

NOVEL SYSTEMS FOR SELECTIVE CATION DETECTION: APPLICATION OF A LIPOPHILIC CARBORANE ANION IN POLYMERIC ION-SELECTIVE ELECTRODES

Martin KRONDAK¹, Radko VOLF² and Vladimír KRÁL^{3,*}

Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic;
e-mail: ¹ martin.krondak@vscht.cz, ² radko.volf@vscht.cz, ³ vladimir.kral@vscht.cz

Received November 9, 2001
Accepted November 16, 2001

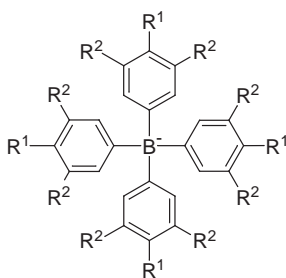
Selectivity and sensitivity of PVC membrane electrode are dramatically influenced not only by the specific receptor, but also, mainly for neutral ionophores, by additional lipophilic co-receptor. For cation detection, tetraphenylborate derivatives have been commonly used. Here, we describe novel systems based on conjunction of the classic cation receptors and a highly lipophilic cobalticborane anionic species. The superiority of this novel co-receptor is demonstrated by application of dibenzo-18-crown-6 and dicyclohexano-18-crown-6 as ionophores in conjunction with the classic lipophilic additive and the novel additive cobalticborane. The presented data show much higher efficiency which makes this additive co-receptor ideal for cation detection and development of novel sensors.

Keywords: Ion selective electrodes; Ionophores; Co-receptors; Lipophilic additives; Carboranes; Cobalticborane; Tetraphenylborates.

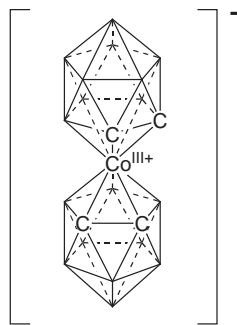
The construction of highly selective electrochemical sensors is one of the leading themes in supramolecular chemistry and technology. Membrane ISE with liquid membrane for potentiometric measurement is a widely used type of sensor with a good power-to-price ratio. This and the wide range of possible analytes makes it a very popular tool in contemporary analytical chemistry.

A key component of each membrane is the receptor – ionophore, which is capable of selectively complexing the ion of interest. To date, many various ionophores are available and development of new ones with better selectivity or selectivity to new analytes is the subject of scientific competition. But properties of ion-selective PVC electrodes (ISE) are influenced by other membrane components, too. Typically, the ratio of PVC matrix and plasticizer determines mechanical properties of the membrane. The lipophilicity of plasticizer determines the interferent influence¹ and also the lipophilic additive strongly affects the electrode response of both neu-

tral and charged ionophore electrodes². The complex mechanism of membrane ISE was addressed by recent studies³. If membrane consists of a neutral ionophore capable of complexing analyte ions, the resulting charge of the complex is equal to the charge of analyte. Thus the counterion is required to maintain the overall charge equilibrium. Impurities from other membrane components can act as counterions, but their amount is very uncertain and the function of this membrane may be very poor, not giving reproducible response. Commonly, highly lipophilic anions or cations are used as lipophilic additives (or, better, co-receptor). Presently, commonly used anionic lipophilic additives are alkali metal tetraphenylborates (TPB). The simplest representative of the TPB family – sodium tetraphenylborate (**1**) – is not lipophilic enough and can leach from membrane. This leaching, although relatively small, is reflected in the lowered membrane lifetime⁴. A better choice is a chlorinated derivative of TPB (**2**). The best to date, in terms of lipophilicity, are tetrakis[3,5-bis(trifluoromethyl)phenyl]borate and tetrakis[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxypropan-2-yl)phenyl]borate⁴ (**3** and **4**). Also hydrophobic sulfonic acid derivatives were used as structurally different lipophilic additives⁵. These have relatively low lipophilicity and thus they were copolymerized with the polymeric matrix of the membrane in order to prevent leaching. In comparison with TPBs, they have charge concentrated in a small space and this leads to increasing interference of other ions due Coulombic interaction between the analyte and lipophilic additive⁵.



	R ¹	R ²
1	H	H
2	Cl	H
3	H	CF ₃
4	H	C(CF ₃) ₂ OCH ₃

**5**

The non-marked atoms are borons, the lines depict the shape of molecule, not bonds

General requirements for a lipophilic co-receptor additive are: (i) high lipophilicity, (ii) delocalized positive or negative charge and (iii) adequate stability. In accordance with those requirements, we introduce the cobalticborane anion **5** as a lipophilic additive for PVC membrane ISE. This co-receptor increases the present assortment of lipophilic additives.

Cobalticborane⁶ (**5**) is a weakly coordinating anion capable of acting as a lipophilic additive in liquid membrane ISE. Cobalticborane and some other common carborane derivatives are large anions with strongly delocalized charge and thus they are hot candidates for the use in ISE. Due to high lipophilicity, they are currently used as counterions in organic synthesis for crystallization. Another advantage of these novel co-receptors is the possibility of modifying them on the periphery of the carborane cage, *e.g.* by halogenation⁷, thus further increasing lipophilicity, and also of modifying binding properties by the introduction positive or negative charge. This general methodology opens a new way for the construction of ISE.

EXPERIMENTAL

In order to verify whether cobalticborane can operate as a lipophilic additive, a standard experimental setup with a PVC membrane containing 2-nitrophenyl octyl ether (NPOE) as the plasticizer (33% PVC, 64% NPOE) was used. Classic cation binding receptors, dibenzo-18-crown-6 (DB18C6) and dicyclohexano-18-crown-6 (DCH18C6) were used as ionophores (1%); both of which are known for their selectivity to potassium ions. They are well examined receptors with known properties and thus they provide a good platform for testing of other membrane components, specifically counterion binding co-receptors. The influence of cobalticborane **5** was compared with the simplest representative of the tetraphenylborate family – sodium tetraphenylborate (50 mole % relative to the ionophore). The scheme of potentiometric measuring cell was: SCE/0.1 M NaCl/test solution/PVC membrane/0.1 M NaCl/AgCl/Ag. Testing solutions were chlorides of Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ and NH₄⁺ in water. Concentrations were from 10⁻¹ to 10⁻⁸ mol/l.

RESULTS AND DISCUSSION

The results of the potentiometric measurements are collected in Table I, which summarizes sensitivities and working ranges for the electrodes depending on the cations tested.

Responses of cations are mainly determined by their affinity to the ionophore and by their hydrophilicity/lipophilicity. It is not surprising that potassium ions provide the best response, because both used ionophores are well known for their affinity to K⁺. Hydrophilic lithium cations provide a much lower response in a close working range. Sodium and rubidium ions

TABLE I
Sensitivities and working ranges of tested PVC ISE-membranes

Active component	Li ⁺		Na ⁺		K ⁺		Rb ⁺		Cs ⁺		NH ₄ ⁺	
	slope mV/dec	range mol/l	slope mV/dec	range mol/l	slope mV/dec	range mol/l	slope mV/dec	range mol/l	slope mV/dec	range mol/l	slope mV/dec	range mol/l
1	2	^a	3	^a	15	10 ⁻⁴ -10 ⁻¹	18	10 ⁻⁵ -10 ⁻¹	25	10 ⁻⁴ -10 ⁻¹	16	10 ⁻⁵ -10 ⁻¹
5	6	10 ⁻³ -10 ⁻¹	12	10 ⁻⁴ -10 ⁻¹	24	10 ⁻⁴ -10 ⁻¹	12	10 ⁻⁴ -10 ⁻¹	33	10 ⁻⁴ -10 ⁻¹	8	10 ⁻³ -10 ⁻¹
DB18C6	3	^a	7	10 ⁻² -10 ⁻¹	10	10 ⁻⁴ -10 ⁻¹	12	10 ⁻³ -10 ⁻¹	8	10 ⁻⁴ -10 ⁻¹	8	10 ⁻³ -10 ⁻¹
DCH18C6	14	10 ⁻⁵ -10 ⁻¹	17	10 ⁻⁵ -10 ⁻¹	28	10 ⁻⁵ -10 ⁻¹	29	10 ⁻⁵ -10 ⁻¹	19	10 ⁻⁵ -10 ⁻¹	28	10 ⁻⁵ -10 ⁻¹
DB18C6 + 1	11	10 ⁻³ -10 ⁻¹	27	10 ⁻⁵ -10 ⁻¹	49	10 ⁻⁵ -10 ⁻¹	37	10 ⁻⁵ -10 ⁻¹	29	10 ⁻⁵ -10 ⁻¹	37	10 ⁻⁵ -10 ⁻¹
DCH18C6 + 1	22	10 ⁻² -10 ⁻¹	24	10 ⁻⁴ -10 ⁻¹	46	10 ⁻⁵ -10 ⁻¹	37	10 ⁻⁵ -10 ⁻¹	31	10 ⁻⁴ -10 ⁻¹	35	10 ⁻⁵ -10 ⁻¹
DB18C6 + 5	14	10 ⁻² -10 ⁻¹	36	10 ⁻⁴ -10 ⁻¹	55	10 ⁻⁵ -10 ⁻¹	41	10 ⁻⁵ -10 ⁻¹	38	10 ⁻⁵ -10 ⁻¹	30	10 ⁻⁵ -10 ⁻¹
DCH18C6 + 5	27	10 ⁻² -10 ⁻¹	27	10 ⁻⁴ -10 ⁻¹	51	10 ⁻⁵ -10 ⁻¹	41	10 ⁻⁵ -10 ⁻¹	32	10 ⁻⁵ -10 ⁻¹	43	10 ⁻⁵ -10 ⁻¹

^a The working range could not be evaluated.

show response between K^+ and Li^+ . These data are consistent with the well known ionophore selectivity. The relatively high response of cesium ions can be explained by their high lipophilicity compared with other alkali metal cations. The ammonium cation (NH_4^+) is the most important interferent for K^+ sensors based on crown ether ionophores, because of very similar steric requirements – it can fit in the cavity of the crown. The diameter of NH_4^+ cation is 143 pm and that of K^+ ions is 133 pm.

On the other hand, data can be interpreted in terms of membrane compositions. The membrane containing only the PVC–NPOE matrix (not shown in Table I) did not show any response, as expected; its potential was approximately constant. The next compared systems were membranes containing only a lipophilic additive – TPB **1** or cobalticborane **5**. Their responses to analytes in question are determined by non-specific Coulombic interaction of the analyte cation and the lipophilic additive anion. Thus these responses reflect mainly the analyte lipophilicity. The third set of control experiments was measurement of membranes with receptor only, *i.e.* with dibenzo-18-crown-6 and dicyclohexano-18-crown-6. The membranes based on neutral ionophores cannot function without a lipophilic additive co-receptor (membrane impurities partially often work as a lipophilic additive, if it is absent). The function of these membranes cannot be and is not optimum, but data show preference of potassium cations, because the main driving force is the analyte–receptor interaction.

The last four tested membranes contained both an ionophore and lipophilic additive. There was a clear preference of K^+ cations, which show a response from 46 to 55 mV per concentration decade in the range from 10^{-5} to 10^{-1} mol/l. In this case, selectivity of ISE is determined by selectivity of the used ionophore. Overall, membranes with cobalticborane **5** show better response than those with tetraphenylborate **1**. AAS analysis (monitoring cobalt concentration in solution) showed only small leakage of the co-receptor into the water phase under the experimental conditions used for testing membranes (less than 4 μ g of Co).

CONCLUSIONS

In conclusion, the work presented here demonstrates the possibility of using cobalticborane anions as a lipophilic additive co-receptor for liquid-membrane ion-selective electrode. The data showed that cobalticborane works in an ISE better than the commonly used TPB salts and thus improves the electrode performance. Furthermore, carborane properties important for ISE application, such as lipophilicity, can be affected by

substitution of the carborane cage, such as fluorination. Also, a delocalized positive or negative charge can be introduced. Thus, the charged co-receptors open a possibility of cation or anion sensing depending on the chosen member of carborane family. Therefore, carboranes seem to be attractive compounds for electrochemical sensor development.

This work was supported by Howard Hughes Medical Institute (grant No. 75195-541101 for V. K.) and the Ministry of Education, Youth and Sports of the Czech Republic (project CEZ:J19/98:223400008). Special thanks of the authors are due to Ms J. Komínková for her help with AAS analysis.

REFERENCES AND NOTES

1. Koryta J., Štulík K.: *Ion-Selective Electrodes*. Academia, Prague 1984.
2. a) Petrukhin O. M., Frakiisky Ye. V., Kharitonov A. B., Urusov Yu. I., Baulin V. Ye.: *Anal. Chim. Acta* **1999**, *385*, 125; b) Amemiya S., Bühlmann P., Pretsch E., Rusterholz B., Umezawa Y.: *Anal. Chem.* **2000**, *72*, 1618.
3. a) Amemiya S., Bühlmann P., Pretsch E., Rusterholz B., Umezawa Y.: *Anal. Chem.* **2000**, *72*, 1618; b) Kroncak M., Shishkanova T. V., Holakovský R., Volf R., Stibor I., Král V.: *Anal. Chim. Acta* **2001**, in press; c) Král V., Sessler J. L., Shishkanova T. V., Gale P. A., Volf R.: *J. Am. Chem. Soc.* **1999**, *121*, 8771.
4. Bakker E., Pretsch E.: *Anal. Chim. Acta* **1995**, *309*, 7.
5. Rosatzin T., Bakker E., Suzuki K., Simon W.: *Anal. Chim. Acta* **1993**, *280*, 197.
6. a) Hawthorne M. F., Young D. C., Andrews T. D., Howe D. V., Pilling R. L., Pitts A. D., Reintjes M., Warren L. F., Jr., Wegner P. A.: *J. Am. Chem. Soc.* **1968**, *90*, 1907; b) Sivaev I. B., Bregadze V. I.: *Collect. Czech. Chem. Commun.* **1999**, *64*, 783.
7. a) King B. T., Michl J.: *J. Am. Chem. Soc.* **2000**, *122*, 10255; b) Santos E. C., Pinkerton A. B., Kinkead S. A., Hurlburt P. K., Jasper S. A., Sellers C. W., Huffman J. C., Todd L. J.: *Polyhedron* **2000**, *19*, 1777.