin polymer membranes (0.04 mm thickness) were used. The absorbance increases were 0.5088 and 0.8761, respectively in one minute with the ICED-immobilized thin membranes. These results are in agreement with shrinking in polymer dimensions. Dye-immobilized polymeric membranes can be used as sensors practically for both of the ions but sensitivity is higher towards  $\text{Cu}^{2+}$  ions.

## INTRODUCTION

Dye indicator chemistry has been the almost widely used analytical technique for decades due to the fact that dye indicator reactions as well as dye coupled reactions are potentially available for almost any measurement [1]. Ion-selective chromogenic reagents, alone or with masking agents have been used for colorimetric determination of most commonly found metal ions. Of these, the most recent and the most promising ones are the crown ether dyes [2] which are crown ethers that have added ion-selective chromophoric functional groups within the molecule. They are, however, still in the developmental stage and receive practical significance for the determination of metal ions. Yet a substantial number and variety have been developed for a range of applications [3].

Since these dyes bring about specific color changes when they interact with ions, they can serve as selective photometric reagents and can be used in making chemical sensors or probes. The chromophoric groups can be ionic with one or two dissociable protons or can be non-ionic. There has been considerable interest in chemical sensors consisting of immobilized indicator dyes coupled to a spectrometer through fiber optics to determine alkali, alkaline earth and metal ions. A variety of methods for immobilizing indicator dyes and attaching them to optical fibers can be used [4-14]. Ionomer films are useful as hosts for various dyes since dyes can be readily bound via coulombic interactions, with the binding being assisted by hydrophobic interactions [12-14].

The aim of this study was to develop new fiber-optic chemical sensors based on polymer swelling and absorbance measurements for metal ions using a new ionomer host which has been developed as a proton-conducting membrane for fuel cell technology [15].

For this purpose, two dyes with ion-selective crown ether systems have been synthesized. The complexation of these crown ether dyes with cations influences the ground and excited states of the chromophore to a different extent. A neutral crown ether dye (NCED), (4-Nitrophenyl)[4-(4,7,10,13,16-pantaoxa-1-aza-

cyclooctadecyl)phenyl] diazen and an ionic crown ether dye (ICED), 1-Methyl-{2-[4-(4,7,10,13,16-pentaoxa-1-azacyclooctadecyl)phenyl]ethenyl}pyridinium iodide were successfully immobilized on sulfonated hydrocarbon-based block copolymer ionomer.

Our novel idea was to use these crown ether compounds in fiber optic chemical sensors based on polymer swelling, and to evaluate their feasibility both in terms of economic benefits as well as facilitation of sensor measurements.

## EXPERIMENTAL

### Materials

The crown ether dyes, NCED and ICED were synthesized using a method reported previously [16].  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) of NCED,  $\delta$  from TMS: 8.33 (d, 2H, arom. CH ortho to  $-\text{NO}_2$ ), 7.91 (d, 2H, arom. CH meta to  $-\text{NO}_2$ ), 7.85 (d, 2H, arom. CH meta to  $-\text{NCH}_2$ ), 6.90 (d, 2H, arom. CH ortho to  $-\text{NCH}_2$ ), 3.58-3.82 (m, 24H,  $\text{CH}_2\text{O}$  and  $\text{CH}_2\text{N}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) of ICED,  $\delta$  from TMS: 8.70 (d, 2H, arom. CH ortho to  $-\text{N}^+\text{CH}_3$ ), 7.85 (d, 2H, arom. CH meta to  $-\text{NCH}_2$ ), 6.90 (d, 2H, arom. CH ortho to  $-\text{NCH}_2$ ), 6.65 (d, 2H, arom. CH meta to  $-\text{N}^+\text{CH}_3$ ).

The sulfonated block copolymer was a gift from the Dais Corp., Palm Harbor, FL.

### Methods

Each of the synthesized dyes, NCED and ICED, were immobilized on two polymeric membranes with thicknesses of 0.04 mm and 0.20 mm. After immobilization, the membranes were used for the determination of  $\text{Ba}^{2+}$  and  $\text{Cu}^{2+}$  ions. Two approaches were used for these determinations:

1. The determination of swelling-shrinking amounts by measuring the surface area of the membrane (triangular-shaped polymer samples were used in all the experiments and swelling-shrinking amounts were measured by a ruler for area calculations),

2. The absorbance measurements of the membranes after treatments in different solutions.

### Immobilization of the Dyes and Determination of Ions

The triangular shaped polymer membranes were soaked in 0.03 M NaOH solution and stirred for an hour where they were swollen. These swollen polymers were soaked in pure water and stirred for half an hour. Any change was not

observed in the polymer dimensions. The same membranes above were soaked in the dye solution and stirred for a while and shrinking was observed. These shrunk polymers were soaked in ion solutions which were being determined ( $\text{Cu}^{2+}$  or  $\text{Ba}^{2+}$  ion solutions) and stirred for a while again and more shrinking in polymer dimensions were observed.

### Reagents

Tridistilled water was used in all experiments. A 0.03 N NaOH solution was used. Barium thiocyanate trihydrate and copper (II) nitrate trihydrate, used in complexation with NCED and ICED, were of reagent quality. Solutions of  $\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were used as the sources of Ba (II) and Cu (II) ions, respectively.

### Apparatus

A miniature fiber-optic spectrometer (Ocean Optics SD 1000) connected to an IBM compatible computer, employing a software called 'Spectra-Scope' has been used for the processing of absorbance measurements.

## RESULTS AND DISCUSSION

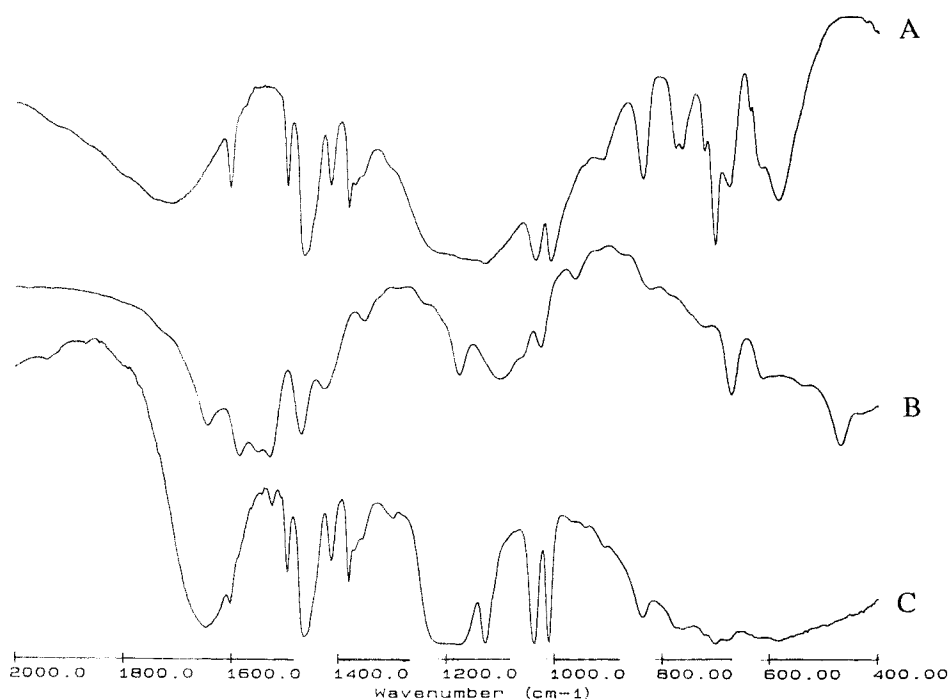
In this study, ionic and neutral crown ether dyes, NCED and ICED, were immobilized to polymer membrane (film) and they were successfully used for  $\text{Cu}^{2+}$  and  $\text{Ba}^{2+}$  ion determinations ([17, 18]).

When the polymer membrane was soaked in NaOH solution,  $\text{H}^+$  of sulfonate groups of the polymer were exchanged with  $\text{Na}^+$  ions and an increase in polymer dimensions were observed. Thus, swelling of thin membrane (173%) was higher than thick membrane (133%). Polymer samples were then soaked in distilled water and no change in polymer dimensions were observed.

In literature, the first step of the synthesis of NCED and ICED were common for both of the dyes and included the reaction between N,N-bis(2-hydroxyethyl)aniline (1) and 1,11-dichloro-3,6,9-trioxaundecan (2a) to give compound 3. We have synthesized compound 3 both by using 2a or tetraethylene glycol di-p-toluene sulfonate (2b) and observed a higher yield when 2b was reacted with compound 1. The yield of the reaction corresponded to 32.5% reported in the literature and our yield was almost the same by using 2a and 96% by using 2b. Also, the product was approximately 90% or greater in purity by  $^1\text{H-NMR}$  by using 2b.

ICED and NCED solutions in water were prepared for the immobilization of the dyes to polymer membranes, where 1:1 mole ratios of dye to  $-SO_3H$  group content of the polymer membranes were used. Measured samples of polymer membrane were immersed in dye solutions and the dye uptake was carried out while stirring at room temperature. ICED was immobilized to the membrane in 30 minutes, whereas, 80 minutes was necessary for the immobilization of NCED to the membrane to get reasonable absorbance values. In order to avoid future leakage of the dye during complexation with ions, the membranes were held in distilled water for half an hour while stirring. There was no leakage in any of the adsorption media which suggested that the washing procedure was quite satisfactory for the removal of physically adsorbed ICED or NCED molecules from the polymer membrane. The binding of ICED with the polymer is expected to be primarily via coulombic interactions as the sulfonated block copolymer is a cation exchanger. NCED does not bear a group and thus the binding is expected to be weaker and principally via hydrophobic interactions. The orange color of ICED-immobilized and the light red color of NCED-immobilized polymer membranes clearly indicate the presence of dyes in the polymer membranes. FTIR spectroscopy was also used to show the incorporation of NCED and ICED within the polymer membranes. Figure 1 shows the FTIR spectra of the plain and the derivatized polymer membranes, with ICED itself for comparison. The band observed at  $1520\text{ cm}^{-1}$  indicated aliphatic  $C=C$  stretching of ICED, as also seen on the structure of ICED. In case of NCED incorporation within the polymer membrane, the characteristic bands of NCED were overlapped with the bands of polymer membrane. Since the vibrational characteristics of  $C-O-C$  system in ethers would not be expected to differ greatly from  $C-C-C$  system, the responses to  $C-O-C$  stretching of ether group of the dyes and  $C-C-C$  of polymer structure are in the same general region ( $1240\text{ cm}^{-1}$ - $1100\text{ cm}^{-1}$ ). A sharp band which appeared at  $1131\text{ cm}^{-1}$  after the immobilization of NCED or ICED to the polymer membrane belong to asymmetrical  $C-O-C$  stretching vibration of the crown ether group. The broad band at  $1715\text{ cm}^{-1}$  in FTIR spectra of the polymer membrane is the combination or overtone band indicative of substituted aromatics. The large decrease in the frequency (to  $1643\text{ cm}^{-1}$ ) and the increase in the intensity of this absorption band in both NCED and ICED-immobilized polymer membrane spectra are due to the dyes as they have aromatic groups.

The uptake of dyes by polymer membranes caused shrinking in the polymer dimensions. The amount of shrinking was higher for NCED-immobilization and it was always the same even when different polymer samples were subjected to immobilization with the dyes. The results are given in Table 1.

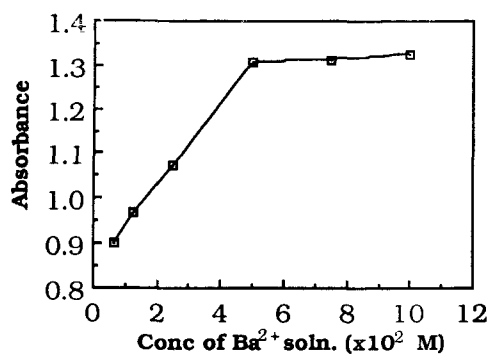


**Figure 1.** FTIR spectra: (A) Plain polymer membrane; (B) ICED; (C) ICED-immobilized polymer membrane.

In recent literature, complexations of these dyes with metal ions in organic solvents, free from water, have been reported. It was claimed that, on variation of the crown ether ring width, the expected selective complexation occurred with added alkali and alkaline earth metal ions, which led to widely varying shifts or changes in intensity of the absorption bands where concentrations of ligand-salt were  $<1:10$ . In our study, ICED solution was prepared with a 1:1 methanol-water solvent mixture. During immobilization much smaller amounts of dyes were used up. After the dye-uptake was realized the membranes (thickness is 0.20 mm) were placed in  $\text{Ba}^{2+}$  or  $\text{Cu}^{2+}$  ion solutions for complex formation and stirred for 2 hours at room temperature. The calibration curve for the complexation of  $\text{Ba}^{2+}$  ion with the ICED-immobilized thin membrane is given in Figure 2. The best absorbance increase was obtained by  $5.0 \times 10^{-2}$  M  $\text{Ba}^{2+}$  ion solution, thus, all the complexation experiments were realized by using the same concentration. In water solutions, no significant shift in wavelength was observed but increases in the intensity of the absorption

TABLE 1. The Comparison of the Properties of ICED- and NCED-Immobilized Polymer Films

Properties	Thick Film		Thin Film
	ICED	NCED	ICED
Immobilization Type	Coulombic interactions	Hydrophobic interactions	Coulombic interactions
Immobilization Time	30 min	80 min	10 min
Wavelength	462	479.9	462
Absorption in ionic soln.	Increases	Increases	Increases
Operational stability of the film	High	High	High
Shrinking in dye	85.9% (in 30 min)	90.0% (in 80 min)	93.0% (in 10 min)
Shrinking in Ba <sup>2+</sup> soln.	76.7% (in 2 h)	84.7% (in 2 h)	86.7% (in 1 min)
Shrinking in Cu <sup>2+</sup> soln.	83.3% (in 2 h)	91.0% (in 2 h)	93.8% (in 1 min)



**Figure 2.** Calibration curve for the complexation of Ba<sup>2+</sup> ion with the ICED-immobilized thin polymer membrane.



TABLE 2. Adsorption Characteristics of NCED- and ICED-Immobilized Thick and Thin Polymer

Thick Films				Thin Films		
Complexing ion	t <sup>a</sup> (min)	ΔA <sub>NCED</sub> <sup>b</sup>	ΔA <sub>ICED</sub> <sup>c</sup>	Complexing ion	t <sup>a</sup> (min)	ΔA <sub>ICED</sub> <sup>d</sup>
Ba <sup>2+</sup>	120	0.1488	0.1664	Ba <sup>2+</sup>	1	0.5088
					5	0.7609
	240	0.3547	0.3906		15	0.8710
Cu <sup>2+</sup>	5	0.0223	—	Cu <sup>2+</sup>	1	0.8761
					5	1.1918
	30	0.0667	—		15	1.1920
	60	0.1242	—			
	120	0.2446	0.3710			
	240	0.4175	0.4393			

a: Complexation time of the dye-immobilized thick or thin polymer membranes

b: Absorbance increases of NCED-immobilized thick polymer membranes during complexations at the given time intervals (Immobilization Time: 80 min, λ<sub>max</sub>: 479.9 nm)

c: Absorbance increases of ICED-immobilized thick polymer membranes during complexations at the given time intervals (Immobilization Time: 30 min, λ<sub>max</sub>: 462.0 nm)

d: Absorbance increases of ICED-immobilized thin polymer membranes during complexations at the given time intervals (Immobilization Time: 10 min, λ<sub>max</sub>: 462.0 nm)

bands and shrinking in polymer dimensions were detected. The shrinking percentages and the absorbance data are given in Table 1 and 2, respectively. In FTIR spectra, C-O-C stretching bands of the crown ether group are shifted to lower frequencies (longer wavelengths) because of resonance after treatment of the dye-immobilized polymer membranes with Ba<sup>2+</sup> and Cu<sup>2+</sup> ion solutions upon complex formation. A broad band appeared between 1235 cm<sup>-1</sup> and 1172 cm<sup>-1</sup> in ICED-immobilized polymer membrane spectrum near a sharp band at 1129 cm<sup>-1</sup> which

also belongs to the ether stretching frequency. These bands are shifted between 1215  $\text{cm}^{-1}$  and 1159  $\text{cm}^{-1}$  after complexation with  $\text{Cu}^{2+}$  ions, together with the shift to 1124  $\text{cm}^{-1}$  of the sharp band. Besides the shifts of C-O-C stretching vibrations, the characteristic band of  $\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$  at 2066  $\text{cm}^{-1}$  appeared at 2059  $\text{cm}^{-1}$  in the complex spectrum. Metal alkoxides,  $\text{M}(\text{OR})_n$  (R, alkyl group), exhibit the M-O stretching below 650  $\text{cm}^{-1}$ , in general. The significant cumulated bands appeared below 700  $\text{cm}^{-1}$  after complexation with  $\text{Ba}^{2+}$  and  $\text{Cu}^{2+}$  ions are due to metal-oxygen stretching vibrations.

It is quite interesting to note that the complexation capacities of both ICED and NCED-immobilized polymer membranes for  $\text{Cu}^{2+}$  ions were higher than that for  $\text{Ba}^{2+}$  ions since higher increases in absorbance values under the same reaction conditions were obtained in  $\text{Cu}^{2+}$  ion solution. The complexation of dye-immobilized polymer membranes with  $\text{Cu}^{2+}$  or  $\text{Ba}^{2+}$  ions caused more shrinking. The amount of shrinking for  $\text{Cu}^{2+}$  ions was higher than the shrinking for  $\text{Ba}^{2+}$  ions for both NCED and ICED-immobilized membranes. The leakage of ICED from the polymer membrane during complexation with the ions implies that these ions interact with ICED-immobilized polymer membrane not only through the crown ether group by complexation, but also through  $\text{SO}_3^-$  groups of the polymer membrane by cation exchange at that medium. No leakage was observed during complexation of  $\text{Ba}^{2+}$  or  $\text{Cu}^{2+}$  ions with NCED-immobilized polymer membranes.

Thin membranes (0.04 mm thickness) were prepared and used for both absorbance and swelling-shrinking measurements to decrease the response time of complexation of the dye-immobilized polymer membranes with  $\text{Cu}^{2+}$  and  $\text{Ba}^{2+}$  ions. A significant absorbance was obtained in 1 minute when ICED-immobilized thin membrane was used. The degree of NCED-immobilization to thin membrane was not enough to get reasonable absorbance. When swelling-shrinking amounts of thick and thin membranes were compared, thin membranes had higher swelling-shrinking values. The swelling-shrinking amounts of the thin membrane are compared to that of the thick membrane in Table 1. The absorbance data of the thin membrane is given in Table 2.

When absorbance data of the thick and thin membranes were compared, the absorbance increases ( $\Delta A$ ) of thick membranes became larger after 120 minutes of complexations with both  $\text{Ba}^{2+}$  and  $\text{Cu}^{2+}$  ions, which implies that the complexations were not completed but for thin membranes the absorbance increases ( $\Delta A$ ) became smaller after 1 minute of complexations.

## CONCLUSION

From the data presented here, it can be concluded that NCED and ICED-immobilized polystyrene block copolymer membranes may effectively (means with high absorption rates and rapid swelling-shrinking properties) be used for the determination of  $\text{Cu}^{2+}$  and  $\text{Ba}^{2+}$  ions from aqueous solutions. The dye-immobilized polymer membrane used as a fiber-optic sensor is much smaller and more convenient to handle compared with a spectrophotometric assay using cuvettes. Our method is capable of continuous, low cost *in situ* measurement of metal ions, although there are certainly other methods that are capable of measuring high concentrations of metal ions. Our future studies will be focused on the regeneration of the dye-immobilized polymer membranes, pH of the medium, response time, detection limit, interference studies and determination of other ions (e. g. ,  $\text{Ni}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ).

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