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Di-*n*-octyl Phenyl Phosphonate: A Plasticizer of Poly(vinyl chloride) Matrix Membrane Electrodes Behaving As a Li^+-selective Agent

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Synopsis. PVC matrix membrane electrodes, which are composed of dioctyl phenylphosphonate (DOPP) as a plasticizer and potassium tetrakis(4-chlorophenyl)borate (KTCPB) as a lipophilic anionic additive, without any other ionophore, exhibit appreciable Li^+-selectivity. The electrode has selectivity coefficients (log $k_{\mathrm{LiM}}^{\mathrm{Pot}}$for Li^+ over Na^+ up to −1.2, over K^+ up to −1.8, over Mg^{2+} up to −1.8, and over Ca^{2+} up to −1.2. The detection limit for Li^+ was about 5.0×10^{-5} mol dm^{-3}.

During the last decade much attention has been focused on the use of neutral carrier compounds as membrane components; they can be used together with different plasticizers in ion-selective membrane electrodes, especially for alkali and alkaline earth metal ions.[1] A number of neutral carriers for ion-selective electrodes have been reported thus far, such as noncyclic polyethers,[2,3] crown ethers,[4] and bis-crown ethers.[5] Moreover, the effects of the plasticizers on the behavior of the ion-selective electrodes have also been investigated, and the change in the selectivity coefficients brought about by plasticizers, together with neutral carriers, have been observed.[6] However, in order to discriminate among cations within a given group of the periodic system, the influence of the solvent/plasticizer with neutral carrier sensors has been considered of minor importance.[7] In this paper, we wish to report on the phenomenon that the selectivity for cations within a given group of the periodic system without any other neutral carrier changes completely depending on the kind of plasticizer.

Experimental

Materials. The plasticizers, dioctyl phenylphosphonate (DOPP) and *o*-nitrophenyl octyl ether (NPOE), and potassium tetrakis(4-chlorophenyl)borate (KTCPB), were commertially available (Dojin Lab.) and were used without further purification. Poly(vinyl chloride) (PVC) (degree of polymerization $n \fallingdotseq 1100$), which was also commertially available from Wako Pure Chemical Industries, Ltd., was used after the polymer had been dissolved in tetrahydrofuran (THF), followed by reprecipitation in methanol.

Preparation of Electrodes. A plasticizer (250 mg), PVC (100 mg), and KTCPB (3 mg) were dissolved in 4 ml of THF. The solution was then poured into a Petri dish (42 mm in diameter) which was held horizontally on a mercury pool, and the THF was evaporated slowly at room temperature. A transparent homogeneous membrane ca. 0.2 mm thick was thus obtained. A disk of the polymeric membrane 5 mm in diameter was cut out from the membrane obtained and was then mounted on an Orion model 92 electrode body for electromotive force (EMF) measurements. The cell assemblies of the ion-selective electrode were as follows: Ag/AgCl/ 10^{-2}mol dm^{-3} LiCl//membrane// test solution/ 1 mol dm^{-3} $LiOCOCH_3$/ sat. KCl/AgCl/Ag, where a silver-silver chloride electrode in a double-junction configuration was used as the external reference electrode.

EMF-Response Measurements. Test solutions were prepared from analytical-grade chlorides of alkali and alkaline earth metals and deionized water (specific conductivity 5×10^{-7} $\Omega^{-1}\,cm^{-1}$). The EMF response of the testing solutions at 25 °C was measured with an Orion model 701A digital ionanalyzer (input impedance 10^{13} Ω) and was recorded by means of a strip-chart recorder and a printer. The time for the electrode to attain the stationary potential value within ±1 mV for the lapse of 30 sec. was referred to as the response time. The potentiometric selectivity coefficient $k_{\mathrm{i,j}}^{\mathrm{Pot}}$ of the i ion over the j ion was determined by the separate-solution method.[8] The concentrations of interference ions referred to by this calculation ranged from 10^{-1} to 1 mol dm^{-3}.

Results and Discussion

Figures 1 and 2 show the plots of the EMF response vs. the logarithm of ion activity (log *a*) when DOPP and NPOE respectively were used as plasticizers. In both cases, the PVC membrane electrodes show a near-Nernstian response for the ions examined except for those with a low EMF response. The electrode exhibits a marked Li^+-selectivity over Na^+, K^+, Mg^{2+}, and Ca^{2+} when DOPP is used, whereas the K^+-selectivity over Li^+, Na^+, Mg^{2+}, and Ca^{2+} is obtained when NPOE is used. When KTCPB was not included in the membranes, the near-Nernstian response for cations was not observed; rather, the response for anions was observed in the case of NPOE.[9] It has been reported

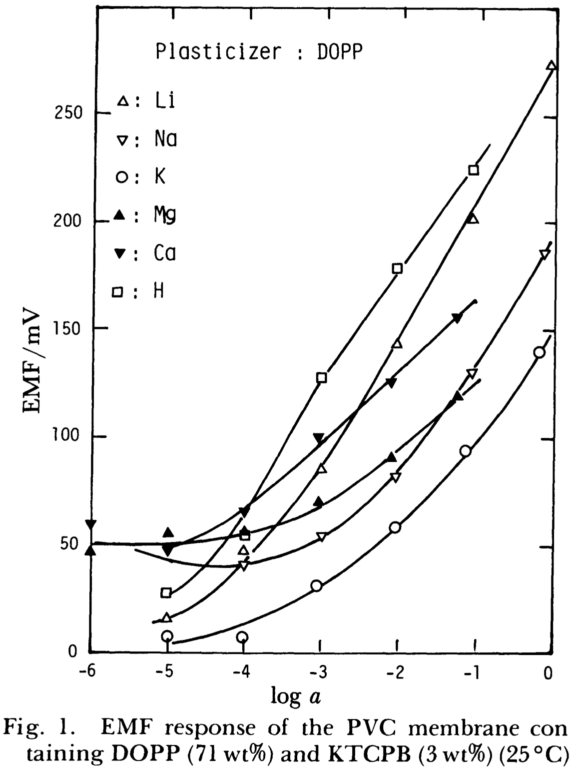

Fig. 1. EMF response of the PVC membrane containing DOPP (71 wt%) and KTCPB (3 wt%) (25 °C).

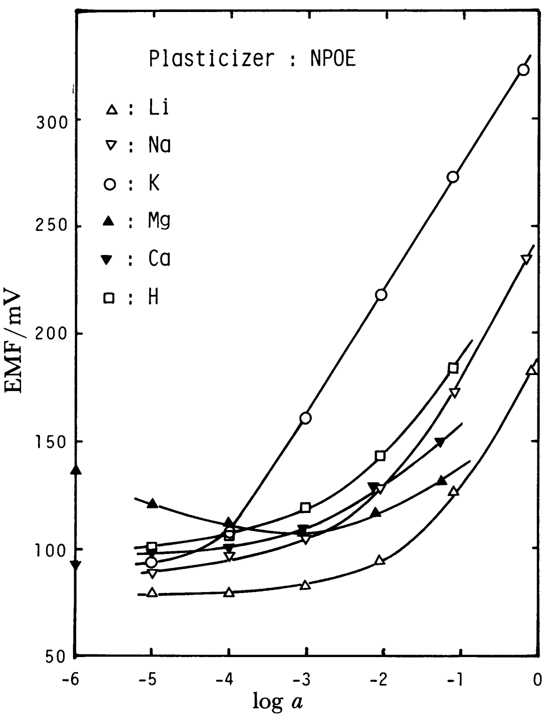

Fig. 2. EMF response of the PVC membrane containing NPOE (71 wt%) and KTCPB (3 wt%) (25 °C).

that DOPP is favorable for Ca^{2+}-selective electrodes containing an organophosphate salt-carrier.[10] It is also well known that a membrane based on tetraphenylborate in nitrobenzene or related solvents, e.g., NPOE, shows a monotonic preference for large over small cations, that is, for lipophilic over hydrophilic cations,[11] as is depicted in Fig. 2. However, when DOPP and KTCPB were used without any other ionophore, the electrode has appreciable selectivity coefficients for Li^+ over Na^+, K^+, Mg^{2+}, and Ca^{2+}. Apparently, DOPP can reverse its ion-selectivity from large to small alkali ions, that is, from lipophilic to hydrophilic cations.

Furthermore, the effect of the mixing of the plasticizers, DOPP and NPOE, on the selectivity coefficients for cations was investigated. The results are also summarized in Fig. 3. The mixing ratios apparently influence the selectivity for cations. The Li^+-selectivity is still retained even when the mixture composed of 3 wt% of DOPP and 68 wt% of NPOE is present in the membrane, as if DOPP hehaved as a Li^+-ionophore. This fact reminds us that certain organic phosphorous compounds and other compounds can improve ion-selectivity in the membrane electrodes.[13–15] It should be noted that the membrane electrode composed of a mixture of NPOE 57 wt% and DOPP 14 wt% as plasticizers has maximum selectivity coefficients for Li^+ over Na^+ of up to −1.3 compared with the other electrodes shown in Fig. 3. Thus, it is a new finding that appreciable Li^+-selectivity appears when a PVC membrane containing DOPP and KTCPB, without any other ionophore, is used.

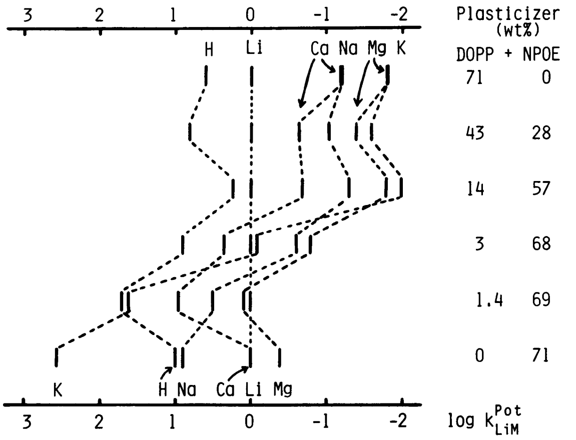

Fig. 3. Influence of the plasticizers on the potentiometric selectivity coefficients.[12]

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$$E = E_i^\circ + \frac{2.3RT}{Z_i\mathrm{F}} \log\left[a_i' + \sum_{j\neq i} k_{ij}^{\mathrm{Pot}}(a_j')^{Z_i/Z_j}\right].$$

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