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Novel Ammonium Ionophores Based on Glycol Dibenzyl Ethers for an Ion-Selective Electrode

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Based on the finding that dibenzyl ether (DBE) exhibited a relatively high selectivity for ammonium ion relative to potassium ion, four types of dibenzyl ethers were synthesized and their ammonium ion selectivities over alkali and alkaline-earth metal ions were examined with potentiometric measurements.

Practically employed ionophores in the ammonium ion selective electrodes have only been nonactin or its derivatives.[1a-h] The main problem found in the use of nonactin is its low selectivity for NH_4^+ relative to K^+, because K^+ is the closest in ionic size to the ammonium ion. This limits its application to a low salt environment[1c, d] and produces the need for other treatments to avoid interference with K^+.[1e] Some efforts to find an ionophore which is highly selective to ammonium ion have been reported,[2] but so far the selectivity is still inferior compared to nonactin.

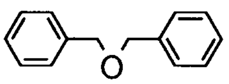
Surprisingly, we found that a membrane electrode based on dibenzyl ether (DBE), exhibited a relatively high NH_4^+ selectivity over K^+. Based on this finding, we report here on novel ammonium ionophores based on dibenzyl ethers (**2** to **5**), and also describe several factors that affect the ammonium ion selectivity of the synthesized ionophores, which will be important for further designing and synthesizing of new ammonium ionophores.

The procedures for synthesizing ionophore **2** - **5** are as follows: Sodium hydride (2.5 eq) was added to 1 eq of the appropriate diol compound (1,3-propanediol, 2,4-dimethyl-2,4-pentanediol, 1,4-butanediol, or 2,5-dimethyl-2,5-hexanediol) dissolved in THF, and the reaction mixture was stirred for 30 min in an ice bath. Benzyl bromide (2.5 eq) was then added dropwise and the mixture was refluxed overnight. After the THF was evaporated, the residue was extracted with chloroform and washed with water. The product was purified by column chromatography (silica gel, hexane/ethyl acetate: 9/1) to yield a colorless oil. The structures of the synthesized ionophores were confirmed by ^{1}H-NMR, IR and elemental analysis.

The solvent-polymeric membranes were prepared with 69 wt % of the ionophore, which also served as the membrane plasticizer, 30 wt % poly(vinyl chloride) (PVC), and 1 wt % of potassium tetrakis(p-chlorophenyl)borate (KTCPB) which prevents anion interference as well as reduces the membrane resistance. The membrane thickness was ca. 100 μm. A 7-mm diameter circle was cut from the prepared membrane and mounted on the tip of the electrode body (Philips IS-561, Philips Japan. Ltd., Tokyo, Japan). The prepared electrodes were immersed in a 1 M NH_4Cl solution for over 24 h for conditioning before use. Electrode cells of the type:

Ag;AgCl, 3 M KCl|0.3 M CsCl|sample|membrane|0.1 M NH_4Cl, AgCl;Ag

were used for the emf measurement. The electrode response potential (emf) measurements were performed according to the reported procedure.[3)] The selectivity coefficients were calculated from the response potentials in an alkali or alkaline earth metal chloride solution by the separate solution method (SSM) and were also partially determined by the fixed interference method (FIM).[4)]



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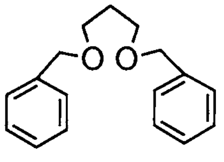

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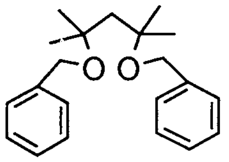

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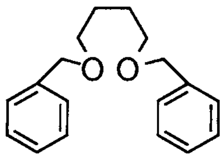

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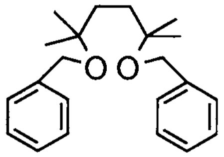

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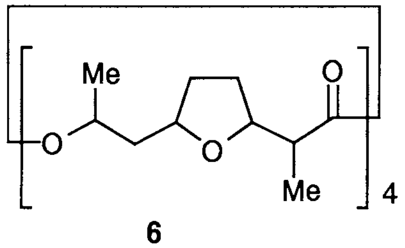

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The selectivity coefficients of the electrodes based on DBE(**1**), the four type of synthesized ionophores (**2** - **5**) and nonactin (**6**) are presented in Table 1.

Potassium ion tends to preferably form hexacoordinate or heptacoordinate complexes, while ammonium ion tends to form a tetracoordinate complex.[5)] DBE molecule preferably forms a complex of the latter type. By considering this coordinating feature, we have designed and synthesized four diether compounds, **2** - **5**, which are expected to form more stable 2:1 complexes with an ammonium ion than that formed with the DBE. When two benzyl groups were connected with propylene glycol (**2**), it was observed that its ammonium ion selectivity for other ions was lower than that of DBE (**1**), especially the selectivity of the Li^+ was drastically lowered. This can be explained by the fact that the distance between the two etheral-oxygen atoms is too short to fit with the hydrogen atom of the ammonium ion. By exchanging this propylene bridge between the two ethers with butylene (**4**), the ammonium ion selectivity toward alkali ions was greatly improved.

Table 1. Comparison of selectivity coefficients, $\log k^{pot}_{NH_4^+,j}$, of NH_4^+-selective ionophores

	$\log k^{pot}_{NH_4^+,j}$ a)								
Ionophore	j= Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
DBE (**1**)	-1.3	-1.7	-1.1	-0.4	0.6	-2.8	-2.7	-2.9	-2.9
Compound **2**	-0.1	-0.9	-0.6	-0.5	0.1	-2.0	-2.0	-2.1	-2.2
Compound **3**	-1.6	-2.1	-1.4	-0.7	0.3	-3.0	-3.0	-2.9	-3.2
Compound **4**	-1.4	-1.8	-1.4	-1.0	-0.3	-2.3	-2.2	-2.4	-2.5
Compound **5**	-1.9	-2.3 (-2.2)	-1.7 (-1.7)	-1.1	-0.1	-3.2	-3.4	-3.2	-3.4
nonactin (**6**)[b]	-3.5	-2.4 (-2.5)	-1.0 (-0.8)	-1.5	-2.4	-4.0	-3.8	-3.6	-4.0

a) Data obtained by the separate solution method (0.1 M cation chloride). Values evaluated by the fixed interference method (j= 0.01 M) are given in parentheses.

b) membrane composition: 3 wt% ionophore, 0.5 wt% KTCPB, 66.5 wt% Bis(2-ethylhexyl sebacate) (BEHS) and 30 wt% PVC.

Propylene and butylene glycols are thought to be too flexible to bind ammonium ions firmly, therefore, we attempted to introduce dimethyl group in the propylene or butylene bridge section to reduce the flexibility of the ammonium ligand by preparing the compounds **3** and **5**. These dimethyl groups also serve as blocking groups to prevent the formation of a "sandwich complex" with larger size ions (Cs^+, Rb^+) . Based on these results, the ammonium ion selectivities of these compounds, **3** and **5**, were greatly improved over those of **2** and **4**. The ammonium ion selectivity over K^+ of compound **5** was twice as good as that of nonactin, which is obviously the best ammonium ionophore developed to date.

The novel approach to design a highly selective ammonium ionophore to replace the use of nonactin has been described. This report will provide the idea for designing a novel ammonium ionophore, because the most ionophores developed to date are highly selective to K^+ rather than to NH_4^+.[6)]

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