UIT Report Vol.13, No.1, pp.113~120, 1982 연구논문집 제13권 제1호 pp.113~120, 1982

Studies on the development of Ion-Selective Electrode to dye and dichromate species

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(Received December 30, 1981)

〈**Abstract**〉

An attempt has been made for the development of ion selective electrode to a dye species.

The PVC electrodes using Crystal violet-dichromate, Bismark brown-Indigo carmine and Bismark brown-Sunset yellow among nine kinds of sensing materials prepared here have been tested for their function to certain dye solution.

Anion or cation enchange resin substituted the site by an acid dye molecule or metal ion such as Cu^{2+}, Fe^{3+} was pulverized into the size of 200 mesh and also used for the preparation of the PVC membrane electrode for testing their responsibility to a dye solution.

Polyurethane membrane and liquid state electrodes were also prepared and tested their function to dye species along with the PVC membrane electrode.

The most satisfactory result was obstained with the PVC membrane electrode made of the sensor, Crystal violet-dichromate for the dichromate solution of the concentration range of 10^{-2}M down to 10^{-4}M. The slope factor was almost nernstian value, 27—30mV/decade.

In general, the responsibility of electrodes was not so good as the theoretical value for the food colours, Sunset yellow, Tartrazine, Green S, Amaranth, and Indigo carmine.

염료 및 $Cr_2O_7^{2-}$에 선택성인 전극의 개발에 관한 연구

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〈**요 약**〉

본 연구에서는 식용 색소 및 $Cr_2O_7^{2-}$에 선택적인 전극 개발을 시도하였다. 9가지의 감응물질을 제조하였으며 그 중에서 3가지만 선정하여 PVC막 제조에 사용하였다. 또한 음 및 양이온 교환수지에 산성 염료분자나 혹은 금속 양이온(Cu^{2+}, Fe^{3+})을 교환시킨 것을 200mesh로 분쇄하여 감응물질(sensor)로 사용한 PVC 전극등도 제작하였으며, 폴리우레탄막으로 만든 전극 및 liquid state 전극등도 제작하여 염료 용액에 대한 반응성을 시험하였다.

가장 성공적인 전극은 Crystal-violet-dichromate를 sensor로 사용한 것으로서 $Cr_2O_7^{2-}$ 용액에 대하여는 10^{-2}M—10^{-4}M 범위에서 이론치에 가까운 27—30mV/decade의 반응성을 보였다. 여러가지 전극들을 Sunset yellow, Tartrazine, Green S 및 Amaranth와 같은 식용 색소에 대하여 반응성을 시험하여 보았으나, 일반적으로 이론값보다 월등 낮은 nernstian slope factor를 보였다.

Ⅰ. Introduction

The extensive bibligraphies on the ion selective electrodes were included in the reviews(1—4). Moody and Thomas, who have developed PVC-based liquid ion exchanger membranes published a large number of papers [5~9,14] and a book[10] which covers both theoretical and practical aspects of ion selective electrodes together with several other books[11~13]. Only a few attempts among the works on ion selective electrode, however, have been made for the determination of organic dye ions[15,16,17,28].

Methods[27] proposed for the analysis of both natural and artificial colours used in foods, drugs, and cosmetics include paper chromatography[18,19], thin layer chromatography[18,19], high performance liquid chromatography[20~22], ion-pair extraction followed by polarography[23, 26] and ultraviolet-visible spectrophotometry[24, 25]. In general, chromatographic procedures offer specific methods that can discriminate against impurities and degradation products. Whereas almost all the methods mentioned above require the separation of the colour components to be determined from a foodstuffs prior to the analytical procedure, the ion selective electrode is simpler than others and the least expensive method. Authors decided it is worth-while to prepare and study an indicator electrode sensitive for a food colour that is capable of forming complexes or precipitates with certain components.

In the present work, the electrodes with the PVC membranes incorporating a slightly soluble compounds in water such as Crystal violet-dichromate were investigated. The electrical response of the electrode showed a good trend to the colour solution, Sunset yellow for range of concentration from 10^{-2}M down to 10^{-5}M. The slope factors of the electrode, however, were super nernstian (32mV/decade) for the high concentration range and much less than the theoretical value for the concentration range of 10^{-3}M to 10^{-5}M. An anion exchange resin in acid dye form and cation exchange resin in a heavy metallic form were prepared and used for the sensing materials as well as several dye compounds, which were insoluble in water.

Ⅱ. Experimental

All the potentiometric measurements were made with a pH meter (EIL 46A vibret) using the ion selective PVC membrane electrodes prepared here in conjuction with a saturated calomel electrode (SCE). Dye and all the chemicals used were reagent grade, and double distilled water was used throrghout the work.

PVC matrix membrane electrodes were fabricated according to the methods of Craggs, Moody, and Thomas[7], and the liquid state electrode body was made of Teflon which is one of the most resistive materials to acids, basis, and organic solvents. Nine kinds of compounds which were slightly soluble in water have been synthesized to use as sensing meterial in the preparation of PVC membrane. The compound, Crystal violet-dichromate, for example, was synthesized by adding 100ml of Crystal violet agueouse solution including 0.5g of pure solid sample into 200ml of 0.02M potassium dichromate solution at 70°C with continuous stirring.

The precipitate was washed with distilled water and was filtered onto a No.4 glass filter, and washed continuously with water untill colourless washings were obtained. The precipitate was dried in a vacuum oven at 70°C for 2 hours, and made into powder (200mesh) using mortar grinder (motor driven mortar). Other compounds were also prepared by the similar procedure described above. They are as follows: (1) Crystal violet-dichromate (yield, 95%) (2) Bismark brown-dichromate (95%),

Table.1 Solubility test of several sensors in solvents

Solvents \ sensors	Crystal violet-dichromate	Bismark brown-indigo carmine	Bismark brown-sunset yellow	Remarks
1) Dioctylphthalate(D.O.P)	(△)	(×)	(×)	
2) Chlorinated paraffine	(△)	(×)	(×)	
3) S.A.I.B & ethanol	(○)	(×)	(×)	miscible with water
4) D.M.P & ethanol	(○)	(×)	(×)	immiscible with water
5) Paraflex G-60	(△)	(×)	(×)	
6) Paraflex G-30	(○)	(×)	(×)	immiscible with water
7) o-dichloro benzene	(△)	(×)	(×)	
8) Tri-n-octylamine with ethanol	(△)	(×)	(×) (○)	immiscible with water
9) Dibutylphthalate (D.B.P) with ethanol	(△)	(×) (○)	(×) (○)	immiscible with water
10) Trixylenylphosphale (T.X.P) with ethanol	(△)	(×) (○)	(×)	immiscible with water
11) Diethanol-amine with ethanol	(○) (○)	(○) (○)	(○) (○)	miscible with water

△ : slightly soluble, × : Insoluble, ○ : Soluble

(3) Bismark brown-sunset yellow (75%), (4) Bismark brown-tartrazine (21%), (5) Bismark brown-amaranth (40%), (6) Bismark brown-indigo carmine (83%), (7) Bismark brown-phosphotungstate (70%), (8) Crystal violet-orange G (15%), and (9) Tetraphenylphosphonium-indigo carmine (90%). The sensing materials to be used have been tested for their solubilities to eleven kinds of viscous solvents in order to disperse the material into the membrane as homogeneously as possible. Three kinds of sensors which showed the highest yield of others have been selected to test their solubility in the solvents as shown on table 1.

An anion exchange resin in acid dye form and cation exchange resin in a heavy metallic form were also prepared and used for the sensing materials instead of dye compounds after pulverization of the stuff into the size of 200 mesh. 2-nitrophenyl-n-butyrate was synthesized and used for the preparation of PVC membranes together with the solvent.

2-nitrophenyl-n-butyrate[29] was prepared as follows: First of all, n-butyryl chloride was syntnesized by making the reaction of 56g $SOCl_2$ (0.47mole) and 35.2g n-butyric acid (0.40mole) at 15°C in a distillation flask with a separatory funnel and a water cooling condenser, and by collecting the distillate at 100—102°C from a column with a good efficiency.

The n-butyryl chloride prepared was made the reaction with the equivalent amount of nitrophenol to form the ester, 2-nitrophenyl-n-butyrate for one hour at 100°C in a refluxing flask with a water cooling condenser.

Finally the reasonably pure ester, 2-nitrophenyl-n-butyrate (conformed by IR spectrum) was separated from impure one by vacuum distillation.

The PVC membrane electrodes were prepared by pouring the homogeneous mixture of 0.15g sensor, 0.03g solvent mediator, 0.025g plasticizer, 0.15g PVC, and 6ml tetrahydrofuran onto a glass or aluminium ring (4.0cm inside diameter) and sticking the circular PVC membrane (1.0cm diameter) cut out from the prepared master membrane on the end of a glass tube.

Polyurethane membrane was made by similar process of the PVC one: 0.40g NIAX polyol

Table.2 The composition of membranes for an electrode

component \ No. of electrodes	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Crystal violet-dichromate(gr)	0.15	0.15		0.15				0.25						
Bismark brown-sunset yellow(gr)			0.15		0.15									
Bismark brown-indigo carmine(gr)						0.15	0.15							
Anion-exchange resin-Amaranth(gr) (Diaion) SA 20 AP)									0.15					
Anion-exchange resin-sunset yellow (gr) (Diaion SA 20 AP)												0.15		
Anion-exchange resin-sunset yellow (gr) (IRA 400C, Amberlite)										0.15				
Cation exchange resin-copper(gr) (Diaion SK-1B-Cu)											0.15			
Cation-exchange resin-Cu^{2+}(gr) (Diaion CR-10-Cu^{2+})														0.15
Cation-exchange resin-Fe^{3+}(gr) (Diaion CR 10-Fe^{3+})													0.15	
Dimethylphthalate (D.M.P) (gr)	0.30													
o-nitrophenyl-n-butyrate(gr)	0.03	0.03	0.03	0.03	0.02	0.02	0.03		0.02	0.03	0.03	0.03	0.03	0.03
PVC powder(gr)	0.15	0.15	0.15	0.15	0.15	0.15	0.15		0.15	0.15	0.15	0.15	0.15	0.15
Saccaroseacetate isobutyrate(g) (SAIB)		0.03												
Ethanol(ml)		0.5			0.5	0.5	0.5							
Dioctylphthalate(D.O.P)(gr)		0.02		0.02					0.06		0.06		0.06	
Diethanolamine(gr)			0.03											
Dibutylphthalate(D.B.P)(gr)			0.02		0.02	0.03	0.02			0.06		0.06		0.06
Tetrahydrofuran(ml)	6	6	6	6	6	6	6		5	5	6	6	6	6
Paraflex G-30(g)				0.03										
Tri-n-octylamine (gr)					0.02									
Trixylenylphosphate(gr)							0.03							
NIAX polyol, PCP-021(gr)								0.40						
Hexamethylene diisocyanate								0.10						
Ethyl acetate								1.0						
5% dibutyltinlaurate soln								0.1						

(PCP-021, Union Carbide Co), 0.10g of 5% dibutyltinlaurate(DBTDL) solution in toluene, 1.0g ethyl acetate, 0.10g hexamethylene diisocyanate (HMDI), and 0.25g sensor, Crystal violet-dicromate were made a homogeneouse mixture. It was poured into a glass ring (5.0cm diameter) and formed a flexible membrane within 24 hours.

The electrodes with a membrane prepared by a suitable recipe on table 2 were used for the test of their electrical function to certain solution. A liquid state electrode made from acrylonitril and Teflon were specially designed and used for the test of a membrane function.

The metallic conductor, Ag/AgCl made from silver wire (1mm diameter) was prepared by dissolving the surface in dilute nitric acid for 3—5 minutes, washing with distilled water and anodic oxidation in 0.1N hydrochloric acid using the current density of 2—5mA for four hours.

The silver wire covered with the homogeneouse silver chloride layer were dipped into 1M potassium chloride solution of an electrode

body with a membrane to be tested. The half cell system described above forms the indicator electrode to acertain component.

Ⅲ. Results and discussion

In general, the membrane electrodes prepared according to the method recommended here have showed better responsibility than the one without using solvent mediator such as 2-nitrophenyl-n-butyrate prepared.

The electrod (D) on table 2 only showed a good trend of electrical response to the colour solution, Sunset yellow for the range of concentration from 10^{-2}M down to 10^{-5}M. Super nernstian response (32mV/decade) resulted for the high concentration range. Poor responsibility such as 12mV/decade, however, come out for the concentration range of 10^{-3}M to 10^{-5}M (see Fig.1). The electrode (D), (F) and (G) showed the near nernstian slope factor, 27—30mV/decade, to the dichrmate solution for the range of the concentration from 10^{-2}M to 10^{-4}M (see Fig.2).

The response curves of electrodes tend to decrease at lower concentration (10^{-6}M) due to their slow response time.

The electrodes (D) and (I) seem to be responsive towards the colour solution, Tartrazine. On the other hand, the electrodes (C) and (H) did not respond to the same colour solution as shown on Fig.3.

The response curve for the colour solution, Amaranth seemed to be positive only towards the electrode (I) as can be seen on Fig.4.

The electrodes (B), (F), (G) and (H) responded to the cationic dye, Bismark brown solution. The electrdes (I) and (L) were responsive to Green S and Tartrazine solution for the range of 10^{-2}M to 10^{-4}M.

The electrode (M) and (N) showed an opposite response curve towards Sunset yellow and Tartrazine solution respectively (see table 3).

The phenomena may indicate that those electrodes were responding to alkli metal ions

Fig.1 Electrical responses of electrodes to Sunset yellow colour

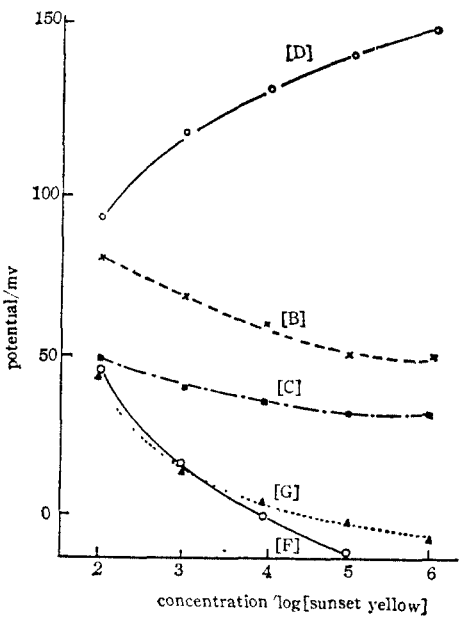
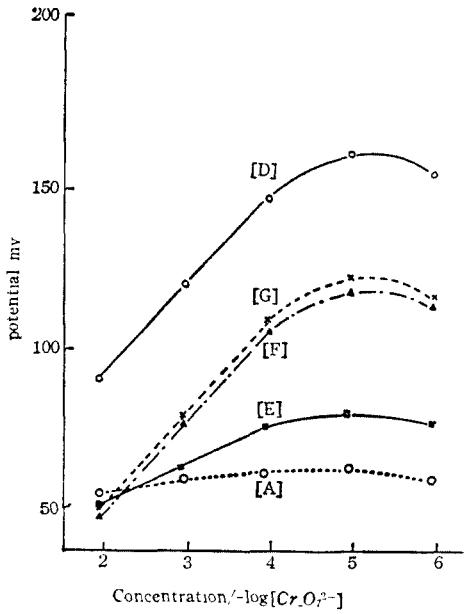


Fig.2 Electrical responses of electrodes to dichromate solution



such as Na^+ contrary to our expectation of forming complex structure between food colour molecule and metal ion.

The membrane electrodes simiar to (M) and (N) made of the corporate body such as a chelate cation exchange resine (Diaion CR-10) substituted with a cation (Cr^{3+}, Co^{2+}, and Ni^{2+}) were examined for the response to a food colour and turned out likely to be a contrary concept for the acid food colours, i.e. Orange G and Amaranth. But the only response curve to the colour, Indigo carmine, appeared to be the theoretical trend.

Therefore, the electrode could be applicable for the determination of Indigo carmine by more careful control of its membrane compost-

Fig. 3 Electrical responses of electrodes to Tartrazine

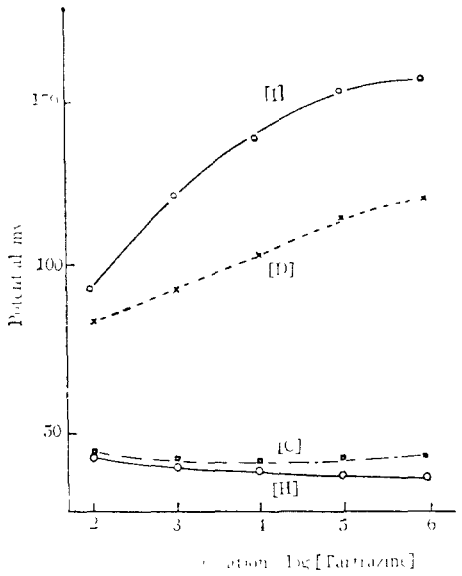


Fig. 4 Electrical responses of electrodes to Amaranth

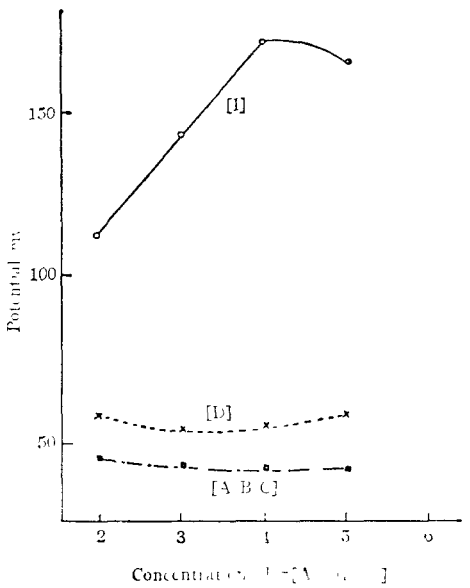


Table. 3 Electrical responses of electrodes to dye solution

No of Electrodes / Dyes determined(M)	potential/mV							
	B	F	G	H	I	L	M	N
Bismark brown(or Tartrazine)								
1×10^{-2}	47.5	42.0	45.5	47.5	(95.0)	—	—	(40.0)
1×10^{-3}	56.0	51.0	62.5	68.0	(124.0)	—	—	(34.5)
1×10^{-4}	50.0	37.5	48.0	62.0	(144.5)	—	—	(21.0)
1×10^{-5}	32.5	14.5	25.5	40.0	(157.0)	—	—	(10.5)
1×10^{-6}	12.5	−8.0	4.0	17.5	(159.5)	—	—	(−4.0)
Green S (or Sunset yellow)								
1×10^{-2}	—	—	—	—	88.0	141.0	(43.0)	—
1×10^{-3}	—	—	—	—	119.5	129.5	(32.5)	—
1×10^{-4}	—	—	—	—	150.0	158.0	(24.0)	—
1×10^{-5}	—	—	—	—	156.0	163.0	(18.0)	—
1×10^{-6}	—	—	—	—	—	—	(11.5)	—

tion to get a bigger slope factor than the small one, 10mV/decade, obtained here at the range of 10^{-2}M to 10^{-4}M.

The poor responsibility of the electrodes to food colour solution presumably due to the bad permeability of a dye molecule into the PVC membrane in spite of the expectation of strong affinity between the dye molecule and sensor components in a membrane.

The liquid state electrode made of Teflon showed similar reactions to various dye solution as the other electrodes did.

The main drawback of this electrode, however, was on the use o organic solvents (plasticizers) which could dissolve the PVC membrane as well as the sensing materials prepared. Such property of organic solvent makes the life of PVC membrane too short to use.

A polyurethane membrane for the liquid state electrode like the one (H) on table 2 was almost insoluble to the solvents tested, but shown non-response or the worse response than the electrode with PVC membrane to a food colour solution.

The preparation of polyurethane membrane rather more porouse and resistive to organic solvent would be very helpful to develope the dye sensitive ion selective electrode for further work.

Ⅳ. Conclusion

The slightly soluble compounds, i.e. Crystal violet-dichromate, Bismark brown-Indigo carmine, and Bismark brown-Sunset yellow were prepared and used for the preparation of membrane electrodes.

The PVC electrode based on the sensor, Crystal-violet-dichromate has shown remarkable response charactor to dichromate solution, but it was not so much successful to food colour solutions such as Sunset yellow, Tartrazine, Green S, and Amaranth.

The reason may presumably be on the fact that the large dye molecule can not easily permeate into the PVC membrane in spite of the expectation of strong affinity between the dye molecule and sensor component.

Polyurethane and PVC membrane electrode with a sensor like ion exchange resin would be valuable to study further for the development of dye sensitive ion selective electrode.

Ⅴ. Acknowledgement

Authors wish to thank to the Korean Traders Scholarship Foundation for the financial support in the presentation of this work.

They are also indebted to Mr. T.S.Lee, and Mr. S.S.Yoon for their assistance.

Refereces

1. R.P. Buck, Anal. Chem., 46, 28R(1974).
2. R.P.Buck, Anal. Chem., 48(5), 23R(1976).
3. R.P. Buck, Anal. Chem., 50(5), 17R(1978).
4. A.K.Covington, Critical Reviews in Analytical Chemistry, 3, 355(1974).
5. G.J. Moody and J.R.R. Thomas, Lab Practice, 27, 285(1978).
6. J.D.R. Thomas, Lab. Practice, 27, 857(1978).
7. A. Craggs, G.J. Moody, and J.D.R. Thomas, J. Chem. Educ., 51, 541(1974).
8. G.J. Moody, N.S. Nassory, and J.D.R. Thomas, Analyst, 103, 68(1978).
9. S.K.A.G. Hassan, G.J. Moody and J.D.R. Thomas, Analyst, 105, 147(1980).
10. G.J. Moody and J.D.R. Thomas, Selective Ion Sensitive Electrodes, Merrow, England (1971).
11. P.L. Bailey, Analysis with Ion-Selective Electrodes, Heydon, London (1976).
12. G.E. Bailescu and V.V. Cosofret, Applications of Ion-Selective Membrane Electrodes in Organic Analysis, Ellis Horwood Ltd. Pub.

(1977).

13. J. Koryta, Ion-Selective Electrodes, Camb ridge Univ. Press (1976).
14. A. Graggs, G.J. Moody, J.D.R. Thomas, and B.J. Birch, Analyst, 105, 426 (1980).
15. A.G. Fogg and K.S. Yoo, in Ion Selective Electrodes edited by E. Pungor, p369, Budapest Conference, Sept. 5-9, 1977, Elsevier scientific pub. co. (1978).
16. M. Kataoka, M. Shin, and T. Kambara, Talanta, 24, 261 (1977).
17. A.R. Rajput, M. Kataoka, and T. Kambara, J. Electroanal. Chem., 66, 67 (1975).
18. D. Pearson, The Chemical Analysis of Foods, seventh edition, Churchill Livingstone, Edinburgh, (1976).
19. K. Venkataraman, Editor, "The Analytical Chemistry of Synthetic Dyes", John Wiley, New York, (1977).
20. J.H. Knox, and G.R. Laird, J. Chromatography, 122, 17 (1976).
21. J. Chudy, N.T. Crosby and I. Patel, J. Chromatography, 154, 306 (1978).
22. N.P. Boley, N.G. Bunton, N.T. Crosby, A.E. Johnson, P. Roper, and L. Somers, Analyst, 105, 589 (1980).
23. A.G. Fogg, and K.S. Yoo, Analyst, 104, 723 (1979).
24. H. Sasaki, Shokuhin Eiseigaku Zasshi, 19, 1 (1978).
25. A.F. Fell and J.G. Allan, Analytical Proceedings, 18 (7), 291 (1981).
26. A.G. Fogg, and K.S. Yoo, Analyst (London), 104, 1087 (1979).
27. K.G. Sloman, A.K. Foltz, J.A. Yeransian, Anal. Chem., 53 (5) 248R (1981).
28. A.G. Fogg, A.A. Al-Sibaai, and K.S. Yoo, Anal. Lett., 10, 173 (1977).
29. Organic Synthesis (Collective Vol. 3)., ed. by E.C. Horning, pp.714-715, John Wiley, (1941).