

Sulphonamides as Ionophores for Ion-Selective Electrodes. I

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Abstract. A series of new compounds: di-sulphonamides and mono-sulpho-mono-carboxy-di-amides has been synthesized. Comparison of the ionophoric properties of these compounds in liquid membrane electrodes was performed and the correlation between the chemical structure and potentiometric ion-selectivity has been studied.

Key words. Ion-selective electrodes, inclusion, sulphonamides.

1. Introduction

The inclusion complexation between a metal cation as a guest and an ionophore as a host molecule and the extraction of metal-ions from aqueous solution into a liquid membrane face is responsible for the ion-selective properties of liquid membrane electrodes. In searching for sensors for ion-selective electrodes it was found that certain lipophilic diamides of dicarboxylic acids behave as good ionophores in ion-selective liquid membrane electrodes [1–3]. The high polarity of the amide carbonyl group ensures sufficient strength of interaction of such ligands with mono- and divalent cations. It has also been reported that lipophilic *N, N*-bis(octadecyl) mono-amides of certain dicarboxylic acids are suitable as active materials in solvent polymeric membranes [4]. A version of sodium ion-selective electrodes has been based on carboxylic acid derivatives of crown ethers [5]. A number of papers have been concerned with modification of the active sites of neutral ion-carriers [6].

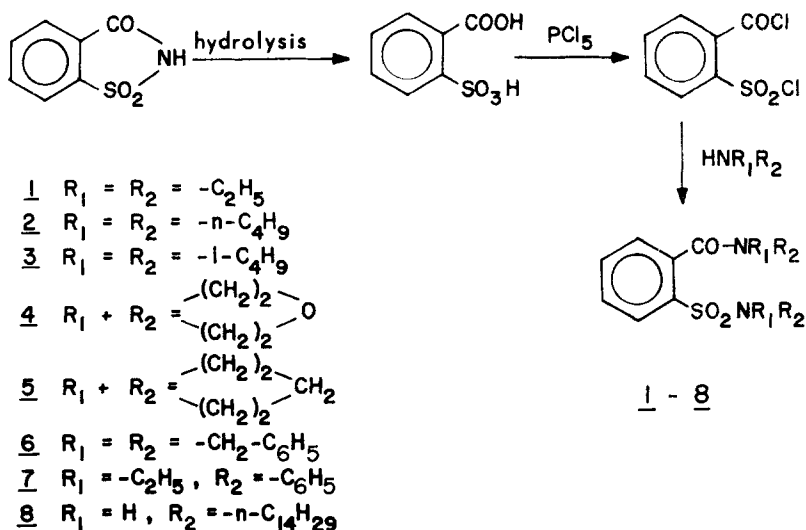
Here, we report on a new modification of the active site of ionophores. Instead of the carbonamide group we introduced the sulphonamide group assuming that the two oxygen atoms bonded to the sulphur atom would act as electron donors. Such a substitution should cause a significant change in the geometric location of the electro-negative oxygen atoms.

A series of compounds: *N, N, N', N'*-tetrasubstituted amides of: *o*-sulphobenzoic acid (1–8), *o*-benzene-disulphonic acid (9–12) and 2'-sulpho-4'-*t*-butylphenoxy)acetic acid (13–17) were synthesized. Also 18 and 20, the carbonyl compounds analogous to 3 and 15, respectively, and 19, the well known ionophore for the lithium ion [2] were synthesized for comparison. The ion-selective properties of PVC-membrane electrodes based on these compounds were studied.

2. Experimental

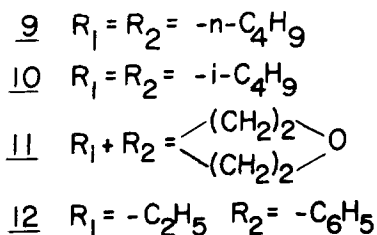
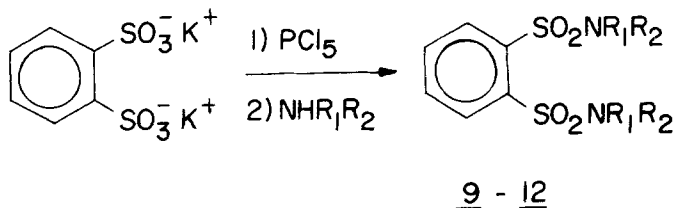
2.1. PREPARATIONS

The ionophores 1–8 were synthesized by the following reaction scheme:



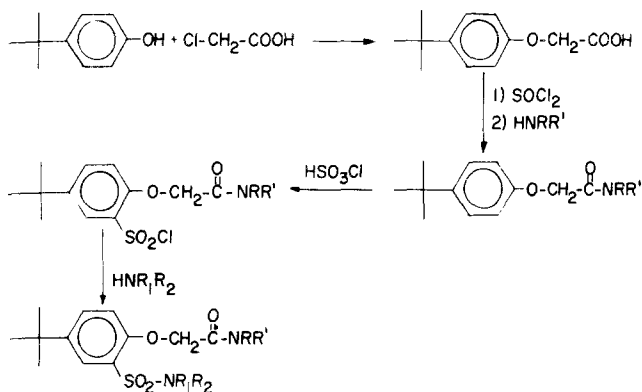
Scheme I.

The ionophores **9–12** were synthesized by a similar procedure starting from the potassium salt of *o*-benzene-disulphonic acid.



Scheme II.

The amides **13–17** were synthesized, starting from *p-t*-butyl phenol, by the following reaction scheme:



13 - 17

13 $R = R' = -n-C_4H_9$; $R_1 = -C_2H_5$; $R_2 = -C_6H_5$

14 $R = R' = -n-C_4H_9$; $R_1 + R_2 = \begin{matrix} (CH_2)_2 \\ \diagdown \quad \diagup \\ O \end{matrix}$

15 $R = R' = R_1 = R_2 = -i-C_4H_9$

16 $R = R' = -i-C_4H_9$; $R_1 = -C_2H_5$; $R_2 = -C_6H_5$

17 $R = R' = -n-C_4H_9$; $R_1 = R_2 = -CH_2-C_6H_5$

Scheme III.

The compounds 18–20 (see Figure 1) were synthesized starting from *o*-phthalic acid, *cis*-cyclohexyldicarboxylic acid and salicylic acid, respectively by similar methods to the above.

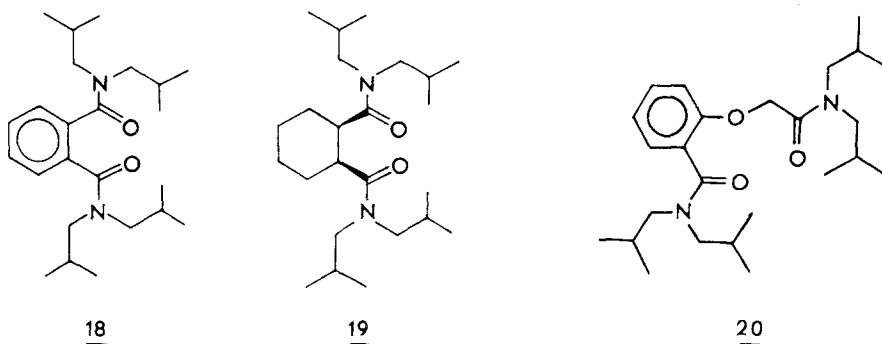


Fig. 1.

The proton nuclear magnetic resonance (NMR) spectra were recorded on a Tesla spectrometer at 60 MHz. Mass spectra were obtained on a Varian MAT 711 mass spectrometer, using the field desorption (FD) technique.

The 1H -NMR spectra and mass spectra of all compounds confirmed their structure and purity.

Compound	The data from $^1\text{H-NMR}$ spectra in CDCl_3 δ [ppm]
1	1.0 (m, 12H), 3.15 (m, 8H), 7.2 (m, 3H), 7.6 (d, 1H).
2	0.85 (2t, 12H), 1.3 (m, 16H), 3.0 (m, 8H), 7.3 (m, 3H), 7.65 (d, 1H).
3	0.7 (m, 24H), 1.8 (m, 4H), 2.85 (m, 8H), 7.2 (m, 3H), 7.75 (d, 1H).
4	3.15 (m, 8H), 3.65 (m, 8H), 7.2 (m, 3H), 7.5 (d, 1H).
5	1.4 (m, 12H), 3.0 (m, 8H), 7.1–7.7 (m, 4H).
6	4.0–4.8 (m, 8H), 7.0 (s, 20H), 6.9–7.6 (m, 4H).
7	1.0 (t, 3H), 1.13 (t, 3H), 3.26 (q, 2H), 3.9 (q, 2H), 6.7–7.7 (m, 14H).
8	1.0 (m, 54H), 3.1 (m, 4H), 7.2 (m, 3H), 7.65 (d, 1H).
9	0.83 (t, 12H), 1.2 (m, 16H), 3.13 (t, 8H), 7.4 (m, 2H), 7.9 (m, 2H).
10	0.7 (2t, 24H), 1.7 (m, 4H), 3.0 (d, 8H), 7.5 (m, 2H), 8.0 (m, 2H).
11	3.13 (2t, 8H), 3.56 (t, 8H), 7.55 (m, 2H), 8.0 (m, 2H).
12	1.0 (t, 3H), 1.13 (t, 3H), 3.85 (q, 4H), 7.0 (s, 10H), 6.96–7.63 (m, 4H).
13	0.8–1.6 (m, 27H), 1.2 (s, 9H), 3.3 (t, 2H), 3.8 (q, 2H), 4.7 (s, 2H), 6.6–7.6 (m, 8H).
14	0.8 (t, 6H), 1.2 (s, 9H), 1.0–1.8 (m, 8H), 3.2 (m, 8H), 3.7 (t, 4H), 4.7 (s, 2H), 6.7–7.8 (m, 3H).
15	0.8 (d, 24H), 1.2 (s, 9H), 1.8 (m, 4H), 2.5 (2d, 8H), 4.8 (s, 2H), 6.6–7.9 (m, 3H).
16	0.7–1.5 (m, 24H), 1.9 (m, 2H), 3.0 (d, 4H), 3.7 (q, 2H), 4.6 (s, 2H), 6.6–7.9 (m, 8H).
17	0.8–1.8 (m, 14H), 1.2 (s, 9H), 3.2 (d, 2H), 4.8 (s, 2H), 6.6–8.1 (m, 3H), 7.2 (s, 10H).
18	0.73 (d, 24H), 1.75 (m, 4H), 2.95 (m, 8H), 6.8–7.2 (m, 4H).
19	0.75 (d, 24H), 1.3 (m, 8H), 1.8 (m, 4H), 3.0 (m, 8H).
20	0.7 (m, 24H), 1.7 (m, 4H), 2.9 (d, 8H), 4.5 (s, 2H), 6.6–7.2 (m, 4H).

The characteristics of ligands **1–20** are given in Table I.

Table I. The characteristics of ligands **1–20**

Ligand	Yield %	m.p. °C	M ⁺ (FD)	Ion preference	Slope [mV]	Linear range
1	50	oil	312	Na ⁺	40	4–1
2	55	oil	424	Ca ²⁺	26	4–1
3	30	76–8	424	K ⁺	51	3.5–1
4	75	173–5	340	K ⁺	50	4.5–1
5	43	103–5	336	K ⁺	47	4–1
6	62	155–8	560	K ⁺	50	3.5–1
7	21	82–5	408	K ⁺	47	4–1
8	54	56–8	592	Ca ²⁺	25	4.5–1.5
9	70	66–9	460	K ⁺	49	3.5–1
10	50	74–8	460	K ⁺	45	3.5–1
11	88	163–5	376	K ⁺	44	4.5–1
12	25	121–3	444	K ⁺	50	3.5–1
13	35	103–5	502	K ⁺	50	3.5–1
14	43	oil	468	K ⁺	47	3–1
15	40	132–4	510	K ⁺	44	3–1
16	25	105–8	502	K ⁺	34	2.5–1
17	33	oil	578	Ca ²⁺	20	4.5–1
18	35	49–50	388	Li ⁺	35	3–1
19	62	oil	392	Li ⁺	58	4–1
20	37	111–3	418	K ⁺	50	3–1

2.2. ELECTRODE SYSTEM

The poly(vinyl chloride) membranes were prepared conventionally, as described elsewhere [7, 8] using 5–6 wt% of ligand (1–20), 35–36 wt% of PVC-S-72 and 59–60 wt% of di-n-butyl phthalate (DBP) as plasticizer. Tetrahydrofuran was used as the solvent. The PVC membranes were incorporated into Ag/AgCl electrode bodies, with 0.01M KCl as the internal electrolyte. A double-junction reference electrode of the Radelkis 0P0820P type (Ag/AgCl, KCl) was used with 0.1M tetraethylammonium nitrate in the bridge cell.

2.3. E.M.F. MEASUREMENTS

All potentials were measured at 20 ± 1 °C using a N 517 (MERA ELWRO) pH-meter equipped with a V 541 digital voltmeter, which allowed a reading accuracy up to ± 0.1 mV. Selectivity coefficients ($\log K_{Li/M}$) were obtained by the separate solution method [2, 3, 7].

3. Results and Discussion

All the synthesized compounds behave as ionophores in ion-selective electrodes, however not all of the electrodes possess fully satisfactory characteristics. In Table I are presented the ions of preference and the slopes of the electrode response to solutions of the preferred metal chlorides.

The potentiometrically determined ion selectivities of the synthesized compounds are presented in Figure 2. The selectivity coefficient ($\log K_{Li/M}$) indicates the preference of the membrane system for the M ions, such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} in relation to Li^+ .

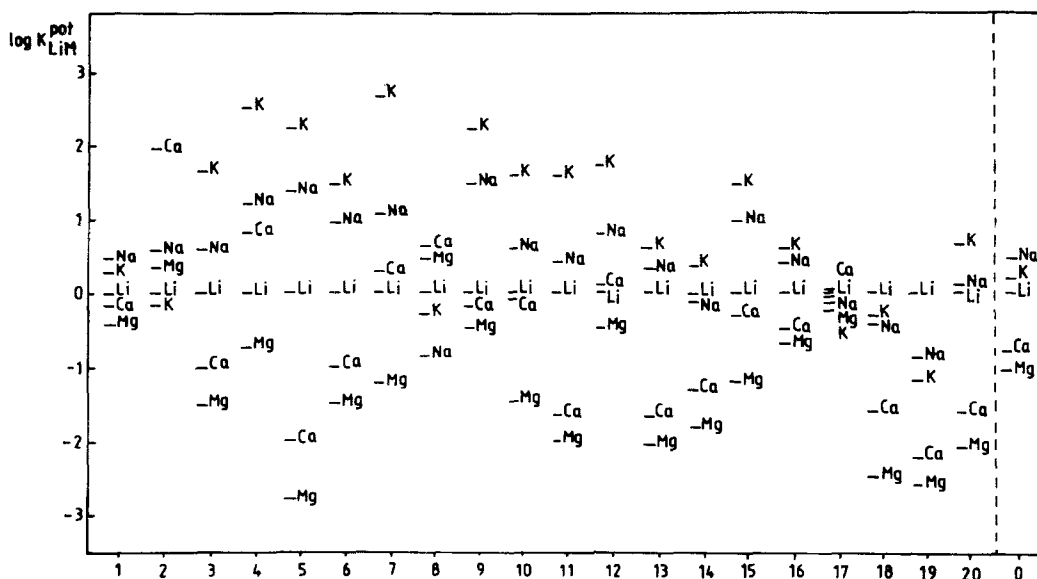


Fig. 2. The selectivity coefficients $\log K_{Li/M}^{pot}$ for ion-selective electrodes based on ligands 1–20, measured by the separate solution method ($M = Mg^{2+}$, Ca^{2+} , Na^+ , K^+ , 0 – for the blank membrane).

Most of the ligands investigated, **3–7**, and **9–16**, show a preference towards big monovalent cations. The comparison of the results obtained for **3** and **10** with those for **18** or **19** suggest that the sulphonamide group induces some selectivity changes among alkaline metal ions, causing the preference for K^+ rather than Li^+ . Rather surprisingly, the observed selectivity sequence differs from that for ligands **2**, **8** and **17**. The electrodes based on these ligands are most selective for the Ca^{2+} ion.

The mutual interaction of the two amide groups in the investigated compounds is to a large extent responsible for the selectivity behaviour of the membrane. The single crystal X-ray structure determination of compound **3** revealed that the carbonyl oxygen and the sulphonyl group oxygens are located very close to one another and form an electron rich site [10].

The changes of substituents on nitrogen atoms cause a change of ligand conformation and in this way modify their ionophoric properties.

Our results are in agreement with the suggestion that the increase in the thickness of the ligand layer may lead to a preference for monovalent over divalent ions of the same size [9]. Indeed, the bulky amide group, for instance in **3**, **4**, **7** or **13** leads to membranes selective for alkali metal ions. Rather long amide chains in **2** or **8** leads to a membrane sensitive for divalent cations.

Acknowledgement

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