

Anion-Sensing Electrodes Based on Nickel(II) Mixed Ligand Complexes

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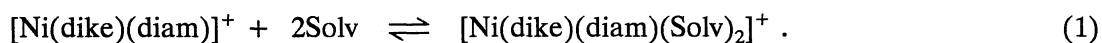
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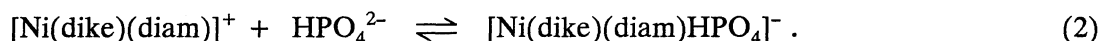
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We have prepared hydrogenphosphate ion-sensing electrodes containing Ni(II) mixed ligand complexes, $[\text{Ni}(\text{dike})(\text{diam})]\text{X}$ where dike= β -diketonate, diam= $\text{N,N}'$ -polyalkylated ethylenediamine, and $\text{X}=\text{ClO}_4^-$ or $\text{B}(\text{C}_6\text{H}_5)_4^-$ which are non-coordinating anions. In the case of electrodes containing perchlorate complexes as a sensing material, an electrochemical response to hydrogenphosphate ions has been observed, but not in the case of the tetraphenylborate complexes.

We have studied a series of Ni(II) mixed ligand complexes, $[\text{Ni}(\text{dike})(\text{diam})]\text{X}$ where dike= β -diketonate ion, diam= N -alkylated ethylenediamine, X =an uncoordinating anion such as ClO_4^- or $\text{B}(\text{C}_6\text{H}_5)_4^-$, which are red, diamagnetic, and square planar structures in the solid state. We were able to observe a characteristic chromotropism of these complexes in solution; solvatochromism and thermochromism were observed depending upon the solvent coordination ability.¹⁻⁵⁾



Using an intermediate coordinating solvent such as acetone or bulky alcohols, we were easily able to obtain an equilibrium solution between the square planar species and the octahedral one. This led us to expect that these square planar chelates, $[\text{Ni}(\text{dike})(\text{diam})]^+$, could exist in an equilibrium state even if coordinating anions are introduced instead of solvent molecules in Eq. 1; i.e., these chelates could act as an anion-sensing material. In the present work, hydrogenphosphate ions (HPO_4^{2-}), which were expected to become a bidentate ligand in this case as shown in Eq. 2, were used:



Acetylacetonate (acac) and benzoylacetonate (bzac) ions were used as a β -diketonate ligand, $\text{N,N,N}',\text{N}'$ -tetramethylethylenediamine (tmen), $\text{N,N,N}'$ -triethylethylenediamine (trien), and $\text{N,N}'$ -dimethyl-1,4-diazacycloheptane (dmdach) as N -alkylated ethylenediamine, and perchlorate and tetraphenylborate ($\text{B}(\text{C}_6\text{H}_5)_4^-$) ions as an uncoordinated anion (counter ion X^-). These mixed ligand

complexes, $[\text{Ni}(\text{dike})(\text{diam})]\text{X}$, were synthesized as described previously.⁶⁾

Ion-sensing electrodes containing these complexes were made as follows: the Ni complex 1.3%, 2-fluoro-2'-nitrodiphenyl ether (FNDPE, Dojindo Laboratories), 65.8%, were used as an ion-sensing material and a plasticizer, respectively, and polyvinyl chloride (PVC)($n=1100$, Wako Chemicals), 32.9%, formed the matrix. A tetrahydrofuran (THF) solution of these membrane materials was prepared and a silver electrode electroplated with silver chloride was dipped into this THF solution. It was then dried in a nitrogen atmosphere. The procedure was repeated several times, until the membrane thickness reached about $100\ \mu\text{m}$. The electrode potential of the ion-sensing electrode thus prepared was measured in aqueous solutions of various hydrogenphosphate concentration against a reference silver/silver chloride electrode (Toa Electronics) without a salt bridge. As a source of hydrogenphosphate ions, potassium salts were used. It was experimentally proved that potassium ions had no influence on the potential measurements; that is, potassium perchlorate and potassium tetraphenylborate which could be precipitated in the membrane phase or at the interface between the membrane and the solution did not affect potential measurements. All the measurements were carried out at room temperature.

The potential responses of these electrodes with membranes containing perchlorate complexes are given in Fig. 1. Linear relations between the potential and the hydrogenphosphate activity were obtained with a slope of approximately $-21\ \text{mV}/\text{decade}$, revealing that these complexes acted as

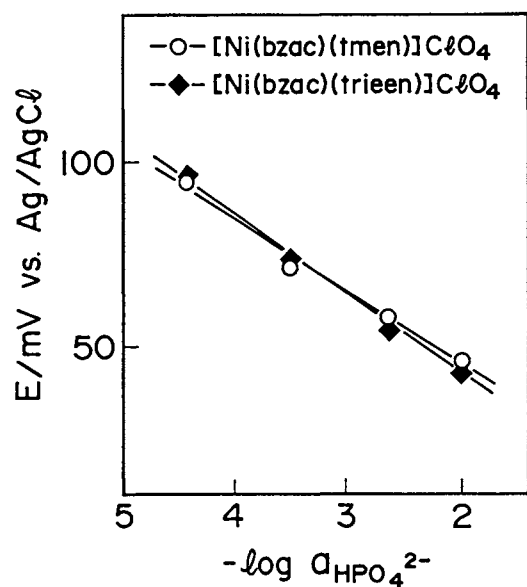


Fig. 1. Responses of membrane electrodes containing perchlorate complexes.

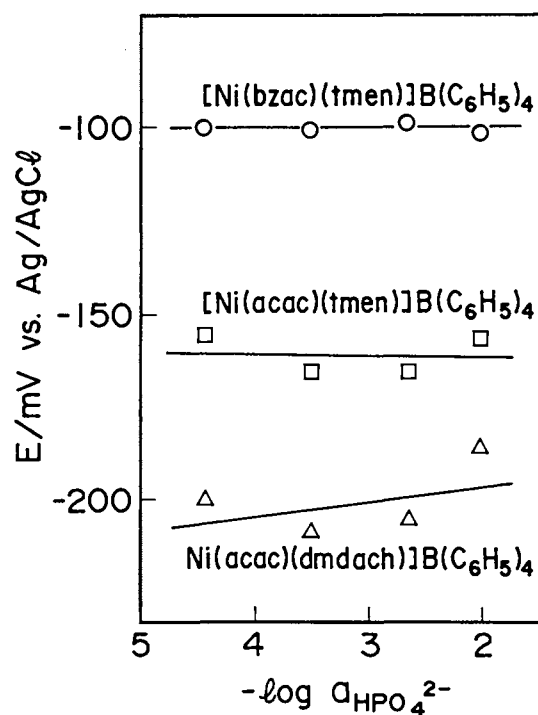


Fig. 2. Responses of membrane electrodes containing tetraphenylborate complexes.

hydrogenphosphate ion-sensing materials. On the contrary, it turned out that electrodes with tetraphenylborate complexes did not show any response to the hydrogenphosphate activity (Fig. 2). This could be attributed to the fact that the tetraphenylborate ion is so bulky and hydrophobic that it prevents hydrogenphosphate ions from interacting with the complex in the membrane phase.⁷⁾

A series of somewhat detailed investigations was carried out on the perchlorate complex which interacted with hydrogenphosphate ions. Electronic spectra in solid state for $[\text{Ni}(\text{bzac})(\text{tmen})]\text{ClO}_4$ are measured by using the Spectro Multi Channel Photo Detector (Otsuka Electronics, MCPD-1000). The spectra are shown in Fig. 3, in which the solid line and broken line represent the spectrum before and after immersing the pellet made from the complex into 0.1 M hydrogenphosphate solution, respectively ($1\text{ M}=1\text{ mol dm}^{-3}$). Before immersion, the pellet was red and the main absorption peak was typical of four-coordinate square planar Ni(II) complexes characterized by the appearance of the absorption band at about 490 nm, assigned to the $^1\text{A}_{2g} \leftarrow ^1\text{A}_{1g}$ transition,⁸⁾ although coexistence of a six-coordinate octahedral complex, probably having two water molecules as ligand, was also suggested by the shoulder at about 680 nm and another peak at about 1040 nm. After immersing the pellet into the solution containing hydrogenphosphate for 15 minutes, the spectrum changed into the broken line, revealing the disappearance of the square planar species.

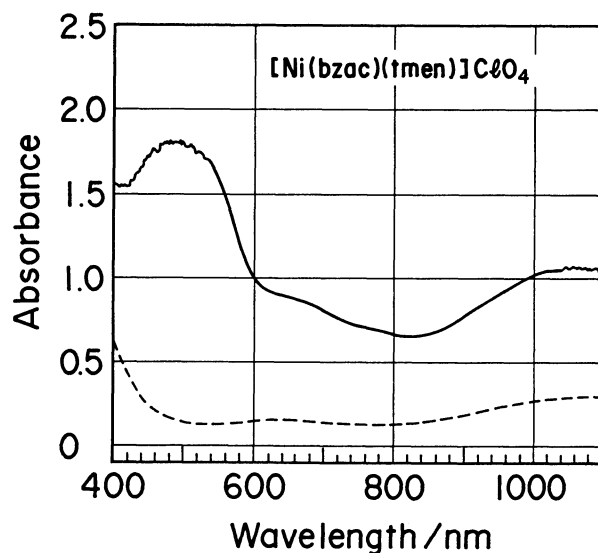


Fig. 3. Electronic spectra in solid state for $[\text{Ni}(\text{bzac})(\text{tmen})]\text{ClO}_4$ before(—) and after(----) immersing the pellet into the hydrogenphosphate solution.

In order to elucidate changes which occurred in the complex at this time, surface analysis was performed on the pellet using an energy dispersive X-ray microanalyzer (Kevex delta-class analyzer). The results are presented in Figs. 4 and 5. In the case of the perchlorate, only Cl and Ni peaks were detected before immersion, while the peaks of P and K atoms appeared in addition to the Cl and

Ni peaks after immersion (Fig. 4). On the other hand, in the case of the tetraphenylborate complex $[\text{Ni}(\text{bzac})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$, in which only the counter ion differed from the complex mentioned above, no peak for P atoms was detected even after immersion (Fig. 5). Therefore, it is concluded that perchlorate complexes of $[\text{Ni}(\text{dike})(\text{diam})]^+$ type could act as phosphate-sensing materials through the equilibrium of square planar and octahedral structure conversion.

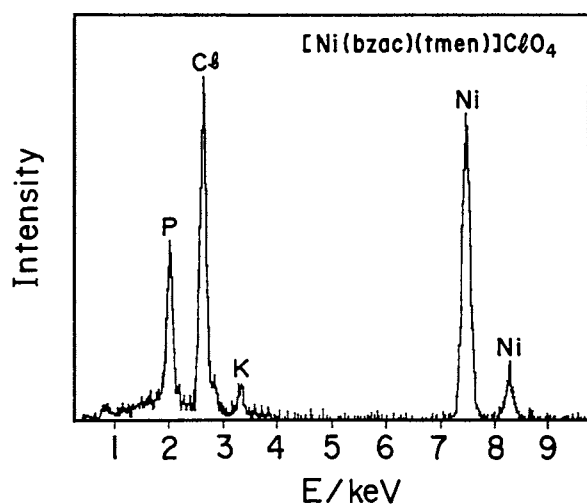


Fig. 4. EPMA spectrum for Ni(II) perchlorate complex after immersion in the hydrogenphosphate solution.

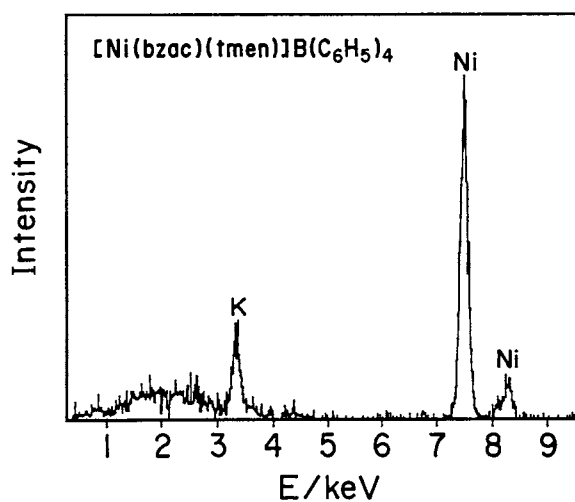


Fig. 5. EPMA spectrum for Ni(II) tetraphenylborate complex after immersion in the hydrogenphosphate solution.

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