Water-Soluble Acidochromic Dyes Lipophilized with Quaternary Ammonium Cations as Tunable Chromoionophores for Polymeric Optodes

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Lipophilic hydrogen chromoionophores used in bulk optodes are mainly derivatives of acid-base indicators lipophilized by introducing long-chain radicals. The latter is a challenging task due to the complex structure of the parent compounds and the intricacy of product purification. This leads to a limited choice of available chromoionophores, and, in turn, of their acidities. An alternative approach to enhance the lipophilicity of water-soluble acidochromes is converting them into an ion pair with a lipophilic counterion [1].

We report here a systematic study of the optical properties of lipophilized acidochromic dyes and their behavior in polymeric sensor matrix. Lipophilic ion pairs of bromophenol blue (BPB), bromothymol blue (BTB) and thymol blue (TB) and quaternary ammonium cations were synthesized, and their optical properties in PVC–DOS phase were investigated (Fig. 1A). The effect of the nature of acidochrome and counterion on the lipophilicity and acidity of the resulting ion pair was evaluated (Fig. 1B). The partition coefficients of the obtained dyes and their acidity constants in the polymeric phase were estimated. The pH- and Cl‑- response of the optodes containing synthesized ion pairs was studied and analyzed in terms of the theoretical model described in [2] (Fig. 1C).



Fig. 1. A: UV-Vis spectra of BTB in water and its ion pair with tetraoctylammonium in PVC–DOS film. B: leaching of TOctA+ ion pair with various acidochromic anions (deprotonated form) from the polymeric phase upon contact with aqueous solution. C: response of optodes containing BTB-TOctA+ ion pair as a chromoionophore. Lines: approximation with model proposed in [2].

The ease of preparation makes lipophilic acidochromic ion pairs a viable alternative to conventional chromoionophores, and a wide variety of available water-soluble precursor indicators allows obtaining chromoionophores with tunable acidity. In addition, the response of the obtained sensors is less prone to cross-sensitivity towards electrolyte activity in the solution (Fig. 1C) compared to conventional optodes, which opens prospects for their further investigation as sensors for individual ionic activity.

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1. W.I.S. Galpothdeniya, K.S. McCarter, S.L. De Rooy, et al., Ionic liquid-based optoelectronic sensor arrays for chemical detection. RSC Adv. **2014**, *4*, 7225

2. N. V. Pokhvishcheva, I.S. Prozherin, A. V. Kalinichev, M.A. Peshkova, Response Patterns of Chromoionophore-Based Bulk Optodes Containing Lipophilic Electrolytes: Toward Background-Independent pH-Sensing. ACS Sens. **2023**, *8*, 3086