Tetrafluoroborate Selective Urushi Electrode as a Membrane Matrix

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Urushi, a kind of natural oriental lacquer, has excellent durability and mechanical strength. Therefore, its use as a membrane matrix for tetrafluoroborate ion selective electrode was examined. A linear potential-concentration curve was obtained within the concentration range 10^{-1} – 10^{-5} mol dm⁻³ tetrafluoroborate. The slope of the linear part of the curve was 55 mV per decade change of the concentration with the electrode prepared from 50 wt% of tri-*n*-octylmethylammonium tetrafluoroborate and 50 wt% of raw Urushi latex. This electrode exhibited a constant potential within the pH range 2–6. The static response time of the electrode was about 1 min and the dynamic response time was about 10 s. Utilization of other kinds of ion-exchanger and Urushi latex as electrode membranes was also examined. The selectivity coefficient for each electrode was measured. Two types of flow-through electrodes were prepared. They showed similar potential-concentration curves to that for the usual type electrode. The electrode was applied to the measurement of the formation rate of tetrafluoroborate from boric and hydrofluoric acids. The electrode could be used for more than 5 months.

Keywords Tetrafluoroborate selective electrode, tri-*n*-octylmethylammonium tetrafluoroborate, flow-through type tetrafluoroborate electrode

Urushi is an oriental natural lacquer used extensively for Japanese lacquer-ware.¹ As Urushi lacquer has excellent durability and mechanical strength, it was examined for use as a matrix of ion selective electrodes.

In our previous report, an iodide selective electrode based on Urushi and powdered silver iodide has been described.² Liquid ion-exchangers could also be used as the electro-active material, and solidification of the ion selective liquid membrane was possible. Perchlorate selective³, nitrate selective⁴ and thiocyanate selective⁵ electrodes have been developed with Urushi and various liquid ion-exchangers such as tri-*n*-octylmethylammonium ion-pair.

Several tetrafluoroborate selective liquid membrane electrodes have also been studied.^{6–11} The solidification of the liquid tetrafluoroborate ion selective electrode membrane has been examined using PVC as the matrix.^{12,13} In this work, a new tetrafluoroborate selective electrode was prepared by using Urushi as the membrane matrix, for the purpose of obtaining a more rigid, more durable and easier to handle tetrafluoroborate electrode. The characteristics of the electrode were studied. The electrode was also applied to the measurement of the rate of formation of tetrafluoroborate from boric and hydrofluoric acids.

Experimental

Apparatus

The electrode potential was measured with an Orion Model 801/Digital pH Ion Analyzer and an Orion double junction reference electrode, Model 90-01.

For the hardening of Urushi membrane, a specially designed air oven, which could provide 80–90% relative humidity at room temperature, was used. A rotating electrode holder for obtaining uniform thickness of the electrode membrane was attached to the air oven and was operated during the hardening process. Another air oven equipped with the rotating electrode holder was also used for the hardening of the Urushi membrane at 130°C.

Chemicals

Several kinds of Urushi latex were obtained from Saito Co., Ltd. Tri-*n*-octylmethylammonium chloride was obtained from Wako Pure Chemical Co. Ltd., tri-*n*-dodecylmethylammonium chloride from Polysciences Inc., tri-*n*-octylpropylammonium bromide from Pfaltz and Bauer, Inc., and cetyltrimethylbenzylammonium hydroxide and chloride from Tokyo Kasei Kogyo Co. Ltd. All other chemicals were of analytical reagent grade.

Preparation of ion exchangers

A mixed solution of boric acid (0.1 mol dm^{-3} , 50 ml) and hydrofluoric acid (20 mol dm^{-3} , 10 ml) was shaken with 1 g of tri-*n*-octylmethylammonium chloride, tri-*n*-dodecylmethylammonium chloride, tri-*n*-octylpropylammonium bromide, or cetyldimethylbenzylammonium hydroxide or chloride dissolved in chloroform (20 ml) for about 10 min in a polyethylene separatory funnel.

After the extract had been passed through a dry filter paper into a beaker, the chloroform was removed by evaporation over a period of three days from the beaker covered with a watch glass.

Construction of electrode

Each tetrafluoroborate ion-exchanger thus obtained was mixed with Urushi latex in different portions and each mixture was used to coat a copper disc of the electrode body (12 mm in diameter, 120 mm in length) made from polycarbonate resin. An internal screened cable was connected to the inside of the copper disc.

After the coating, the mixture was hardened in the air oven at $25\text{--}35^\circ\text{C}$ (80–90% relative humidity). The mixture required 5–15 d for complete hardening, depending on the composition of the mixture. The hardening was also possible at 130°C . The complete hardening was attained within 5–7 h at the higher temperature. Details of the construction and the structure of the electrode were already reported.⁴

Measurement of the potential

The potential of the electrodes was measured at $25 \pm 0.1^\circ\text{C}$. The solution was stirred with a magnetic stirrer. Before use, each electrode was soaked for 2–3 h in $10^{-2} \text{ mol dm}^{-3}$ standard tetrafluoroborate solution prepared as described later.

A tetrafluoroborate stock solution (0.1 mol dm^{-3}) was prepared by mixing 50 ml of boric acid solution (0.2 mol dm^{-3}), 10 ml of hydrofluoric acid solution (20 mol dm^{-3}) and water up to 100 ml. A standard tetrafluoroborate solution ($10^{-2} \text{ mol dm}^{-3}$) was prepared by mixing 10 ml of the stock solution, 10 ml of acetic acid–sodium acetate buffer solution (4:1, 1.0 mol dm^{-3}) and water up to 100 ml. Following the same procedure, other dilute standard tetrafluoroborate solutions were prepared.

Results and Discussion

Potential–concentration curves

The electrode showed a linear potential–concentration curve within the concentration range $10^{-1}\text{--}10^{-5} \text{ mol dm}^{-3}$ tetrafluoroborate, when it was prepared by mixing 50wt% of tri-*n*-octylmethylammonium tetrafluoroborate ion-exchanger and 50wt% of raw Urushi latex. The slope was 55 mV per decade change in the tetrafluoroborate concentration. The slope of the potential–concentration curve decreased to 54 mV or

53 mV when 45wt% or 40wt% of the ion-exchanger was used, although the same linear range of the curve was maintained. When the membranes were prepared from 55wt% and 60wt% of the ion-exchanger, they did not harden sufficiently, as the amount of Urushi was too small for complete hardening of the membranes. The best amount of the ion-exchanger was therefore 50wt%.

The electrode membranes prepared by mixing 50wt% of tri-*n*-dodecylmethylammonium tetrafluoroborate, tri-*n*-octylpropylammonium tetrafluoroborate and cetyldimethylbenzylammonium tetrafluoroborate with 50wt% of raw Urushi latex showed lower slopes of 43 mV, 41 mV and 52 mV, respectively. In these cases, the linear range of the potential–concentration curves was also $10^{-1}\text{--}10^{-5} \text{ mol dm}^{-3}$. These results show that the best ion-exchanger was tri-*n*-octylmethylammonium tetrafluoroborate. Cetyldimethylbenzylammonium tetrafluoroborate also gave an excellent potential–concentration curve.

When the electrode membrane composed of 50wt% of tri-*n*-octylmethylammonium tetrafluoroborate and 50wt% of raw Urushi latex was hardened at the higher temperature (130°C), the potential–concentration curve was linear within the concentration range $10^{-4.5}\text{--}10^{-1} \text{ mol dm}^{-3}$, and the slope was also 55 mV.

Electrode response as a function of pH

The pH effect on the electrode potential was measured for $10^{-3} \text{ mol dm}^{-3}$ tetrafluoroborate. The pH adjustment of the tetrafluoroborate solution was made by changing the mixing ratio of the acetic acid–sodium acetate buffer added for keeping the ionic strength at about 0.1. A small amount of sodium hydroxide or sulfuric acid solution was added for the adjustment of the pH value of the tetrafluoroborate solution, when the required pH value was not attained with the acetate buffer solution.

A pH glass electrode could not be used for the measurement of pH value of the tetrafluoroborate solutions because they contained hydrofluoric acid. Therefore, the pH values of the mixed solutions of the same molar concentration of hydrochloric acid as the hydrofluoric and the buffer, were measured with a pH glass electrode.

An almost constant electrode potential was observed when the pH value of the tetrafluoroborate solution was between 2 and 6. A small decrease in the potential was recognized above pH 6.

Response time

The static 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 potential¹⁴.

According to the IUPAC definition, the static response time of the proposed electrode was about 1 min, independently of the tetrafluoroborate concentration within the linear range, when the tetrafluoroborate solution was stirred with a magnetic stirrer, 20 mm

long, in a 60 ml beaker.

The dynamic response time, measured by adding 25 ml of water to 25 ml of 10^{-2} mol dm^{-3} tetrafluoroborate solution was about 10 s. When 10^{-1} mol dm^{-3} tetrafluoroborate solution was added to 10^{-2} mol dm^{-3} solution, a steady potential was attained after 10 s.

Other characteristics of the electrode

Several electrodes were prepared from 50wt% of tri-*n*-octylmethylammonium tetrafluoroborate and 50wt% of two kinds of Japanese and two kinds of Chinese raw Urushi latex. No difference was observed among the potential-concentration curves obtained for the electrodes prepared with these raw Urushi latexes. Therefore, the difference in the place of production of Urushi latex did not affect the characteristics of the electrodes.

The electric resistance of the electrode membranes was measured before their use with a Toa Electronics Ltd. Super Megohmmeter, Type SM-15. The electric resistance of the membranes prepared with tri-*n*-octylmethylammonium tetrafluoroborate was about 0.1 M Ω , independently of its content of 40–50wt%. The thickness of the membranes was 0.25–0.30 mm.

Selectivity of the electrode

The selectivity coefficients for the electrode prepared from 50wt% of tri-*n*-octylmethylammonium tetrafluoroborate and 50wt% of raw Urushi latex were measured with the mixed solution and separate solution methods.

The selectivity coefficients were similar to those measured with a commercial tetrafluoroborate selective liquid membrane electrode¹⁵.

As shown in Table 1, the order of selectivity coefficients for the halide ions is $K_{\text{BF}_4^-, \text{Cl}^-}^{\text{Pot}} < K_{\text{BF}_4^-, \text{Br}^-}^{\text{Pot}} < K_{\text{BF}_4^-, \text{I}^-}^{\text{Pot}}$ which agrees with the order of increasing ionic radii. For the halogenate ions the order of selectivity coefficients is $K_{\text{BF}_4^-, \text{IO}_3^-}^{\text{Pot}} < K_{\text{BF}_4^-, \text{BrO}_3^-}^{\text{Pot}} < K_{\text{BF}_4^-, \text{ClO}_3^-}^{\text{Pot}}$.

Preparation of flow-through type electrodes

Two types of flow-through tetrafluoroborate selec-

tive electrode were prepared. A mixture of 50wt% of tri-*n*-octylmethylammonium tetrafluoroborate ion-exchanger and 50wt% of raw Urushi latex was coated inside two copper tubes (8 mm in inner diameter, 20 mm in length and 4 mm in inner diameter, 10 mm in length) and the coating was hardened. Urushi latex was coated outside the tubes to create an insulator coating. The prepared flow-through type electrode was connected as shown in Fig. 1 with a reference electrode and a cup for the reference. The flow rate of the tetrafluoroborate solutions was adjusted at 5.0 and 3.5 ml/min. The flow-through type electrodes showed linear potential-concentration curves within the range 10^{-1} – 10^{-5} mol dm^{-3} tetrafluoroborate. The slope of the potential-concentration curves was 55–50 mV per decade change in tetrafluoroborate concentration.

Another type of electrode membrane was prepared

Fig. 1 Flow-through type electrode (A)

Fig. 2 Flow-through type electrode (B)

Table 1 Selectivity coefficients

	Mixed solution method		Separate solution method	
	Concn./ mol dm^{-3}	$K_{\text{BF}_4^-, j}^{\text{Pot}}$	$K_{\text{BF}_4^-, j}^{\text{Pot}}$ at 10^{-1} mol dm^{-3}	$K_{\text{BF}_4^-, j}^{\text{Pot}}$ at 200 mV
Cl^-	10^{-1}	1.0×10^{-3}	3.8×10^{-3}	5.0×10^{-3}
Br^-	10^{-1}	1.0×10^{-2}	3.1×10^{-2}	3.9×10^{-2}
I^-	10^{-2}	0.2	0.5	0.6
ClO_4^-	10^{-3}	2.1	3.8	3.5
ClO_3^-	10^{-3}	1.8×10^{-2}		
BrO_3^-	10^{-1}	8.5×10^{-3}		
IO_3^-	10^{-1}	$< 10^{-4}$		
NO_3^-	10^{-1}	1.2×10^{-2}

Fig. 3 Rate of formation of tetrafluoroborate

by coating with the same mixture of the ion-exchanger and the Urushi latex on a nylon net (80 mesh), then this coating was hardened. The obtained electrode membrane was held between two plastic blocks (70×70×25 mm) and a flow-through type electrode was constructed with inlet and outlet of tetrafluoroborate solution, silver-silver chloride electrode and four bolts and nuts, as shown in Fig. 2. A potential-concentration curve having the same linear range and the slope as the usual type electrode was obtained, when the tetrafluoroborate solution was passed at a flow rate of 5.0 ml/min through the electrode assembly.

Rate of formation of tetrafluoroborate

The tetrafluoroborate electrode prepared from 50wt% of tri-*n*-octylmethylammonium tetrafluoroborate and 50wt% of raw Urushi latex was applied to the measurement of formation of tetrafluoroborate from boric and hydrofluoric acids. Boric acid solution (2×10^{-2} mol dm⁻³ 40 ml) and hydrofluoric acid solution (2×10^{-1} mol dm⁻³, 40 ml) were mixed. The mixed solution was kept in a water bath maintained at $24 \pm 0.1^\circ\text{C}$ and the potential change was recorded with the tetrafluoroborate electrode immersed into the solution with continuous stirring.

The result is shown in Fig. 3. It was found that the equilibrium of formation of tetrafluoroborate was attained completely within 7–8 h at $24 \pm 0.1^\circ\text{C}$.

In conclusion, a new tetrafluoroborate ion selective electrode was prepared from tri-*n*-octylmethylammonium tetrafluoroborate and Urushi, a kind of natural lacquer, and the characteristics of the electrode were

measured.

The electrode had almost the same characteristics as the liquid membrane electrodes previously reported.

The proposed electrode is easier to handle than the liquid membrane electrode and has a hard, lustrous and smooth membrane surface. The electrode can be used for more than 5 months with several hours use each day.

References

1. "Encyclopaedia Chimica", Vol. 1, p. 807 (1960), (Kyoritsu Pub. Co., Tokyo).
2. K. Hiirō, T. Tanaka and A. Kawahara, *Bunseki Kagaku*, **25**, 653 (1976).
3. K. Hiirō, A. Kawahara and T. Tanaka, *Anal. Chim. Acta*, **110**, 321 (1979).
4. K. Hiirō, A. Kawahara and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **46**, 1447 (1980).
5. K. Hiirō, A. Kawahara and T. Tanaka, *Bunseki Kagaku*, **31**, E33 (1982).
6. C. Liteanu, E. Hopirtean and E. Stefaniga, *Rev. Roum. Chim.*, **22**, 653 (1977); Chem. Abstr., **87**, 45916r (1977).
7. E. Hopirtean, M. Preda and C. Liteanu, *Chem. Anal. [Warsaw]*, **21**, 861 (1976); Chem. Abstr., **86**, 100277q (1977).
8. A. S. Pathan, A. G. Fogg and D. T. Burns, *Proc. Soc. Anal. Chem.*, **11**, 162 (1974); Chem. Abstr., **83**, 21398q (1975).
9. A. G. Fogg, A. S. Pathan and D. T. Burns, *Anal. Lett.*, **7**, 545 (1974).
10. R. Reinsfelder and F. A. Schultz, *Anal. Chim. Acta*, **65**, 425 (1973).
11. C. J. Coetzee and A. J. Basson, *Anal. Chim. Acta*, **126**, 217 (1981).
12. A. L. Grekovich, S. E. Didina and E. A. Materova, *Ionnyi Obmen Ionometriya*, **2**, 150 (1979); Chem. Abstr., **92**, 208308p (1980).
13. Kuo-Xiong Chang, Hui-Chu Fu, Wei-Xin Chen, Hou-Chi Wang and Qun Yuan, *Hua Hsueh Hsueh Pao*, **38**, 223 (1980); Chem. Abstr., **94**, 182464a (1981).
14. IUPAC Secretariat: "Recommendations for Nomenclature of Ion-Selective Electrodes, Appendices on Provisional Nomenclature, Symbols, Units and Standards—Number 43", January, Oxford, (1975).
15. G. J. Moody and J. D. R. Thomas, "Selective Ion-sensitive Electrodes", p. 22 Merrow, Watford, (1971).

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