

Polarizability of the Interface Between the Room-Temperature Molten Salt and Water

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Room-temperature molten salts (RTMS) composed of hydrophobic cations and anions can form both electrochemically polarized and nonpolarized interfaces upon contact with an aqueous electrolyte solution (W), depending on the relative magnitude of the hydrophobicity of the ions that the RTMS consist of and also the type of ions present in the aqueous phase [1,2]. This type of the liquid-liquid two-phase systems are important for constructing a new extraction systems that are environmentally benign in comparison of those relied on volatile organic compounds.

In order to understand the extraction properties of RTMS|W systems, the polarizability of the interface should be clearly defined. As the ion transfer across the RTMS|W interface is supposed to be facile, the width of the polarized potential window is primarily determined by the thermodynamic properties of the ions as well as their diffusion coefficients. This is in marked contrast with the polarizability of conventional electrode-aqueous solution interfaces, where the hydrogen overvoltage is crucial.

We will show that the width of the polarized potential window is directly related to the solubility product of the RTMS, which is in turn related to the difference in the standard ion-transfer potentials of the RTMS-constituting ions. The current rise at the edge of the potential window is determined by the transfer of hydrophobic cations and of the hydrophobic anions at the negative and positive end of the polarized potential window, provided that the solubility of the ions in the W phase in the RTMS phase is hydrophilic enough to be negligible. Here the potential of the W phase with respect to the RTMS phase has been taken to be positive.

The current-potential characteristic is determined by the diffusion and migration of the ions constituting the RTMS and is obtained by solving the Nernst-Planck equation for the transfer of the ions in the RTMS in conjunction with and the diffusion equation for the transfer of these ions in W. This is exactly the same as that reported for the transfer of a supporting electrolytes at the liquid|liquid interface [3,4]. The charge transfer resistance due to the transfer of the ions constituting the RTMS is proportional to the inverse of the square-root of the solubility product. For a planar interface with semi-infinite boundary conditions for both phases, the charge transfer resistance, R_{ct} , at the current is given by:

$$\begin{aligned} R_{ct} &\approx \frac{RT}{2F^2A} \left(\frac{\sqrt{\pi t}}{c_S^R} \right) \left(\frac{1}{D_{C^+}^W D_{A^-}^W} \right)^{1/4} \exp \left[\frac{F}{2RT} (\Delta_R^W \phi_{A^-}^0 - \Delta_R^W \phi_{C^+}^0) \right] \\ &= \frac{RT}{2F^2A} \left(\frac{\sqrt{\pi t}}{c_S^R} \right) \left(\frac{1}{D_{C^+}^W D_{A^-}^W} \right)^{1/4} \frac{1}{\sqrt{K_s^W}} \end{aligned}$$

where t is time elapsed after the interface is formed, c_S^R is the concentration of the RTMS in the RTMS phase, D_i^W is the diffusion coefficient of i in W, $\Delta_R^W \phi_i^0$ is the standard ion-transfer potential of i between the RTMS and W, and K_s^W is the solubility product of the RTMS in W, and, R , T , F , and A have their usual meanings.

We will demonstrate this simple prediction for several

different types of RTMS that are based on quaternary ammonium cations and bis(perfluoroalkylsulfonyl) imide anions.

References

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