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*DITHIOCARBOXYLATES IN ION SELECTIVE  
MEMBRANES*

Summary of doctoral thesis

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## **SHORTENINGS.**

- ADiOE - diisooctylester of adipic acid
- BAE - amilester of benzene acid
- DBF - dibutylphthalate
- EAS - electrode-active substance
- IR - infrared
- izo-TBF - izotributylphosphate
- ISE - ion selective electrode
- NBOE - octylester of p-nitrobenzene acid
- NC - 2-nitro-p-cimol
- PVC - polyvinylchloride
- SDiBE - diisobuthylester of sebacic acid
- TBF - tributylphosphate

For more than 25 years the Department of Analytical chemistry of the University of Latvia has been dealing with the synthesis and investigation of dithiocarboxylic acids. Till the beginning of 1980s these investigations were mainly conducted by use of spectrophotometric methods. This work resulted in photometric extraction methods for the determination of various metal ions.

These investigations laid the basis for further systematic studies in the field of ionometry. The use of dithiocarboxylates in ion selective electrodes extends the limits of their application. Many dithiocarboxylates can not be used in spectrophotometry because of their little reaction contrast, whereas they can frequently be successfully applied in ionometry where the colour is not relevant.

Chelate compounds were first reported in literature in 1967 when Shatkay and his co-workers introduced calcium theonyltrifluoroacetate into a polyvinylchloride matrix. Several other chelate compounds have been reported in literature. Dialkyldithiophosphates studied at the Department of Physical Chemistry of St. Petersburg University under the leadership of the academician Nicolsky are the closest among them. There have been attempts to introduce dithizonates, but they have led to no considerable success. The survey of publications shows that the use of chelates in plasticized membranes, which are considered to be the most promising ones, has been insignificant (only four chelates). It is partly due to the small number of publications on the investigations of chelates in solvents which are plasticizers as well (e.g. tributylphosphate, dibutylphthalate or sebacic and adipic acid esters). It makes the investigations easier.

As the theory explaining the activity of ion selective electrodes has not been worked out completely so far, ionometric studies of dithiocarboxylates were started with benzenedithiocarboxylates and their compounds with metal ions. Benzenedithiocarboxylic acid is the simplest one among aromatic dithiocarboxylic acids. Besides, it is produced commercially as a reagent.

One of the first tasks of the present investigations was to work out the procedure for preparing the film. That included selecting conditions for the introducing of dithiocarboxylates and choosing appropriate plasticizer. Two ways of introducing were tested. According to the first method dithiocarboxylic acid was introduced into the film, and after that keeping the film in a metal ion solution the acid in the film was transformed to the corresponding chelate. When using the second approach, appropriate conditions for the extraction of a corresponding dithiocarboxylate were selected and the extract was subsequently introduced into the polyvinylchloride film. The second so called "extraction method", was more suitable, as the characteristics of the obtained membranes were more stable and reproducible.

The next important step was to find an appropriate plasticizer. It turned out that traditional extracting agents used in spectrophotometry could not be applied, as they did not meet the requirements of plasticizers. Whereas the choice of other plasticizers was limited by the slight solubility of benzenedithiocarboxylates in them. Tributylphosphate turned out to be the most suitable among the plasticizers. In the course of the studies of benzenedithiocarboxylates the introduction of several chelates into plasticized PVC membrane was tested, but only the complex compounds of zinc(II), cadmium(II), cobalt(II) and nickel(II) with benzenedithiocarboxylic proved to be suitable for further investigations. Others were too unstable and decomposed during the preparation of the membrane, or their stability was too high and their dissociation on the boundary surface of the membrane and the liquid was limited. The prepared zinc and cadmium-selective membranes were sensitive to the change of concentration of the corresponding ions in the range pMe 1,0 - 4,5 with slope 26,0 mV/pZn and 25,5 mV/pCd correspondingly. The characteristics of the cobalt and nickel-selective membranes turned out to be slightly worse.

When investigating the plasticized membranes of benzenedithiocarboxylates, it was observed that membrane characteristics depended on the concentration of the electrode-active substance (the corresponding chelate). The solubility of benzenedithiocarboxylates being limited, it was necessary to choose the derivatives of benzenedithiocarboxylic acid whose solubility in tributylphosphate is higher in order to obtain membranes having better characteristics. During subsequent investigations, various hydroxyderivatives of benzenedithiocarboxylic acid were synthesized and studied. The following hydroxyderivatives were used for preparing the plasticized membranes: 2-hydroxybenzenedithiocarboxylates (I), 2,4-dihydroxybenzenedithiocarboxylates (II), 2,3,4-trihydroxybenzenedithiocarboxylates (III), 3-methoxy-4-hydroxybenzenedithiocarboxylates (IV), 4-hydroxybenzenedithiocarboxylates (V). The characteristics of the obtained membrane electrodes are given in table 1 and 2.

These tables show that the concentration of the electrode-active substance in the membrane should be no less than 0,1 mol/l. The reducing of concentration in the membrane affects the characteristics of electrodes. First of all, it reduces the range of the concentrations to be determined. Though, each chelate has its own concentration limit. In the case of II-Zn(II) chelate this concentration is 0,05 mol/l. As results from the data given in table 1 and 2, the best membranes are the ones containing II-Zn(II), IV-Zn(II), II-Cd(II), IV-Cd(II) chelates.

The influence of the anions was studied by use of the membrane containing chelate II-Cd(II). The presence of anions turned out to have no

Table 1.  
Characteristics of Some Plasticized Membrane Electrodes Based on  
Hydroxybenzenedithiocarboxylates.

| Electrode-active substance | Conc. of EAS in membrane, mol/l | Concentration range of linear response, mol/l | Linear slope, mV/pMe | pH range  | Life time of the electrode, weeks |
|----------------------------|---------------------------------|---|----------------------|-----------|-----------------------------------|
| I - Zn (II)                | $5 \cdot 10^{-3}$               | $1 \cdot 10^{-3} - 1 \cdot 10^{-1}$           | 19.0                 | 4.8 - 5.9 | 1                                 |
| II - Zn(II)                | $5 \cdot 10^{-2}$               | $1 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 29.5                 | 3.5 - 6.0 | 12                                |
| V - Zn(II)                 | $5 \cdot 10^{-3}$               | $3 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 25.2                 | 4.6 - 6.4 | 1                                 |
| I - Cd(II)                 | $5 \cdot 10^{-3}$               | $1 \cdot 10^{-3} - 1 \cdot 10^{-1}$           | 16.0                 | 3.5 - 6.5 | 1                                 |
| II - Cd(II)                | $5 \cdot 10^{-2}$               | $5 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 29.0                 | 3.5 - 6.5 | 12                                |
| III - Cd(II)               | $5 \cdot 10^{-2}$               | $5 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 26.0                 | 3.5 - 6.5 | 1                                 |
| V - Cd(II)                 | $5 \cdot 10^{-3}$               | $4 \cdot 10^{-4} - 2 \cdot 10^{-1}$           | 21.0                 | 4.1 - 6.2 | 1                                 |
| II - Ni(II)                | $5 \cdot 10^{-2}$               | $5 \cdot 10^{-4} - 1 \cdot 10^{-1}$           | 24.0                 | 3.0 - 7.0 | 12                                |
| III - Ni(II)               | $5 \cdot 10^{-2}$               | $1 \cdot 10^{-4} - 1 \cdot 10^{-1}$           | 24.0                 | 3.5 - 7.0 | 1                                 |
| II - Co(II)                | $5 \cdot 10^{-2}$               | $5 \cdot 10^{-4} - 1 \cdot 10^{-1}$           | 24.0                 | 3.0 - 7.0 | 12                                |
| III - Co(II)               | $5 \cdot 10^{-2}$               | $1 \cdot 10^{-4} - 1 \cdot 10^{-1}$           | 23.0                 | 3.5 - 7.0 | 1                                 |
| V - Co(II)                 | $5 \cdot 10^{-3}$               | $3 \cdot 10^{-5} - 1 \cdot 10^{-3}$           | 10.0                 | 3.7 - 6.9 | 1                                 |
|                            |                                 | $1 \cdot 10^{-3} - 1 \cdot 10^{-1}$           | 25.0                 | 3.7 - 6.9 |                                   |
| II - Tl(I)                 | $5 \cdot 10^{-2}$               | $4 \cdot 10^{-4} - 1 \cdot 10^{-1}$           | 52.0                 | 3.7 - 6.9 | 4                                 |

Table 2.  
Characteristics of Some Plasticized Membrane Electrodes Based on  
4-Hydroxybenzenedithiocarboxylates.

| Electrode-active substance | Conc. of EAS in membrane, mol/l | Concentration range of linear response, mol/l | Linear slope, mV/pMe | pH range  | Life time of the electrode, months |
|----------------------------|---------------------------------|---|----------------------|-----------|------------------------------------|
| IV - Zn(II)                | $3 \cdot 10^{-1}$               | $1 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 28.5                 | 3.5 - 6.0 | 6                                  |
| IV - Zn(II)                | $2 \cdot 10^{-1}$               | $1 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 28.5                 | 3.5 - 6.0 | 6                                  |
| IV - Zn(II)                | $1 \cdot 10^{-1}$               | $1 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 28.5                 | 3.5 - 6.0 | 6                                  |
| IV - Zn(II)                | $5 \cdot 10^{-2}$               | $5 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 27.0                 | 3.5 - 6.0 | -                                  |
| IV -Cd(II)                 | $3 \cdot 10^{-1}$               | $1 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 28.0                 | 3.5 - 6.5 | 6                                  |
| IV -Cd(II)                 | $2 \cdot 10^{-1}$               | $1 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 28.0                 | 3.5 - 6.5 | 6                                  |
| IV -Cd(II)                 | $1 \cdot 10^{-1}$               | $1 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 28.0                 | 3.5 - 6.5 | 6                                  |
| IV -Cd(II)                 | $5 \cdot 10^{-2}$               | $5 \cdot 10^{-5} - 1 \cdot 10^{-1}$           | 26.0                 | 3.5 - 6.5 | -                                  |
| IV -Co(II)                 | $3 \cdot 10^{-1}$               | $1 \cdot 10^{-4} - 1 \cdot 10^{-1}$           | 9.0                  | 3.0 - 7.2 | -                                  |
| IV -Co(II)                 | $5 \cdot 10^{-2}$               | $4 \cdot 10^{-4} - 1 \cdot 10^{-1}$           | 9.0                  | 3.0 - 7.2 | -                                  |
| IV - Ni(II)                | $3 \cdot 10^{-1}$               | $3 \cdot 10^{-4} - 1 \cdot 10^{-1}$           | 13.0                 | 3.0 - 7.0 | -                                  |
| IV - Ni(II)                | $5 \cdot 10^{-2}$               | $5 \cdot 10^{-4} - 1 \cdot 10^{-1}$           | 13.0                 | 3.0 - 7.0 | -                                  |
| IV - Tl(I)                 | $1 \cdot 10^{-2}$               | $1 \cdot 10^{-3} - 1 \cdot 10^{-1}$           | 38.0                 | 4.1 - 9.0 | 2                                  |

effect on the concentration range of cadmium(II) ions, but it changed the linear slope :



The numerical values of the linear slope are given in the brackets in the line above. The presence of iodide ions reduces twice the sensitivity of the method of determination. This is due to the action of anions upon cadmium ions contained in the chelate.

When studying the plasticized membranes of benzenedithiocarboxylates, it was observed that plasticizers affect the characteristics of electrodes, as they are not inert towards the changes in the activity of ions. It could be observed in the case of TBF which being a polar solvent possesses cation-selective electrode function. But in other plasticizers EAS solubility is not sufficient to ensure invariability of the linear slope and the lowest possible detection limit. In order to reduce the influence of the plasticizer, membranes were prepared from a mixture of plasticizers, apart from TBF there was some other organic solvent. These solvents were different, some being more neutral, others with dominating anion-selective function. Characteristics of the prepared membranes are given in table 3.

Table 3.

Dependence of Membrane Electrode Characteristics of 4-Hydroxy-benzenedithiocarboxylates on the Mixture of Plasticizers.

| Plasticizers   | IV - Zn(II)                           |                      | IV- Cd(II)                            |                      |
|----------------|---------------------------------------|----------------------|---------------------------------------|----------------------|
|                | Linear concentration range, mol/l     | Linear slope, mV/pZn | Linear concentration range, mol/l     | Linear slope, mV/pCd |
| TBF            | $1,0 \cdot 10^{-5} - 1 \cdot 10^{-1}$ | 28.5                 | $1,0 \cdot 10^{-5} - 1 \cdot 10^{-1}$ | 28.0                 |
| TBF: ADiOE=1:1 | $2,5 \cdot 10^{-6} - 1 \cdot 10^{-1}$ | 29.0                 | $4,0 \cdot 10^{-6} - 1 \cdot 10^{-1}$ | 29.0                 |
| TBF: NBOE =1:1 | $1,0 \cdot 10^{-5} - 1 \cdot 10^{-1}$ | 29.0                 | $8,0 \cdot 10^{-6} - 1 \cdot 10^{-1}$ | 29.0                 |
| TBF: NC = 1:1  | $3,8 \cdot 10^{-6} - 1 \cdot 10^{-1}$ | 29.0                 | $5,2 \cdot 10^{-6} - 1 \cdot 10^{-1}$ | 29,0                 |

The table 3 shows that by use of mixture of plasticizers it is possible to increase the range of concentrations to be determined (by extending the lowest limit) and to increase slightly the linear slope, reaching the theoretical Nernstian slope.

When testing the optimum mass ratio, it was found to be 1:1. The tests showed that the influence of various plasticizers and their mixtures on the membrane potential from solution pH was insignificant (about 0,5 pH units).

One of the most important ISE characteristics are their potentiometric selectivity coefficients. It was determined by use of the technique recommended

by IUPAC - the method of "mixed solutions" at constant concentration (0,01 mol/l) of interfering ions. After testing selectivity coefficients of all the prepared membranes, it was found that the best ones are the membranes containing zinc(II) and cadmium(II) 4-hydroxydithiocarboxylates as EAS. Patents for these ion selective electrodes have been issued. Potentiometric selectivity coefficients of these membranes are given in table 4 and 5.

Table 4.

Dependence of Potentiometric Selectivity Coefficients of Plasticized Membranes Based on Zinc(II) 4-hydroxydithiocarboxylate on the mixture of Plasticizers

| Interfering ion, B           | $K_{A/B}^{pot}$     |                     |                     |                     |
|------------------------------|---------------------|---------------------|---------------------|---------------------|
|                              | TBF                 | TBF: ADIOE =1:1     | TBF: NBOE=1:1       | TBF: NC=1:1         |
| Li <sup>+</sup>              | $2,0 \cdot 10^{-1}$ | $5,6 \cdot 10^{-1}$ | $2,2 \cdot 10^{-1}$ | $1,2 \cdot 10^{-1}$ |
| Na <sup>+</sup>              | $2,0 \cdot 10^{-3}$ | $4,1 \cdot 10^{-3}$ | $5,0 \cdot 10^{-3}$ | $7,8 \cdot 10^{-2}$ |
| K <sup>+</sup>               | $3,8 \cdot 10^{-4}$ | $3,9 \cdot 10^{-4}$ | $3,1 \cdot 10^{-4}$ | $4,2 \cdot 10^{-4}$ |
| Rb <sup>+</sup>              | $2,1 \cdot 10^{-4}$ | $1,8 \cdot 10^{-4}$ | $1,9 \cdot 10^{-4}$ | $1,7 \cdot 10^{-4}$ |
| Cs <sup>+</sup>              | $1,0 \cdot 10^{-4}$ | $1,0 \cdot 10^{-4}$ | $1,0 \cdot 10^{-4}$ | $1,0 \cdot 10^{-4}$ |
| NH <sub>4</sub> <sup>+</sup> | $1,9 \cdot 10^{-1}$ | $2,5 \cdot 10^{-2}$ | $2,5 \cdot 10^{-2}$ | $1,1 \cdot 10^{-2}$ |
| Mg <sup>2+</sup>             | $1,9 \cdot 10^{-3}$ | $2,5 \cdot 10^{-3}$ | $2,0 \cdot 10^{-3}$ | $1,0 \cdot 10^{-2}$ |
| Ca <sup>2+</sup>             | $4,0 \cdot 10^{-4}$ | $7,8 \cdot 10^{-4}$ | $6,5 \cdot 10^{-4}$ | $1,1 \cdot 10^{-3}$ |
| Sr <sup>2+</sup>             | $1,9 \cdot 10^{-4}$ | $1,1 \cdot 10^{-4}$ | $1,2 \cdot 10^{-4}$ | $4,0 \cdot 10^{-4}$ |
| Ba <sup>2+</sup>             | $1,0 \cdot 10^{-4}$ | $1,0 \cdot 10^{-4}$ | $1,0 \cdot 10^{-4}$ | $1,0 \cdot 10^{-4}$ |
| Cu <sup>2+</sup>             | 10,1                | 12,3                | 7,5                 | 7,9                 |
| Ag <sup>+</sup>              | disturb             | disturb             | disturb             | disturb             |
| Cd <sup>2+</sup>             | 3,7                 | 2,9                 | 5,6                 | 2,5                 |
| Hg <sup>2+</sup>             | disturb             | disturb             | disturb             | disturb             |
| Pb <sup>2+</sup>             | disturb             | disturb             | disturb             | disturb             |
| Mn <sup>2+</sup>             | $2,0 \cdot 10^{-2}$ | $1,8 \cdot 10^{-2}$ | $1,0 \cdot 10^{-2}$ | $4,8 \cdot 10^{-2}$ |
| Fe <sup>2+</sup>             | $2,0 \cdot 10^{-2}$ | $1,2 \cdot 10^{-2}$ | $9,5 \cdot 10^{-3}$ | $3,7 \cdot 10^{-2}$ |
| Co <sup>2+</sup>             | $6,7 \cdot 10^{-3}$ | $4,1 \cdot 10^{-3}$ | $2,0 \cdot 10^{-3}$ | $2,2 \cdot 10^{-3}$ |
| Ni <sup>2+</sup>             | $6,7 \cdot 10^{-3}$ | $4,1 \cdot 10^{-3}$ | $3,8 \cdot 10^{-3}$ | $4,5 \cdot 10^{-3}$ |

These tables of electrode selectivity coefficients show that the determination of zinc(II) and cadmium(II) is strongly hindered by the presence of lead(II), copper(II) and mercury(II) ions in the solution under analysis. At the presence of these ions, more stable 4-hydroxybenzenedithiocarboxylates are formed in the membrane. As a result, ion exchange with the membrane is strongly reduced, and electrode function is lost, consequently the membrane can not be used in further studies. In the case of a zinc-selective membrane the presence of cadmium(II) ions is not desirable, as they displace zinc(II) ions

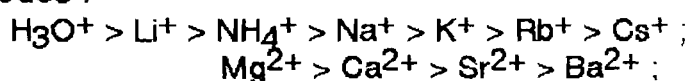
in the chelate with cadmium ions, and the membrane loses its zinc-selective electrode function.

Table 5.

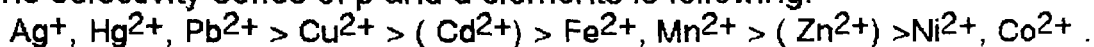
Dependence of Potentiometric Selectivity Coefficients of Plasticized Membranes Based on Cadmium(II) 4-hydroxydithiocarboxylate on the mixture of Plasticizers.

| Interfering ion, B           | $K_{A/B}^{pot}$      |                      |                      |                      |
|------------------------------|----------------------|----------------------|----------------------|----------------------|
|                              | TBF                  | TBF:ADiOE=1:1        | TBF:NBOE=1:1         | TBF:NC=1:1           |
| Li <sup>+</sup>              | 1,0.10 <sup>-1</sup> | 1,4.10 <sup>-1</sup> | 1,5.10 <sup>-1</sup> | 7,5.10 <sup>-2</sup> |
| Na <sup>+</sup>              | 5,9.10 <sup>-3</sup> | 6,5.10 <sup>-3</sup> | 7,9.10 <sup>-3</sup> | 7,2.10 <sup>-3</sup> |
| K <sup>+</sup>               | 6,0.10 <sup>-4</sup> | 6,3.10 <sup>-4</sup> | 7,8.10 <sup>-4</sup> | 7,4.10 <sup>-4</sup> |
| Rb <sup>+</sup>              | 1,8.10 <sup>-4</sup> | 1,9.10 <sup>-4</sup> | 2,5.10 <sup>-4</sup> | 2,4.10 <sup>-4</sup> |
| Cs <sup>+</sup>              | 1,0.10 <sup>-4</sup> | 1,0.10 <sup>-4</sup> | 1,0.10 <sup>-4</sup> | 1,0.10 <sup>-4</sup> |
| NH <sub>4</sub> <sup>+</sup> | 3,0.10 <sup>-2</sup> | 4,1.10 <sup>-2</sup> | 1,1.10 <sup>-2</sup> | 1,1.10 <sup>-2</sup> |
| Mg <sup>2+</sup>             | 2,0.10 <sup>-3</sup> | 1,5.10 <sup>-3</sup> | 1,5.10 <sup>-3</sup> | 1,2.10 <sup>-3</sup> |
| Ca <sup>2+</sup>             | 8,1.10 <sup>-4</sup> | 9,5.10 <sup>-4</sup> | 9,8.10 <sup>-4</sup> | 9,7.10 <sup>-4</sup> |
| Sr <sup>2+</sup>             | 4,0.10 <sup>-4</sup> | 3,5.10 <sup>-4</sup> | 2,5.10 <sup>-4</sup> | 2,7.10 <sup>-4</sup> |
| Ba <sup>2+</sup>             | 1,0.10 <sup>-4</sup> | 1,0.10 <sup>-4</sup> | 1,0.10 <sup>-4</sup> | 1,0.10 <sup>-4</sup> |
| Cu <sup>2+</sup>             | 5,6                  | 5,0                  | 5,6                  | 8,9                  |
| Ag <sup>+</sup>              | disturb              | disturb              | disturb              | disturb              |
| Zn <sup>2+</sup>             | 2,0.10 <sup>-2</sup> | 1,5.10 <sup>-2</sup> | 1,2.10 <sup>-2</sup> | 1,0.10 <sup>-2</sup> |
| Hg <sup>2+</sup>             | disturb              | disturb              | disturb              | disturb              |
| Mn <sup>2+</sup>             | 1,0.10 <sup>-2</sup> | 2,5.10 <sup>-1</sup> | 1,5.10 <sup>-2</sup> | 1,2.10 <sup>-2</sup> |
| Fe <sup>2+</sup>             | 1,0.10 <sup>-2</sup> | 1,0.10 <sup>-1</sup> | 1,5.10 <sup>-1</sup> | 1,8.10 <sup>-1</sup> |
| Co <sup>2+</sup>             | 6,1.10 <sup>-3</sup> | 5,8.10 <sup>-3</sup> | 5,1.10 <sup>-3</sup> | 3,4.10 <sup>-3</sup> |
| Ni <sup>2+</sup>             | 6,1.10 <sup>-3</sup> | 5,9.10 <sup>-3</sup> | 4,5.10 <sup>-3</sup> | 2,3.10 <sup>-3</sup> |
| Pb <sup>2+</sup>             | disturb              | disturb              | disturb              | disturb              |

In accordance with potentiometric selectivity coefficients the following s-element selectivity series can be drawn for all investigated plasticized membrane electrodes :



The selectivity series of p and d elements is following:



Taking into account potentiometric selectivity coefficients, samples to be analysed for the use of electrodes can be selected. In cooperation with the Rostov plant "Almaz" zinc-selective electrode was introduced for the testing of zinc(II) ions during the electrolysis. The calibration curve method was used for



the control of zinc(II) ions. The only procedure to be carried out was its tenfold dilution.

Liquid membranes are one of the widely applied kinds of ISE using chelates as EAS. In order to compare liquid membranes with the plasticized ones, liquid membranes with following dithiocarboxylates were prepared: cadmium(II) 2,4-dihydroxybenzenedithiocarboxylate (I), cobalt(II) 2,4-dihydroxybenzenedithiocarboxylate (II), cobalt(II) 2,3,4-trihydroxybenzenedithiocarboxylate (III).

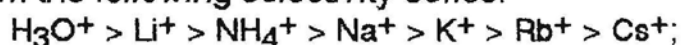
As the organic solvent should be heavier than water, should not mix with water and dissolve in it, should dissolve the chelate well enough, these requirements considerably limit the choice of the solvents. In liquid membranes the mixtures of various esters of phosphoric acid and isoamyl alcohol with chloroform were used as solvents. The characteristics of the prepared membranes are given in table 6 and 7.

Table 6.

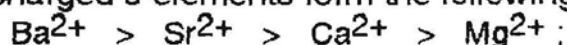
Electrode Characteristics of Liquid Cadmium-selective and Cobalt-selective Membranes.

| Electrode active chelate | Solvent mixture with chloroform (1:1) | Concentration range of linear respons, mol/l | Linear slope, mV/pMe | pH range  | Life time of electrode, weeks |
|--------------------------|---------------------------------------|--|----------------------|-----------|-------------------------------|
| I                        | tributilfosfāts                       | $1 \cdot 10^{-4}$ - $1 \cdot 10^{-1}$        | 28.0                 | 3.5 - 5.5 | 3                             |
| I                        | izoamilspirts                         | $2 \cdot 10^{-4}$ - $1 \cdot 10^{-1}$        | 31.0                 | 3.5 - 5.2 | 3                             |
| I                        | tripentilfosfāts                      | $3 \cdot 10^{-4}$ - $1 \cdot 10^{-1}$        | 30.0                 | 3.5 - 5.5 | 3                             |
| III                      | tributilfosfāts                       | $1 \cdot 10^{-4}$ - $1 \cdot 10^{-1}$        | 30.0                 | 3.2 - 6.3 | 1                             |
| II                       | tributilfosfāts                       | $1 \cdot 10^{-4}$ - $1 \cdot 10^{-1}$        | 25.0                 | 3.1 - 6.5 | 1                             |
| III                      | izoamilspirts                         | $1 \cdot 10^{-4}$ - $1 \cdot 10^{-1}$        | 28.0                 | -         | -                             |
| II                       | izoamilspirts                         | $1 \cdot 10^{-4}$ - $1 \cdot 10^{-1}$        | 24.0                 | -         | -                             |

Depending on the degree of interference on the electrode potential of liquid membranes cations of the singly charged s-elements, hydroxonium and ammonium ions form the following selectivity series:



This series is similar to the one obtained when studying the plasticized membranes. Doubly charged s-elements form the following selectivity series:



This series has the opposite sequence in comparison to the one obtained when studying the plasticized membranes. The selectivity quene for p and d elements is following:



Table 7.

Potentiometric Selectivity Coefficients for Liquid Cadmium-selective and Cobalt-selective Membranes (solvent - the mixture of chloroform with TBF, Ia - chloroform with triphenylphosphate).

| Interfering ion, B           | $K_{A/B}^{pot}$      |                      |                      |                      |
|------------------------------|----------------------|----------------------|----------------------|----------------------|
|                              | I                    | Ia                   | II                   | III                  |
| Li <sup>+</sup>              | $1,48 \cdot 10^{-2}$ | $2,35 \cdot 10^{-2}$ | $5,25 \cdot 10^{-2}$ | $7,40 \cdot 10^{-2}$ |
| Na <sup>+</sup>              | $< 10^{-4}$          | $4,17 \cdot 10^{-3}$ | $8,32 \cdot 10^{-3}$ | $3,35 \cdot 10^{-2}$ |
| K <sup>+</sup>               | $< 10^{-4}$          | $3,31 \cdot 10^{-3}$ | $4,68 \cdot 10^{-3}$ | $2,31 \cdot 10^{-2}$ |
| Rb <sup>+</sup>              | $< 10^{-4}$          | $< 10^{-4}$          | $< 10^{-4}$          | $< 10^{-4}$          |
| Cs <sup>+</sup>              | $< 10^{-4}$          | $< 10^{-4}$          | $< 10^{-4}$          | $< 10^{-4}$          |
| NH <sub>4</sub> <sup>+</sup> | $8,32 \cdot 10^{-2}$ | $7,43 \cdot 10^{-3}$ | $1,68 \cdot 10^{-2}$ | $5,25 \cdot 10^{-2}$ |
| Mg <sup>2+</sup>             | $< 10^{-4}$          | $1,58 \cdot 10^{-3}$ | $1,00 \cdot 10^{-2}$ | $3,98 \cdot 10^{-2}$ |
| Ca <sup>2+</sup>             | $< 10^{-4}$          | $3,16 \cdot 10^{-3}$ | $1,28 \cdot 10^{-2}$ | $6,03 \cdot 10^{-2}$ |
| Sr <sup>2+</sup>             | $1,77 \cdot 10^{-2}$ | $3,98 \cdot 10^{-2}$ | $1,24 \cdot 10^{-1}$ | $1,07 \cdot 10^{-1}$ |
| Ba <sup>2+</sup>             | $2,51 \cdot 10^{-2}$ | $5,25 \cdot 10^{-2}$ | $2,24 \cdot 10^{-1}$ | $2,10 \cdot 10^{-1}$ |
| Cu <sup>2+</sup>             | 4,12                 | 1,82                 | 13,01                | 43,13                |
| Cd <sup>2+</sup>             | 1,0                  | 1,0                  | $6,24 \cdot 10^{-2}$ | $4,31 \cdot 10^{-2}$ |
| Zn <sup>2+</sup>             | $6,24 \cdot 10^{-2}$ | $9,73 \cdot 10^{-2}$ | $4,95 \cdot 10^{-2}$ | $2,11 \cdot 10^{-2}$ |
| Mn <sup>2+</sup>             | $3,16 \cdot 10^{-2}$ | $1,39 \cdot 10^{-1}$ | $1,97 \cdot 10^{-1}$ | $8,42 \cdot 10^{-1}$ |
| Fe <sup>2+</sup>             | $3,00 \cdot 10^{-2}$ | $1,20 \cdot 10^{-1}$ | $1,80 \cdot 10^{-1}$ | $7,95 \cdot 10^{-1}$ |
| Co <sup>2+</sup>             | $9,81 \cdot 10^{-2}$ | $2,48 \cdot 10^{-1}$ | 1,0                  | 1,0                  |
| Ni <sup>2+</sup>             | $3,40 \cdot 10^{-2}$ | $1,40 \cdot 10^{-1}$ | $7,85 \cdot 10^{-2}$ | $7,85 \cdot 10^{-1}$ |

Like in the case of the plasticized membranes, the presence of copper(II) ion in the solution under analysis in the liquid membrane electrodes cause irreversible processes in the composition of the membrane. As a result cadmium-selective or cobalt-selective electrodes lose their electrode function, as a more stable copper(II) chelate is formed in the membrane, whose dissociation is not sufficient for the formation of the electrode function.

Having compared the obtained electrode characteristics of liquid membranes and the electrode characteristics of PVC plasticized membranes, the following conclusions can be made:

1. Plasticized membranes possess a wider range of concentrations to be determined.
2. In the case of plasticized membranes equilibrium potential sets in sooner.
3. The stability of measurements for plasticized membranes is higher and the potential drift is smaller.
4. The life time of the plasticized membrane electrodes is longer.

5. The preparing of electrodes and their handling is more convenient in the case of plasticized membranes.

6. The selectivity of liquid membranes is higher, in the case of s-elements in particular.

Among all the investigated ISE those with zinc and cadmium-selective membranes with the corresponding 4-hydroxybenzenedithiocarboxylates as electrode-active chelates gave the best results. That is why quantitative determination methods for zinc(II) and cadmium(II) ions were worked out making use of these two electrodes. TBF and iso-TBF were used as plasticizers for zinc and cadmium-selective PVC membranes. Silver and silver chloride electrode was used as a reference electrode. As zinc and cadmium membrane electrodes are used in neutral medium, complexone III turned out to be the most suitable titrant. It is cheap and easily accessible for any laboratory.

Though the electrodes are called ion selective electrodes, their selectivity in most cases is limited. It is one of the major drawbacks in ionometry. In order to work out good methods of determination, it is necessary to prevent the interference of adjacent ions. It can be done by choosing a suitable masking agent. The analysis of selectivity tables for zinc and cadmium-selective membranes leads to the conclusion that it is important to eliminate the interference of copper(II), mercury(II), nickel(II), cobalt(II), cadmium(II) and ammonium ions. In order to test the effectiveness of the chosen masking agent, titration was carried out without a masking agent and with the masking agent at the presence of the interfering ion. Thus, the maximum possible amount of the interfering ion which can be successfully masked was determined. All results obtained by use of masking agents are summed up in the table 8 and 9.

All masking agents are reported in literature, but the masking of ammonium ions was done by use of nontraditional method. Elimination of the ammonium ions was carried out in the following way. 0,5 ml of 8,0 M cesium hydroxyde were added to the solution under analysis obtaining a basic solution with pH 9-10. Cesium hydroxyde was chosen because the interference of cesium(I) ion on the zinc-selective membrane is the smallest.

The obtained solution was heated till the gaseous ammonium was completely given off. After cooling the liquid, drops of 6,0 M hydrochloric acid solution were added, till a neutral medium was obtained. Potentiometric titration of zinc(II) and cadmium(II) ions was carried out then. The precision of the potentiometric titration did not exceed 2%.

Table 8.

Masking Conditions for the Potentiometric Titration of Zinc(II) Ions by Use of Zinc-selective Electrode.

| Interfering ion                     | Masking conditions  | Masked amount<br>$c_{\text{interf.}} : c_{\text{Zn}^{2+}}$ |
|-------------------------------------|---|--|
| $\text{Cu}^{2+}$                    | Ascorbic acid (0.1 M) + KJ (0.1 M) = 1:1<br>(tenfold superiority) | 10 : 1   |
| $\text{Hg}^{2+}$                    | Ascorbic acid (0.1 M) (fivefold superiority)                      | 5 : 1  |
| $\text{Co}^{2+}$ , $\text{Ni}^{2+}$ | Sodium diethyldithiocarbamate (0.1 M)<br>(threefold superiority)  | 10 : 1   |
| $\text{Cd}^{2+}$                    | Sodium diethyldithiocarbamate (0.1 M)<br>(twofold superiority)    | 10 : 1   |
| $\text{NH}_4^+$                     | 8 M CsOH (pH=9-10), boiling, 6 M HCl (pH~7)                       | 50 : 1   |

Table 9.

Masking Conditions for the Potentiometric Titration of Cadmium(II) Ions by Use of Cadmium-selective Electrode.

| Interfering ion                     | Masking conditions  | Masked amount<br>$c_{\text{interf.}} : c_{\text{Cd}^{2+}}$ |
|-------------------------------------|---|--|
| $\text{Cu}^{2+}$                    | Ascorbic acid (0.1 M) + KJ (0.1 M) = 1:1<br>(tenfold superiority) | 20 : 1   |
| $\text{Hg}^{2+}$                    | Ascorbic acid (0.1 M) (fivefold superiority)                      | 10 : 1   |
| $\text{Co}^{2+}$ , $\text{Ni}^{2+}$ | Sodium diethyldithiocarbamate (0.1 M)<br>(threefold superiority)  | 50 : 1   |
| $\text{NH}_4^+$                     | 8.0 M CsOH (pH~9-10), boiling,<br>6.0 M HCl (pH~7)                | 50 : 1   |

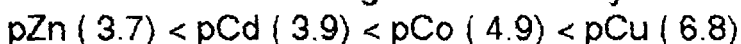
In the ion selective membranes reported in literature so far, only a small part of all the known organic reagents has been used as electrode-active chelates. Each organic reagent can be used for obtaining dozens of chelates. Not all the chelates are known to be useful for preparing ISE. The main difficulties are connected with the choice of EAS for the ion selective membrane. The forecasting of new membranes should be carried out for further studies of the applicability of chelates in ISE membranes.

The chelate stability is known to play a considerable part in the activity of ISE. It would be useful to establish the relationship between stability of the complex compound and the principal characteristics of ISE. Thermodynamic extraction constants of some benzenedithiocarboxylates and their hydroxy-

derivatives in 3-methyl-1-butanol are known, but these constants in TBF have not been investigated.

Nuclear magnetic resonance method was tested for the determination of thermodynamic extraction constants, but it did not give the desired results. That is why spectrophotometric method was chosen for the determination of thermodynamic extraction constants in further studies. Several solvents were chosen to study the influence of a solvent on thermodynamic extraction constants: chloroform, 3-methyl-1-butanol and TBF. These constants were determined for zinc and cadmium benzene- and 4-hydroxybenzenedithiocarboxylates. The logarithmical values of the thermodynamic extraction constants of zinc and cadmium benzenedithiocarboxylates in chloroform are 13,0 and 16,2 respectively. The logarithmical values of these constants of cadmium 4-hydroxybenzenedithiocarboxylates in 3-methyl-1-butanol is 16,2 and in TBF 20,1. These values for zinc 4-hydroxybenzenedithiocarboxylates is 13,1 in 3-methyl-1-butanol and 14,9 in TBF.

The obtained extraction constants lead to the conclusion that the introduction of a hydroxyl group into a benzene ring in p position does not effect substantially the chelate stability. A similar regularity follows from the characteristics of the corresponding ion selective membranes. Insufficient solubility of benzenedithiocarboxylates does not permit to achieve better characteristics. The use of polar solvents for the extraction affects the stability of the complex compound to a greater extent. Replacing 3-methyl-1-butanol with TBF, the extraction constant increases by 2-3 orders. Summing up pMe values determined for 4-hydroxybenzenedithiocarboxylates obtained by Silvija Pastare and in present work the following chelate stability series can be made:



This stability series correlates well with the ISE characteristics. Only nickel chelate extraction constant ( $pNi - 3,8$ ) falls out of this series. It is due to the tendency of nickel ions to form several complex compounds. It has not been determined yet which compound gave the obtained constant. When using TBF as an extracting agent, the most stable chelate is formed at once.

A similar correlation exists between the extraction constants of other studied dithiocarboxylates.

The determination of extraction constants by use of a spectrophotometric method is labour-consuming and demands large amount of organic solvent. It is especially noticeable when using the plasticized membrane solvents as extracting agents, they are often not accessible in sufficient amount. It was one of the main reasons why the extraction constants of just a few chelates in TBF have been determined. Thus, further studies are required in order to establish a more complete correlation between the extraction constants and the characteristics of ISE. Nevertheless, the obtained data lead to a conclusion that dithiocarboxylates suitable for preparing ion selective

membranes are the ones where pMe values are in range 3,5 - 4,5 in the case of 3-methyl-1-butanol and chloroform and about 5,0 in the case of TBF.

Extraction constants give insufficient information about the applicability of chelates in ion selective membranes. In order to get additional information the possibility of using the method of infrared spectrometry was tested. IR spectra of several benzenedithiocarboxylates were obtained. Several fluctuations of the valent bonds can be observed in these spectra. The intensity of these bands depends on the chelate. In the case of zinc and cadmium chelates, the bands of valent bonds are clearly expressed, while in the case of cobalt and nickel chelates, the bands are less intensive and converged. In the case of copper chelate they are extinguished almost completely. It is due to the thermodynamic stability of chelates. All the observed regularities correlate well enough with the characteristics of investigated ion selective membranes.

In the case of ion selective membranes the electrode function decreased in the following series of 4-hydroxybenzenedithiocarboxylates:



This regularity can be attributed to the intensity of the valent fluctuations in IR spectra, too, the greater the thermodynamic stability, the less is the intensity of fluctuations. By use of IR spectra a nickel-selective electrode has been made using nickel(II) 1-phenyl-3-amino-5-pyrazolone-4-dithiocarboxylate as EAS.

Summing up the results of the obtained ion selective membranes, it can be concluded that dithiocarboxylates can be used as EAS in ISE. Though, the number of suitable dithiocarboxylates is limited by the insufficient solubility of several chelates in the solvent used in the membrane. Too stable and unstable dithiocarboxylates are not suitable as well.

### ***BRIEF SUMMARY.***

1. Ion selective membranes of plasticized polyvinylchloride have been obtained using various chelate benzenedithiocarboxylates as electrode-active substances. They were introduced into membranes by means of the extraction method. The electrodes with zinc(II) and cadmium(II) benzenedithiocarboxylates in their membranes turned out to have the best characteristics.

2. The most suitable plasticizer of polyvinylchloride membranes has been found, which simultaneously serves as a solvent in the extraction of benzenedithiocarboxylates. It is tributylphosphate. The solubility of chelate benzenedithiocarboxylates in other organic solvents is worse.

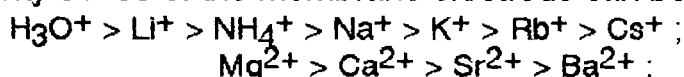
3. When studying the plasticized membranes containing benzenedithiocarboxylates, it was found that the electrode characteristics improved if the concentration of the electrode-active substance in membrane increased. It was

found that solubility of electrode-active substances can be increased by introducing hydroxyl groups into benzene ring.

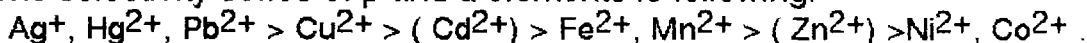
4. The principal characteristics of all the obtained plasticized membrane electrodes have been determined: the linear concentration range, linear slope, optimum concentration of the electrode-active chelate in the membrane, pH range, the electrode life time, the response time and the potentiometric selectivity coefficients.

5. After analysing the obtained data, it was found that the electrodes having 4-hydroxybenzenedithiocarboxylates as electrode-active chelates in the membranes possessed the best characteristics. The principal advantage of these electrodes is their higher selectivity.

6. Taking into account potentiometric selectivity coefficients, the following s-element selectivity series of the membrane electrode can be made:



The selectivity series of p and d elements is following:



7. As plasticizers affect the membrane selectivity and tributylphosphate has a clearly expressed cation-selective function, zinc-selective and cadmium-selective membranes with the mixtures of various solvents used for plasticizing were prepared. Thus, it is possible to extend the detection limit of electrode for half an order, to extend the pH range by 0,5 pH units, as well as to improve the electrode selectivity.

8. The influence of anions on the electrode function was also studied. The presence of interfering ions in the solution was to have no effect on the linear concentration range to be determined, but it changed the linear slope. The influence of anions increases in the following way:



9. Possibility of using zinc-selective electrode for the control of the composition of zinking electrolyte during electrolysis has been demonstrated.

10. In order to compare the plasticized membranes with the liquid one, electrodes containing the membranes of both kinds were prepared, and the characteristics of these electrodes were determined. In liquid membranes various chelate hydroxybenzenedithiocarboxylates were used as electrode-active substances. Comparing the obtained data, the following conclusions can be made:

1. Plasticized membranes possess a wider range of concentrations to be determined.
2. In the case of plasticized membranes equilibrium potential sets in sooner.
3. The stability of measurements for plasticized membranes is higher and the potential drift is smaller.
4. The life time of the plasticized membrane electrodes is longer.

5. The preparing of electrodes and their handling is more convenient in the case of plasticized membranes.

6. The selectivity of liquid membranes is higher, in the case of s-elements in particular.

11. Complexometric methods for the potentiometric titration of zinc(II) and cadmium(II) ions have been worked out using zinc-selective and cadmium-selective membrane electrodes as indicator electrodes. Masking conditions at the presence of various interfering ions have been determined.

12. By use of spectrophotometric method, thermodynamic extraction constants of zinc(II) and cadmium(II) 4-hydroxybenzenedithiocarboxylates in 3-methyl-1-butanol and tributylphosphate and zinc(II) and cadmium(II) benzenedithiocarboxylates in chloroform have been determined. In tributylphosphate these constants were found to be 2-3 orders higher than in less polar solvents. The obtained thermodynamic extraction constants correlate well with the corresponding characteristics of membrane electrodes. It can be used when forecasting new ion selective membrane electrodes.

13. Solid complexes of copper(II), nickel(II), cobalt(II), zinc(II), cadmium(II) benzenedithiocarboxylates and various hydroxyderivatives have been synthesized. Infrared spectra of the obtained chelates have been obtained.

14. Infrared spectra of these chelates were found to be applicable as a source information when choosing electrode-active substances in order to obtain ion selective electrodes with the desired properties.

15. Infrared spectra have been applied to make the nickel-selective electrode where nickel(II) 1-phenyl-3-amino-5-pyrazolone-4-dithiocarboxylate was chosen as an electrode-active substance.



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