Exploring the Limits of Ionic Liquid Reference Electrodes

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Reference electrodes (REs) without liquid junction have attracted significant attention over the last 20 years. These REs typically utilize ionic liquids (ILs) as free-flowing, water-immiscible salt bridges or as lipophilic electrolytes within plasticized polymeric reference membranes. Upon contact with a sample, the IL partitions into the aqueous phase (Fig. 1a), establishing an equilibrium distribution across the interface and a corresponding phase boundary potential, that is generally independent of the sample composition (Fig. 1b). IL-based REs offer an alternative to conventional REs employing aqueous salt bridge electrolytes and present opportunities for achieving integrated potentiometric sensing systems [1]. However, despite their advantages, IL-based REs have yet to achieve widespread commercial adoption, partly due to a lack of comprehensive understanding regarding their limitations. One major concern revolves around the reference membrane lifetime, as there is little quantitative data available on IL partitioning and leaching. The RE potential stability in complex samples is also of great importance. Lipophilic ions and surfactants are known to affect the response of IL-based REs, making it crucial to understand and investigate the underlying mechanisms in more detail.

In this study we explore the working limits of REs based on polymeric reference membranes incorporating ILs. A theoretical framework is developed and experimentally verified to describe the failure of REs in the presence of lipophilic solution ions [2]. The critical concentration at which the RE potential begins to deviate noticeably from its equilibrium value is estimated as the intersection of the separate Nernstian responses to the IL and the solution ion (Fig. 1c). Furthermore, reference membrane lifetimes are assessed based on the IL partition constants acquired for the sensing matrix used in this study. Lastly, we discuss the effectiveness of potential stabilization with highly lipophilic electrolytes to establish the optimal range of IL lipophilicity for RE design.

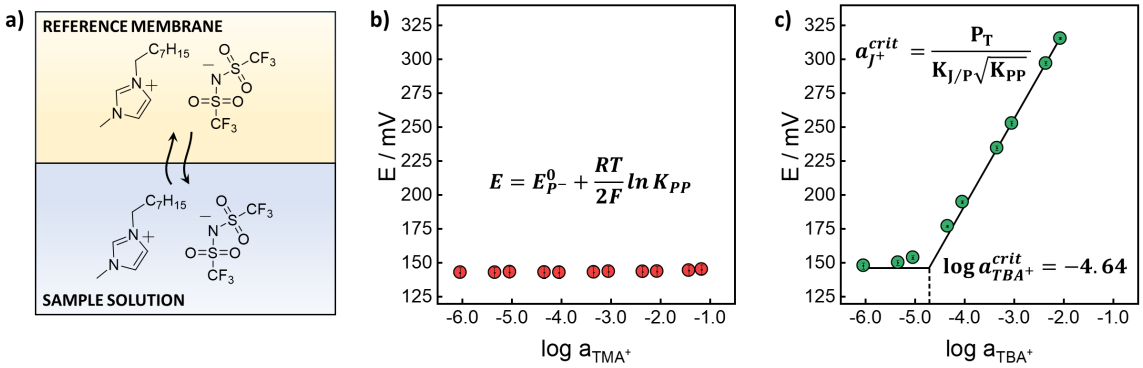

Figure 1. a) Partitioning of the ionic liquid $[C_8mim^+][C_1C_1N^-]$ between the electrode membrane and the sample and the response of the corresponding REs in the presence of different concentrations of b) tetramethylammonium (TMA^+) and c) tetrabutylammonium (TBA^+).

[1] E. Lindner, M. Guzinski, T.A. Khan, B.D. Pendley, *ACS Sensors*, **2019**, 4, 549–561.
[2] N. Y. Tiuftiakov, E. Zdrachek, E. Bakker, *Sensors Actuators, B Chem.*, **2024**, 407, 135474.