Supplementary Data for:

Electrochemical assessment of water|ionic liquid biphasic systems towards cesium extraction from nuclear waste

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# Scan rate experiment

Cell S1, shown below, employed through the micropipette electrolytic cell described in sections 2.2 and 2.3 of the main text was used to explore the diffusion characteristics of the metal ion/metal-ligand complex at the w|IL interface.

 (Cell S1)

Figure S1 illustrates the overlaid cyclic voltammograms (CVs) recorded using Cell S1 with a potential range between −0.140 to 0.400 V and an initial potential of 0.000 V, while the scan rate, *v*, was increased from 0.036 V∙s−1 to 0.049, 0.064, 0.081, and 0.100 V∙s−1. During the forward sweep, from 0.000 to 0.400 V, a peak-shaped wave was observed at ~0.100 V and this is indicative of the facilitated ion transfer (FIT) of Cs+ from w to IL through interfacial complexation with CMPO dissolved in the IL phase; this is analogous to the case described in section 3.3 and Figure 4 of the main text. Similarly, on the reverse scan a return peak of Cs+ transferring from IL to w through interfacial decomplexation was recorded at ~0.015 V. With increasing scan rate the peak current, *ip*, increased. Using equation 3, the Randles-Sevčik equation [[1](#_ENREF_1), [2](#_ENREF_2)], a plot of *ip* versus *v*1/2 can be used to calculate the diffusion coefficient from the slope of the curve as determined through linear regression analysis. Inset in Figure S1 is the *ip* versus *v*1/2 graph for the Cs+-FIT peak (○) along with the ‘line of best fit’ (**—**). An R2 of 0.9394 was obtained for the linear curve fitting, indicating good agreement with equation 3, with a calculated diffusion coefficient of 1.36 (±0.06) × 10−8 cm2∙s−1.



**Figure S1**: Cyclic voltammograms obtained using Cell S1 with an initial potential of 0.000 V, a potential range from −0.140 to 0.400 V, while altering the scan rate from 0.036 V∙s−1 to 0.049, 0.064, 0.081, and 0.100 V∙s−1. Inset is a plot of the peak current, *ip*, versus *v*1/2 for the ion transfer peak located at approximately 0.100 V.

The diffusion coefficient was calculated using the forward scan since the initial, or bulk, concentration of Cs+ is known while ultimately the bulk metal ion-ligand concentration is not. Therefore, the calculated diffusion coefficient is indicative of Cs+ transfer. Typical diffusion coefficients of metal ions in aqueous solutions have magnitudes of 10−5 cm2∙s−1, while the calculated value is 3 orders of magnitude less than that and common to charged species in and IL phase [[3-6](#_ENREF_3)]. It can therefore be concluded that FIT, in this case, is limited by the diffusion of CMPO to the interface. This could mean that the error associated with this measurement may be owing to the relaxation effects of the w|IL interface as described by Kakiuchi *et al.* [[7](#_ENREF_7), [8](#_ENREF_8)], i.e. ion pairing at the aqueous-IL boundary might impose a degree of order that was disrupted by the CV experiment. The error may be caused by a disparity between the initial (relaxed) and final conditions, possibly indicating that more time between CV experiments needs to be given for the system to relax to its initial state. The Cs+ wave is not as high as expected from relative high Cs+ concentration. The FIT process is not limited by Cs+ diffusion in the aqueous phase but by the ligand diffusion from the IL to the interface.

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