Flow Injection Analysis Study of the Effect of Certain Additives on the Response and Selectivity of Liquid Membrane Ion-Selective Electrodes

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Abstract

PVC membrane ion-selective electrodes were prepared using two crown ether carboxylic acids as ionophores. Different amounts of the additive potassium tetrakis (p-chlorophenyl) borate (KTpClPB) were incorporated in the electrode matrices with and without 1% trioctylphosphine oxide (TOPO) additive. The effect of the varying amounts of KTpClPB and TOPO on the responses and selectivities of the electrodes towards alkali and alkaline earth metals were studied.

Introduction

Crown ethers have been used successfully as neutral carriers in ion-selective electrodes (1-7). The response of these electrodes and their selectivity for a certain metal over others depends on the characteristics of the the the carrier (2, 3), the composition of the electrode matrix (1, 8-10), and the composition of the sample solution (9). The effect of the electrode matrix composition on the electrode response depends on the type and amount of the plasticizer used, and the type and amounts of additives such as potassium tetrakis (p-chlorophenyl) borate (KTpClPB) (10) and trioctylphosphine oxide (TOPO) (11). It has been shown that the presence of fixed negative sites confined in the electrode membrane matrix can enhance the electrode response (9). This was achieved by incorporating mobile, lipophilic anions, such as the tetrakis (p-chlorophenyl) borate anion, which will be permanently confined into the membrane. The functions of this anion in the electrode membrane matrix include reduction of interferences from lipophilic anions in the sample solution, of the response time of the membrane electrical resistance, and of the cation exchange energy barrier at the membrane-solution interface (10). The addition of trioctylphosphine oxide to the electrode matrix has been reported to affect the response of the electrode and its selectivity for certain metals with respect to others (11,12).

In this study the response of electrodes of different membrane matrix compositions and their selectivities to certain ions are studied. Two crown ether ionophores, 1 and 2, are used to prepare the matrices with and without TOPO, as well as with different proportions of KTpClPB.

Experimatal

Reagents and Chemicals

Ionophores 1 and 2 were supplied by Professor R.A. Bartsch, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409. The chlorides of cesium, rubidium, potassium, sodium, lithium, strontium, calcium and magnesium were dried at 140° for 48 hours before being used in preparation of standard solutions. Distilled deionized water was used to prepare all the aqueous solutions. Tetrahydrofuran (THF) from E.M. Science, Cherry Hill, New Jersey, was used to dissolve the electrode matrix. Polyvinylchloride (PVC) was obtained from Fluka AG, o-nitrophenyl octyl ether (NPOE) and KTpClPB were from Specialty Organics, Inc., Irwindale, California, and TOPO was from Aldrich Chemicals Co., Milwaukee, Wisconsin.

Apparatus

A flow injection analysis system with a flow cell containing a series of silver wire electrodes, similar to those reported earlier (13), were used in this study. The electrode membranes (prepared as illustrated below) were coated on the tips of the silver wires as thin membranes. Three layers of 2 ul each were coated on the tip of each electrode. After the electrode dried, the channel of the flow cell was closed by a clear plastic sheet with a double sided tape. Then the cell was introduced into the flow system and the electrodes were conditioned overnight in contact with the carrier solution (14 mM NaCl) before use. A silver-silver chloride electrode downstream in the flow cell was used as reference electrode.

A Beckman 3500 digital pH meter and Linear strip chart recorder were used to record the potentiometric FIA signals. Air pressurized reference and carrier stream reservoirs were used in connection with flowmeters and debubblers.

Procedure

Preparation of the Electrode Matrix

Eight electrode matrices were prepared by completely dissolving the electrode matrix mixtures in 350 μl THF. Each electrode has a specific mixture as follows:

- Electrode 1: 1.5 mg ionophore 1, 65 mg NPOE, 0.8 mg KTpClPB, which represents a 0.5 molar ratio to the ionophore, and 33 mg PVC.

- Electrode 2: 1.5 mg ionophore 1, 65 mg NPOE, 0.8 mg KTpClPB, 1 mg TOPO and 33 mg PVC.

- Electrode 3: 1.5 mg ionophore 1, 65 mg NPOE, 3.2 mg KTpClPB, which represents twice the number of moles of the ionophore, and 33 mg PVC.

- Electrode 4: 1.5 mg ionophore 1, 65 mg NPOE, 3.2 mg KTpClPB, 1 mg TOPO and 33 mg PVC.

- Electrode 5: 1.5 ionophore 2, 65 mg NPOE, 1 mg KTpClPB, which represents half the moles of the ionophore, and 33 mg PVC.

- Electrode 6: 1.5 mg ionophore 2, 65 mg NPOE, 1 mg KTpClPB, 1 mg TOPO, and 33 mg PVC.

- Electrode 7: 1.5 mg ionophore 2, 65 mg NPOE, 4 mg KTpClPB, which represents twice the moles of the ionophore and 33 mg PVC.

- Electrode 8: 1.5 mg ionophore 2, 65 mg NPOE, 4 mg KTpClPB, 1 mg TOPO, and 33 mg PVC.

Table 1 summarizes the relative portions of the additives KTpClPB and TOPO.

Potentiometric Procedure

A procedure similar to that described earlier (13) was used. The carrier and the reference electrode streams were 14 mM sodium chloride solutions. The flow rates were 1 ml/1 min. for the carrier stream and 0.2 ml/min. for the reference electrode stream. The sample volume was 200 μl, which is large enough to allow zero dispersion in the middle of the sample plug (4). Potassium ion calibration curves from 0.2 to 200mM were prepared for electrodes 1, 2 and 4, and cesium calibration curves over the same range were prepared for electrodes 3, 5, 6, 7, and 8. Solutions of 100 mM of other ions were injected for selectivity coefficient measurements.

Coefficients

The selectivity coefficients were calculated using the separate solution method (13, 14, 15) by two methods: In the first (Method 1), pure solutions of known concentrations of the interfering metals were injected into the flow system. Due to the large sample volume used, the dispersion is zero at the middle of the sample plug and no mixing with the carrier occurs. The potential was recorded for each solution. The concentration of potassium (for electrodes 1, 2 and 4) or cesium (for electrodes 3, 5, 6, 7 and 8) corresponding to the signal of the interfering ion is obtained from the calibration curves. The selectivity coefficient is then calculated from the equation:

$$K_{Cs,M}^{pot} = \frac{C_{Cs}}{(C_M)^{1/Z_M}}$$

or

$$K_{K,M}^{pot} = \frac{C_K}{(C_M)^{1/Z_M}}$$

C_M is the concentration of the interfering metal injected and Z_M is its valency. In the second method (Method 2), equal concentrations of pure cesium (or potassium) and of interfering metal solutions were separately injected into the carrier stream. The potentiometric FIA signal of each one is recorded, and the selectivity coefficient is calculated from the equation (15):

$$\log K_{Cs,M}^{pot} = \frac{E_2 - E_1}{S} + \left(1 - \frac{1}{Z_M}\right) \log[Cs]$$

or

$$\log K_{K,M}^{pot} = \frac{E_2 - E_1}{S} + \left(1 - \frac{1}{Z_M}\right) \log[K]$$

M is the interfering metal, Z_M is its valency, and S is the slope of the primary ion calibration curve (Ca and K, respectively). Since there is no mixing due to the large sample volume, the signals obtained are the responses of the pure solutions.

For electrode 3, the selectivity coefficients for cesium with respect to other metals were first calculated, then the selectivities for potassium with respect to the other metals were then calculated from these, because the electrode is responsive to cesium much more than to potassium.

Results and Discussion

Calibration Graphs

Table I summarizes the trends observed for different electrode compositions. Figure 1 shows the calibration curves of potassium standards using electrodes 1 (curve A), 2 (curve B), and 4 (curve C), which incorporate ionophore 1. Electrode 3, which also incorporates ionophore 1, shows higher response for cesium than potassium. So a cesium calibration curve was used to calculate the selectivity coefficients.

Table 1. Electrode additive compositions

Electrode	Ionophore	KTpClPB/ Ionophore	% TOPO	Effect
1	1	0.5	0	
2	1	0.5	1	Increased response for K
3	1	2.0	0	Increased Cs selectivity
4	1	2.0	1	Increased response and slope for K
5	2	0.5	0	Low Cs response
6	2	0.5	1	Poor Cs response, non-Nernstian
7	2	2.0	0	Increased Cs response and sensitivity
8	2	2.0	1	Slight decrease in Cs response

The addition of 1 mg TOPO to the electrode matrix which includes 0.8 mg KTpClPB (electrode 2) causes a slight increase in the slope (from 45 to 47 mV/decade) and in the signal itself (curve B). Also, increasing the ratio between KTpClPB and the ionophore from 1:2 to 2:1, with the addition of 1 mg TOPO to the electrode matrix, causes a further increase of the slope, to become completely Nernstian, and the potentiometric signal itself is enhanced (curve C). In the electrode containing ionophore 1 without added TOPO, it was found that increasing the KTpClPB to 200% molar ratio to the ionophore (electrode 3) causes the electrode to become a cesium electrode, i.e. it becomes a poor potassium electrode. This is in agreement with previous studies that show that a large quantity of the lipophilic anion may decrease cation permselectivity for small monovalent cations, due to increased com-

plexation of the ionophore, with the result that the selectivity may be determined by the extractability by the membrane solvent (1, 10). The larger more lipophilic cesium ion is more readily extracted. The addition of TOPO (electrode 4) appears to alleviate the effect of the larger amount of KTpClPB.
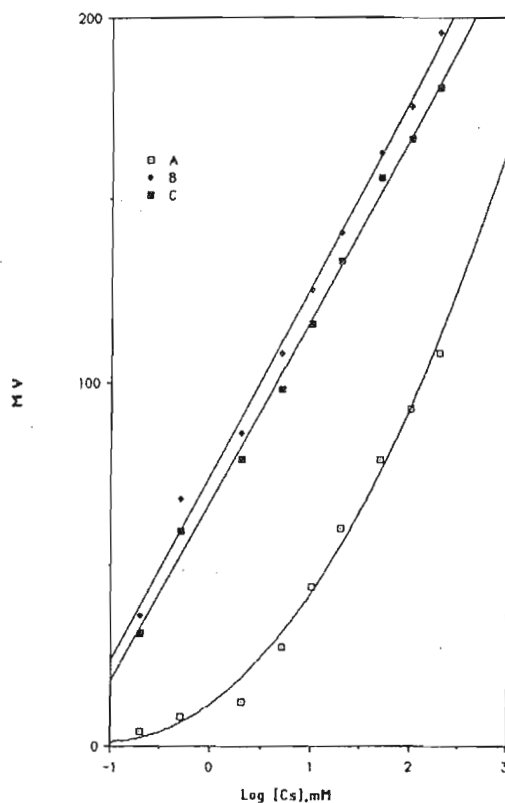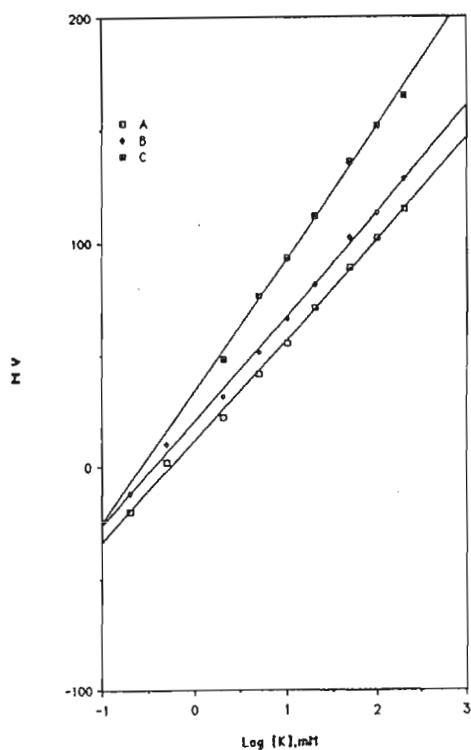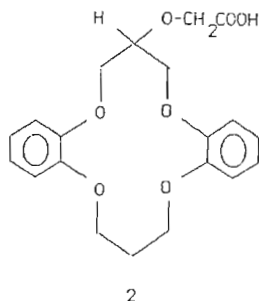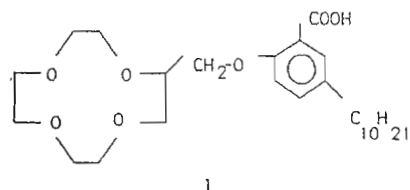

Figure 1. Calibration graphs for potassium standards using electrodes incorporating ionophore 1; curve A, electrode 1, curve B, electrode 2 and curve C, electrode 4.

Figure 2. Calibration graphs for cesium standards, using electrodes incorporating ionophore 2; curve A, electrode 5, curve B, electrode 7, and curve C, electrode 8.

Figure 2 shows the calibration curves for cesium standards using electrodes 5 (curve A), 7 (curve B) and 8 (curve C). Curve A shows a response approaching Nernstian (slope = 50.4 mV/decade) for cesium. Addition of 1 mg TOPO to the electrode matrix (electrode 6) produced poor response with a calibration curve far from Nernstian (slope = 17 mV/decade). The increase in the molar ratio of KTpClPB from half of the ionophore to twice (electrode 7, and curve B) increases the sensitivity, slope and linear portion of the cesium calibration curve. Addition of 1 mg TOPO to the electrode matrix to form electrodes causes a slight decrease in the response and the slope of the calibration curve (curve C) towards cesium.

Selectivity Coefficients

Table II shows the selectivity coefficients and their reciprocals for potassium with respect to cesium, rubidium, sodium, lithium, strontium, calcium and magnesium, using electrodes 1, 2, 3 and 4 incorporating ionophore 1. The selectivity coefficients were determined by both Method 1 (M1) and Method 2 (M2). It is shown, with few exceptions, that the values obtained by the two methods generally either coincide or are very close to each other.

Table II   The selectivity coefficients and their reciprocals for potassium over cesium, rubidium, sodium, lithium, strontium, calcium and magnesium, using electrodes 1–4 incorporating ionophore 1.

Electrode	Elect. Comp.	M / Selectivity	Cs M_1	Cs M_2	Rb M_1	Rb M_2	Na M_1	Na M_2	Li M_1	Li M_2	Sr M_1	Sr M_2	Ca M_1	Ca M_2	Mg M_1	Mg M_2
1	Ionophore 1 + 0.8 mg KTp-ClPB	$K^{pot}_{K,M}$	0.037	0.036	0.59	0.57	0.055	0.054	1.5×10^{-3}	1.5×10^{-3}	0.044	0.043	3.2×10^{-3}	3.2×10^{-3}	4.7×10^{-4}	4.5×10^{-4}
		$\frac{1}{K^{pot}_{K,M}}$	27	28	1.7	1.8	18	18	670	670	23	23	310	310	2100	2200
2	Ionophore 1 + 0.8 mg KTp-ClPB + 1 mg TOPO	$K^{pot}_{K,M}$	0.028	0.029	0.52	0.53	0.028	0.029	2.2×10^{-3}	2.3×10^{-3}	0.026	0.027	3.6×10^{-3}	3.8×10^{-3}	1.9×10^{-3}	2.0×10^{-3}
		$\frac{1}{K^{pot}_{K,M}}$	36	34	1.9	1.9	36	34	450	430	38	37	280	260	530	500
3	Ionophore 1 + 3.2 mg KTp-ClPB	$K^{pot}_{K,M}$	23	23	3	3	3.9×10^{-3}	3.9×10^{-2}	1.8×10^{-3}	1.7×10^{-2}	7.0	37	10	32	0.023	0.034
		$\frac{1}{K^{pot}_{K,M}}$	0.042	0.042	0.33	0.33	260	26	550	59	0.14	0.027	0.10	0.031	43	29
4	Ionophore 1 + 3.2 mg KTp-ClPB + 1 mg TOPO	$K^{pot}_{K,M}$	0.054	0.049	0.72	0.68	0.025	0.025	2.0×10^{-3}	1.9×10^{-3}	4.0×10^{-3}	3.8×10^{-3}	1.8×10^{-3}	5.7×10^{-3}	5.6×10^{-4}	1.8×10^{-3}
		$\frac{1}{K^{pot}_{K,M}}$	19	20	1.4	1.5	40	40	500	530	250	260	550	180	1800	560

M_1: Method 1

M_2: Method 2

Table II shows the selectivity coefficients and their reciprocals for cesium over rubidium, potassium, sodium, lithium, strontium, calcium and magnesium, using electrodes 5, 6, 7 and 8 incorporating ionophore 2. In the case of electrode 6, the selectivity coeffients were not determined by Method 1, due to the low slope of

the curve (17 mV/decade). The selectivity coefficients for cesium with respect to divalent metals were not determined for this electrode, due to the very small and unreproducible signals obtained with divalent ions.

Table III Selectivity coefficients and their reciprocals for cesium over rubidium, potassium, sodium, lithium, strontium, calcium and magnesium, using electrodes 5–8 incorporating ionophore 2.

Electrode	Elect. Comp.	M / Selectivity	Rb M_1	Rb M_2	K M_1	K M_2	Na M_1	Na M_2	Li M_1	Li M_2	Sr M_1	Sr M_2	Ca M_1	Ca M_2	Mg M_1	Mg M_2
5	Ionophore 2 + 1.0 mg KTp-ClPB	$K^{pot}_{Cs,M}$	0.30	0.30	0.15	0.15	0.054	0.055	0.037	0.037	0.28	0.28	0.052	0.052	0.018	0.018
		$\frac{1}{K^{pot}_{Cs,M}}$	3.3	3.3	6.7	6.7	19	18	27	27	3.5	3.5	19	19	56	56
6	Ionophore 2 + 1.0 mg KTp-ClPB + 1 mg TOPO	$K^{pot}_{Cs,M}$	2.6		0.17		0.13		0.87							
		$\frac{1}{K^{pot}_{Cs,M}}$	0.38		5.9		7.7		1.1							
7	Ionophore 2 + 4 mg KTp-ClPB	$K^{pot}_{Cs,M}$	0.21	0.21	0.072	0.076	2.6×10^{-3}	2.7×10^{-3}	1.2×10^{-3}	1.2×10^{-3}	0.022	0.023	4.0×10^{-3}	4.1×10^{-3}	5.7×10^{-4}	9.8×10^{-4}
		$\frac{1}{K^{pot}_{Cs,M}}$	4.8	4.8	14	13	380	370	830	830	45	43	250	240	1800	1000
8	Ionophore 2 + 4 mg KTp-ClPB + 1 mg TOPO	$K^{pot}_{Cs,M}$	0.24	0.20	0.086	0.087	4.3×10^{-3}	4.4×10^{-2}	1.3×10^{-3}	1.5×10^{-3}	0.014	0.014	9.3×10^{-4}	9.5×10^{-4}	7.0×10^{-4}	2.3×10^{-3}
		$\frac{1}{K^{pot}_{Cs,M}}$	4.2	5.0	12	11	230	230	770	620	70	70	1100	1100	1400	430

M_1: Method 1 M_2: Method 2

Effect of the Ratio of KpClPB

The difference in composition between electrodes 1 and 3 is the percentage of KTpClPB, being 50% of the ionophore (molar ratio) in electrode 1 and 200% in electrode 3. From Table II, it is seen that the increase in KTpClPB increases the selectivity towards cesium and rubidium with respect to potassium, increases the selectivity for potassium over sodium, but decreases the selectivity of potassium over lithium and the divalent metals. These effects of the KTpClPB are less obvious between electrodes 2 and 4, which incorporate in addition 1 mg of TOPO, i.e., the TOPO appears to mediate the effect of the lipophilic anion.

In Table III it is clear that the increase of the percentage of KTpClPB enhances the selectivity for cesium with respect to the other ions.

Effect of Trioctylphosphine Oxide (TOPO)

For ionophore I, Table II shows that at low percentage of KTpClPB, TOPO increases the selectivity for potassium over cesium, rubidium, sodium, and strontium, and decreases the selectivity for potassium over lithium, calcium and magnesium, while at high percentage of KTpClPB, it enhances the selectivity of potassium over the rest of the cations except lithium. This is in agreement with previous results (11, 12) that TOPO enhances the selectivity for lithium. For ionophore 1, Table III shows that TOPO decreases the selectivity for cesium over rubidium, potas-

sium, sodium, lithium, and magnesium, but enhances its selectivity with respect to strontium and calcium.

Conclusion

This study demonstrates that the presence and percentages of KTpClPB and TOPO in the electrode matrice, together or alone, may have a remarkable effect on the response of the electrode and its selectivity for a given ion. This effect depends on the type of ionophore, the types of ions involved, and the other components of the electrode matrix. Addition of high concentrations of KTpClPB appear to have the opposite effect of the addition of TOPO. That is, high KTpClPB decreases response towards small monovalent ions while TOPO tends to decrease response to the large ions. By specifying the primary ion to which an ion-selective electrode is needed, it is possible to optimize the composition of the electrode matrix to meet the required function.

Acknowledgement

References

1. D. Ammann, W.E. Morf, P. Anker, P.C. Meier, E. Pretsch and W. Simon, *Ion-Selective Electrode Rev.* **5**, 3–92 (1983).

2. V.P.Y. Gadzekpo, G.J. Moody, J.D.R. Thomas and G.D. Christian, *Ion-Selective Electrode Rev.* **8**, 173–207 (1986).

3. S. Kitazawa, K. Kimura, H. Yano and T. Shono, *J. Am. Chem. Soc.* **106**, 6978–6983 (1984).

4. R.Y. Xie and G.D. Christian, *Anal. Chem.* **58**, 1806–1810 (1986).

5. V.P.Y. Gadzekpo, G.J. Moody and J.D.R. Thomas, *Anal. Proc.* **23**, 62–64 (1986).

6. M. Yamauchi, A. Jyo and N. Ishibashi, *Anal. Chim. Acta* **136**, 399–401 (1982).

7. E. Metzger, R. Dohner, W. Simon, D.J. Vonderschmitt and K. Gautschi, *Anal. Chem.* **59**, 1600–1603 (1987).

8. V.P.Y. Gadzekpo, J.M. Hungerford, A.M. Kadry, Y.A. Ibrahim, R.Y. Xie and G.D. Christian, *Anal. Chem.* **58**, 1948–1953 (1986).

9. P.C. Meier, W.E. Morf, M. Laubli and W. Simon, *Anal. Chim. Acta* **156**, 1–8 (1984).

10. P.C. Meier, W.E. Morf, M. Laubli and W. Simon, *Anal. Chim. Acta* **156**, 1–8 (1984).

11. R.Y. Xie and G.D. Christian, *Analyst* **112**, 61–64 (1987).

12. A.S. Attiyat, G.D. Christian, R.Y. Xie and R.A. Bartsch, *Anal. Chem.*, submitted for publication, 1987.

13. R.Y. Xie, V.P.Y. Gadzekpo, A.M. Kadry, Y.A. Ibrahim, J. Ruzicka and G.D. Christian, *Anal. Chim. Acta* **184**, 259–269 (1986).

14. V.P.Y. Gadzekpo and G.D. Christian, *Anal. Chim. Acta* **164**, 279–282 (1984).

15. IUPAC, *Pure Appl. Chem.* **48**, 129–132 (1976).