THIOCYANATE-SELECTIVE ELECTRODE BY USE OF URUSHI AS THE MEMBRANE MATRIX

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A thiocyanate-selective electrode prepared from a new matrix, Urushi, and tri-*n*-octylmethylammonium thiocyanate ion exchanger is described. The electrode shows linear potential-activity curve with-in the range 1.0×10^{-5} – 0.56×10^0 mol dm⁻³ ammonium thiocyanate and the slope is about 59mV per decade change in thiocyanate activity. The electrode has a fast response. Conditions for the preparation of the electrode such as ratio of the liquid ion exchanger and Urushi, amount of water in the Urushi and temperature for hardening the membrane are studied. The electrode characteristics of pH dependence and selectivity coefficient are also examined. The Urushi matrix membrane is hard, lustrous and smooth.

1 Introduction

Urushi is a natural oriental lacquer and is used for lacquer-ware. It is well known that Urushi lacquer has excellent durability and mechanical strength. For this reason, the authors examined the use of Urushi as a matrix for ion-selective electrodes. An iodide-selective electrode based on Urushi and powdered silver iodide has already been described¹⁾. Not only powdered materials but also liquid ion exchangers can be used as the electro-active material. And solidification of ion-selective liquid membranes is possible when Urushi is used as a matrix for the electrodes. Then, perchlorate-selective²⁾ and nitrate-selective electrodes³⁾ have been developed from Urushi and tri-*n*-octylmethylammonium perchlorate and nitrate liquid ion exchangers.

On the other hand, several thiocyanate-selective liquid membrane electrodes were studied⁴⁾⁻⁸⁾. In this work, a new thiocyanate-selective electrode was prepared by using Urushi as the membrane matrix for obtaining more rigid, durable and easy to handle thiocyanate electrode, and the performance of the electrode was studied.

2 Experimental

2.1 Apparatus

The measurements of the electrode potential were made with a Orion Model 801/ Digital pH Ion Analyzer. Orion double junction reference electrode, Model 90-01 was used. The resistance of the electrode membrane was measured with a Toa Electronics Super Megohmmeter, Model SM-15.

2.2 Chemicals

Several kinds of Urushi were obtained from Saito Co. Ltd. and Nishizawa Urushi Co. Ltd. Acetone powder which was undissolved part obtained by treating Urushi

with acetone, was purchased from Saito Co. Ltd. Synthetic Urushiol made by Mitsubishi Yuka Co. Ltd. was also used. The tri-*n*-octylmethylammonium chloride (Capriquat, Dojindo Laboratories Co. Ltd.) was converted to the thiocyanate form by shaking its solution in chloroform (10g in 40g) with three 40ml aliquots of 0.1 mol dm^{-3} ammonium thiocyanate (analytical-reagent grade, Wako Pure Chemical Industries Co. Ltd.). The chloroform was removed by evaporation over a period of three days from a beaker covered with a watch glass, after the extract has been passed through a dry filter paper into the beaker.

Other chemicals were all analytical reagent grade.

2.3 Construction of Urushi membrane electrode

The thiocyanate ion exchanger was mixed in different portions with Urushi latex on a watch glass of 6cm in diameter. The mixture was coated on the copper internal contact of the electrode body (12mm in diameter, 120mm in length). After coating the mixture was hardened in air at 20-35°C (80% relative humidity). The mixture required 5-15d. for complete hardening. The hardening was also possible at 130-150°C. The complete hardening was attained within 5-7hr at the higher temperature. Details of the construction of the electrode and the structure of the electrode were the same as already reported³⁾.

2.4 Measurement of the potential

Potential of the electrodes vs. the reference electrode were measured at 25.0 $\pm$ 0.1°C. The solution was stirred with a magnetic stirrer. Before use, each electrode was soaked for 2-3hr in $10^{-2} \text{ mol dm}^{-3}$ ammonium thiocyanate solution. From the concentration of thiocyanate solution, activity of thiocyanate ion was calculated.

3 Results and Discussion

3.1 Potential-activity curves

When 45 parts of the tri-*n*-octylmethylammonium thiocyanate ion exchanger and 55 parts of Ise Urushi were mixed and hardened in air at 20-35°C (80% relative humidity), the electrode showed a linear potential-activity curve within the range 1.0×10^{-5} - $0.56 \times 10^{-3} \text{ mol dm}^{-3}$ ammonium thiocyanate. The slope was about 52mV per decade change in thiocyanate activity. By changing the weight ratio of the ion exchanger and Urushi various electrodes were prepared and measured the slope of the potential-activity curve. Three kinds of Urushi, Ise, Tikkei and Sugurome, were compared. The results were shown in Table 1.

Table 1 Effect of ratio of tri-*n*-octylmethylammonium thiocyanate ion exchanger and Urushi on slope of potential-activity curve.

Weight ratio of ion exchanger and Urushi	Slope of potential-activity curve (mV/decade)		
	Ise Urushi	Tikkei Urushi	Sugurome Urushi
40:60	48	52	49
45:55	52	56	50
50:50	58	59	57

As shown in Table 1, when 50 parts of ion exchanger and 50 parts of Tikkei Urushi were mixed, highest slope (59mV) of the potential-activity curve was observed. In this case, the detection limit as defined by a potential difference of 18mV between the potential-activity curve and the extrapolated linear section was $6 \times 10^{-6} \text{ mol dm}^{-3}$. Thus, the response of the proposed electrode was near-Nernstian, it was found that Urushi could be used as a membrane matrix for the thiocyanate-selective electrode. When the membranes were prepared from 55 parts of ion exchanger, they did not harden properly. The best amount of ion exchanger was therefore 50 parts. No difference was found in the linear range (1.0×10^{-5} – $0.56 \times 10^0 \text{ mol dm}^{-3}$) of the electrode responses among these electrodes. By changing the amount of the mixture of the ion exchanger and Urushi applied to the electrode body 2 groups of electrode having different thickness of the membrane were prepared. No large difference in the electrode characteristics was observed between membranes of 0.25 mm and 0.15mm in thickness.

3.2 Hardening conditions

The hardening of Urushi is proceeded under either condition, i.e. at 20–30°C (80% relative humidity) or 100–150°C. For comparing both hardening conditions, 50 parts of tri-*n*-octylmethylammonium thiocyanate ion exchanger and 50 parts of Tikkei Urushi were mixed and the mixture was hardened at 20–35°C (80% relative humidity), 100, 130 and 150°C and prepared the electrodes. The electrode characteristics were shown in Table 2.

Table 2 Effect of hardening condition on electrode characteristics.

Hardening		Potential-activity curve	
Temperature (°C)	Time for complete hardening (hr)	Linear range (mol dm^{-3})	Slope (mV/decade)
20–35	7 (d.)	1.0×10^{-5} – 0.56×10^0	59
100	24	1.0×10^{-5} – 0.56×10^0	53
130	7	1.0×10^{-5} – 0.56×10^0	54
150	5	1.0×10^{-5} – 0.56×10^0	53

When the membranes were prepared at higher temperatures the potential-activity curves were linear within the activity range 1.0×10^{-5} – 0.56×10^0 though the slope was reduced to 53–54mV per decade. However, hardening of the membranes was attained within much shorter period (5–7hr) when they were hardened at 130–150°C.

3.3 Electrodes prepared from other ion exchangers

When 50 parts of tri-*n*-dodecylmethylammonium thiocyanate or tri-*n*-octylpropylammonium thiocyanate was used as the ion exchanger instead of tri-*n*-octylmethylammonium thiocyanate with 50 parts of Tikkei Urushi, almost identical linear potential-activity curves were obtained. The slopes of the linear part of the potential-activity curves were 60 mV per decade change in thiocyanate activity in both cases of tri-*n*-dodecylmethyl- and tri-*n*-octylpropyl-ammonium thiocyanate ion exchangers.

Several pyridinium compounds such as 1-*p*-dodecylbenzyl-4-methylpyridinium thiocyanate, 1-dodecyl-4-(3-phenylpropyl)-pyridinium thiocyanate, 1-hexadecyl-4-

(5-nonyl)-pyridinium thiocyanate and 1-octadecyl-4-methylpyridinium thiocyanate were also used as the ion exchanger. These electrodes did not show improved characteristics.

3.4 Effect of composition of Urushi on the electrode characteristics

The components of Urushi are Urushiol (60-80w/w%), water (10-30w/w%), rubbery substances (7-8w/w%), nitrogen compounds (2-3w/w%) and laccase, an oxidizing enzyme⁹⁾. When Urushi is treated with acetone, Urushiol is dissolved in acetone. By separating the undissolved other components and removing acetone, white powder, called acetone powder, is obtained. The hardening process of Urushi comprises a series of reaction, i.e. the enzyme quinone formation catalyzed by laccase and the subsequent non-enzymic coupling reaction of quinone with the unsaturated side chains or nucleus of Urushiol catalyzed by water give ligomeric materials¹⁰⁾.

Therefore, when the acetone powder is added to Urushi, the hardening of Urushi is supposed to be attained within shorter period. Then, various amounts of acetone powder were added to Tikkei Urushi and mixed with tri-*n*-octylmethylammonium thiocyanate ion exchanger and prepared electrodes. The weight ratio of Urushi and ion exchanger was kept at 50:50. And the time required for the complete hardening of the mixture was measured. The electrode characteristics were also measured.

On the other hand, synthetic Urushiol can be obtained. Therefore, it is considered that a mixture of the synthetic Urushiol and acetone powder could be used instead of natural Urushi. Then, some electrodes were prepared from mixtures of synthetic Urushiol and various amounts of acetone powder, water and tri-*n*-octylmethylammonium thiocyanate ion exchanger. And response of the electrodes was measured. The Weight ratio of Urushiol:water:ion exchanger was kept at 45:10:45. The results were shown in Table 3.

Table 3 Effect of acetone powder on electrode characteristics.

Content of acetone powder in whole mixture (w/w%)	Time for complete hardening (d.)	Potential-activity curve	
		Linear range (mol dm ⁻³)	Slope (mV/decade)
0.0	5	1.0x10 ⁻⁵ -0.56x10 ⁰	59
0.8	5	0.99x10 ⁻⁴ -0.56x10 ⁰	58
5.0	5	0.99x10 ⁻⁴ -0.56x10 ⁰	49
9.4	5	0.99x10 ⁻⁴ -0.56x10 ⁰	44
0.4	18	0.99x10 ⁻⁴ -0.56x10 ⁰	56*
4.4	18	0.99x10 ⁻⁴ -0.56x10 ⁰	28*

*Electrodes prepared from synthetic Urushiol.

As shown in Table 3, the time required for the complete hardening of the electrode membrane prepared from mixtures of Tikkei Urushi and acetone powder was the same as that without acetone powder. As the content of acetone powder increased the slope of the potential-activity curve decreased. Electrodes prepared from the mixtures of Urushiol and acetone powder did not show improved chracte-

ristics.

Another component which acts as a catalyst for the hardening process of Urushi is considered to be water. Then, 0.5g of Ise Urushi was transferred into a watch glass. The watch glass was left in a silica gel desiccator and the Urushi was dehydrated until it reached to a constant weight. From the weight loss of the Urushi, it was found that the water content in the Ise Urushi was 25.6w/w%. The dehydrated Urushi and known amount of water were mixed. From 50 parts of the mixture and 50 parts of tri-*n*-octylmethylammonium thiocyanate ion exchanger, several electrodes were prepared and their characteristics were measured. The results were shown in Table 4.

Table 4 Effect of water content on electrode characteristics.

Water content in Urushi- water mixture (w/w%)	Time for complete hardening (d.)	Resistance (Megohm)	Potential-activity curve		
			Linear range (mol dm ⁻³)	Slope (mV/decade)	Drift after 5d. (mV)
0.0	10	1 -4	1.0×10^{-5} - 0.56×10^0	58	-10
1.5	8	0.1-2	1.0×10^{-5} - 0.56×10^0	58	- 5
3.5	8	0.1-2	1.0×10^{-5} - 0.56×10^0	58	- 5
6.3	8	0.1-2	1.0×10^{-5} - 0.56×10^0	58	+10
15.2	7	0 -0.5	1.0×10^{-5} - 0.56×10^0	58	+14
31.0	7	0 -0.5	1.0×10^{-5} - 0.56×10^0	58	+10
35.4	7	0 -0.1	1.0×10^{-5} - 0.56×10^0	58	+33

From Table 4, as the water content in Urushi increased the time required for complete hardening decreased. It was found that water accelerated the hardening process of Urushi. No difference was observed among the characteristics of these electrodes. After measuring the potential-activity curves, the electrodes allowed to stand 5d. in air. And potential-activity curves were measured again. The potential differences between averages of the first and the second measurements for each 0.75×10^{-1} , 0.90×10^{-2} , 0.96×10^{-3} and 0.99×10^{-4} mol dm⁻³ of thiocyanate activity, were listed in the last column of the Table 4. When the water content in Urushi-water mixture was 1.5 or 3.5w/w%, minimum potential drift (-5mV) was observed. Resistances of the electrodes measured by immersing electrodes in 1 mol dm⁻³ sodium chloride solution were also listed in Table 4. Resistance of the electrode decreased with increasing water content.

3.5 Response time

The response time of an ion-selective electrode is defined by IUPAC as the time taken for the potential to reach a value 1 mV from the final equilibrium potential¹¹⁾. According to the IUPAC definition, the response time of the proposed electrode was about 10s., independently of the thiocyanate activity within the linear range, when the thiocyanate solution was stirred with a magnetic stirrer 2cm long in a 60 ml beaker. In general, the response time of liquid membrane electrodes lies between 10 and 30s. in 0.96×10^{-3} mol dm⁻³ solution¹²⁾. The response

time of the proposed thiocyanate electrode is shorter than that of the liquid membrane electrodes.

3.6 Electrode response as a function of the pH

The pH effect on the electrode potential was given in Fig. 1. The pH adjustment was made by the addition of sodium hydroxide or sulfuric acid. The variation in pH had no effect on the electrode potential over the range from pH 3 to 11 when the thiocyanate activity was 0.96×10^{-3} mol dm $^{-3}$ and from pH 3 to 12 when it was 0.75×10^{-1} mol dm $^{-3}$.

For the comparison these results with the values measured by the marketed electrode the response of Orion's 94-58 solid-state electrode was measured. With the electrode, constant electrode potential was observed over the range from 2.5 to 11. The results was taken to be the same as that found for the proposed electrode.

3.7 Response in non-aqueous media

With all liquid membrane electrodes, the utmost caution is required when working with partially-aqueous media, due to the solubility of the ion exchanger in such media. Potential-activity curves were measured in ethanol-water mixtures containing 0, 5, 10 and 20w/w% of ethanol. The linear ranges and the slopes of the potential-activity curves were 1.0×10^{-5} -, 1.0×10^{-5} -, 1.0×10^{-5} - and 0.99×10^{-4} - 0.56×10^0 mol dm $^{-3}$ and 59, 60, 59 and 49mV, respectively. It was concluded that the electrode could be used in ethanol-water media when the ethanol concentration was less than 10w/w%.

3.8 Selectivity of the electrode

The selectivity coefficients for the electrode in the presence of other ions are listed in Table 5. As shown in Table 5, the order of decreasing selectivity for the halide ions coincides with the order of decreasing ionic radii. The selectivity coefficient $K_{\text{SCN} \cdot \text{NO}_3}$ lies between $K_{\text{SCN} \cdot \text{Br}}$ and $K_{\text{SCN} \cdot \text{I}^-}$. This agrees with the order already reported^{7),8)}.

4 Conclusion

Thiocyanate-selective electrode prepared from a new matrix, Urushi, and tri-*n*-octylmethylammonium thiocyanate ion exchanger is proposed. The electrode has

Fig. 1 Electrode response as a function of pH.

Table 5 Selectivity coefficients by the mixed solution method¹³⁾.

Interfering ion	Activity (mol dm ⁻³)	Selectivity coefficient
F ⁻	0.56x10 ⁰	Less than 10 ⁻⁵
Cl ⁻	0.56x10 ⁰	2.7x10 ⁻⁴
Br ⁻	0.90x10 ⁻²	1.9x10 ⁻²
I ⁻	0.96x10 ⁻³	3.0x10 ⁻¹
NO ₃ ⁻	0.96x10 ⁻³	9.9x10 ⁻²
CN ⁻	0.75x10 ⁻¹	2.6x10 ⁻²
SO ₄ ²⁻	0.16x10 ⁻¹	less than 10 ⁻⁵

linear response range and selectivity similar to those of liquid membrane electrodes already reported. Moreover, the electrode membrane is hard, lustrous and smooth. The electrode can be used continuously for more than 500hr and is easier to handle than the liquid membrane electrode.

It was concluded that Urushi is found to be useful as an excellent membrane matrix for the thiocyanate-selective electrode by using liquid ion exchanger.

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Keyword phrases

ion-selective electrode for thiocyanate;
 Urushi as membrane matrix;
 tri-*n*-octylmethylammonium thiocyanate;

(Received July 15, 1981)