WATER-SOLUBLE ACIDOCHROMIC DYES LIPOPHILIZED WITH QUATERNARY AMMONIUM CATIONS AS TUNABLE HYDROGEN CHROMOIONOPHORES FOR POLYMERIC OPTICAL SENSORS

<u>Prozherin I.S.</u>, Pokhvishcheva N.V., Menshova A.S., Peshkova M.A.

St. Petersburg State University, St. Petersburg, Russia
Student
IljaProzherin@yandex.ru

At present, there is a wide variety of classes of polymeric optical sensors in research practice, among which colorimetric optodes are the most commonly used due to the ease of signal acquisition and response interpretation. Their response mechanism is based on the establishment of heterogeneous equilibria with the participation of an optically detectable component (hydrogen chromoionophore), the protonated and deprotonated forms of which have contrasting colours. Nowadays, hydrogen chromoionophores are mainly derivatives of acid-base indicators lipophilized by introducing long-chain radicals [1]. However, this method of lipophilization can be cumbersome due to the complex structure of the parent compounds and intricacy of the product purification [2].

Acidochromic ionic liquids (ILs) may become a viable alternative to conventional hydrogen chromoionophores due to their ease of synthesis and tunable characteristics [3]. However, an overview of existing attempts to utilize acidochromic ILs as lipophilic hydrogen chromoionophores highlights the focus on exploring only a few specific applications of optical sensors based on such indicators.

Here we report a systematic study of the optical properties of lipophilized acidochromic dyes and their behavior in a polymeric sensor matrix, with the aim of finding a path toward readily available chromoionophores with tunable acidity. Lipophilic ion pairs of several sulfonaphthalein dyes with quaternary ammonium cations are synthesized and used as chromoionophores in coextraction-based PVC–DOS optodes. It is shown that the nature of the acidochrome and counterion determine the lipophilicity (fig. 1A) and acidity (fig. 1B) of the resulting ion pair. The partition coefficients of the obtained dyes are in the range from 10^4 to 10^6. Finally, the possibility of utilising the previously reported theoretical description [4] in order to predict the properties of optodes based on such indicators was demonstrated (fig. 1C).

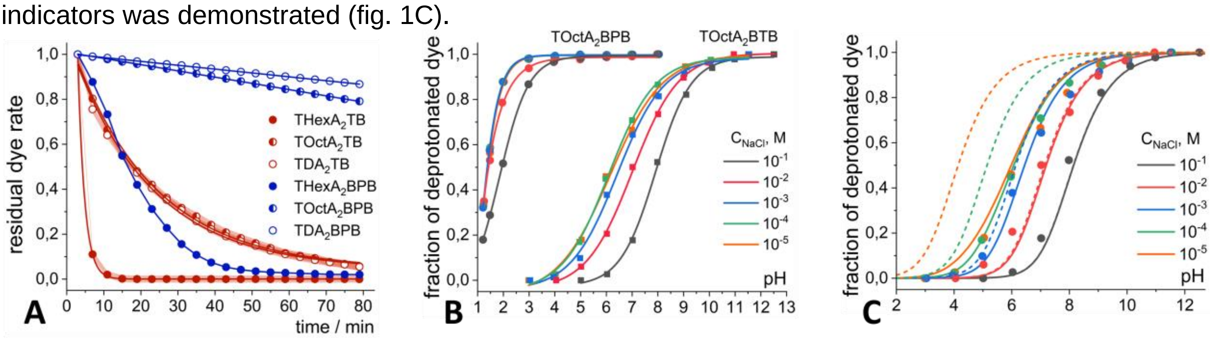

Figure 1. A: Residual amount of lipophilized dyes in deprotonated form relative to their initial content in the polymeric film, versus time of contact with the aqueous phase. B: pH-response curves of optodes containing bromophenol blue and bromothymol blue ion paired with $TOctA^+$ as pH-chromoionophores. C: pH-response curves of optodes containing bromothymol blue ion paired with $TOctA^+$ as pH-chromoionophores. Symbols: experimental data, dashed lines: prediction using conventional theory of the optode response, solid lines: prediction using generalized theory of the optode response [4].

References

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