



Thallium extraction from hydrochloric acid media into a deep eutectic solvent using bis(2-ethylhexyl) phosphate

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Introduction

The chemical properties of the superheavy elements with $Z > 108$ are relatively unknown due to their short half-lives and difficulty of production. To prepare for a future experiment with element 113, one of the recently IUPAC accepted superheavy elements, the behavior of its homologs, Tl and In, are studied using separation techniques. The future experiments will provide information on whether the periodic trends are maintained for superheavy elements.

Figure 1: Periodic table with the symbols of the four newly accepted superheavy elements [1]

Ionic liquids are organic salts with a melting point below 100°C, where some are liquid at room temperature. Hydrophobic, room temperature ionic liquids are nonvolatile, nonflammable, and less toxic than conventional solvents, such as kerosene or benzene. Because of the favorable chemical properties, previous work used those ionic liquids for suitable substitute solvent in liquid-liquid extraction for metal extraction.[2]

Deep Eutectic Solvents

Additional work focused on liquid-liquid extraction with a class of ionic liquids called deep eutectic solvents[3]. A deep eutectic solvent (DES) is a mixture of at least two compounds with a melting point lower than its substituent parts. This work uses a DES composed of a 2:1 molar ratio of DL-menthol and lauric acid (DES M:LA). This DES M:LA is biodegradable and less toxic, making it an attractive candidate for the organic solvent in liquid-liquid extraction. Pure DESs can be used as extracting agent but also as a solvent for an additional compound to act as an extracting agent. This work focuses on the effects of adding an extracting agent, bis(2-ethylhexyl) phosphate (HDEHP) to the DL-menthol and lauric acid mixture.

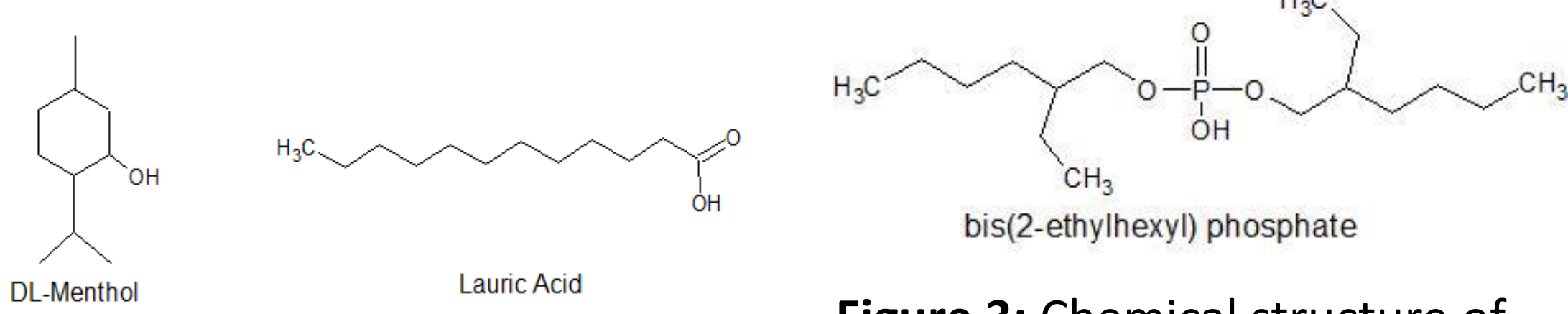


Figure 2: Chemical structures of DL-menthol and lauric acid, which are the two components of the DES

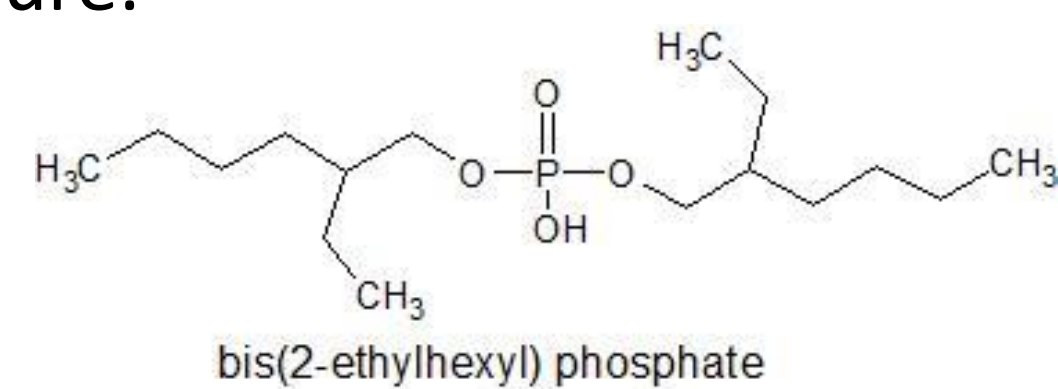


Figure 3: Chemical structure of bis(2-ethylhexyl) phosphate, also known as HDEHP, the extracting agent added in the DES

Deep Eutectic Solvents

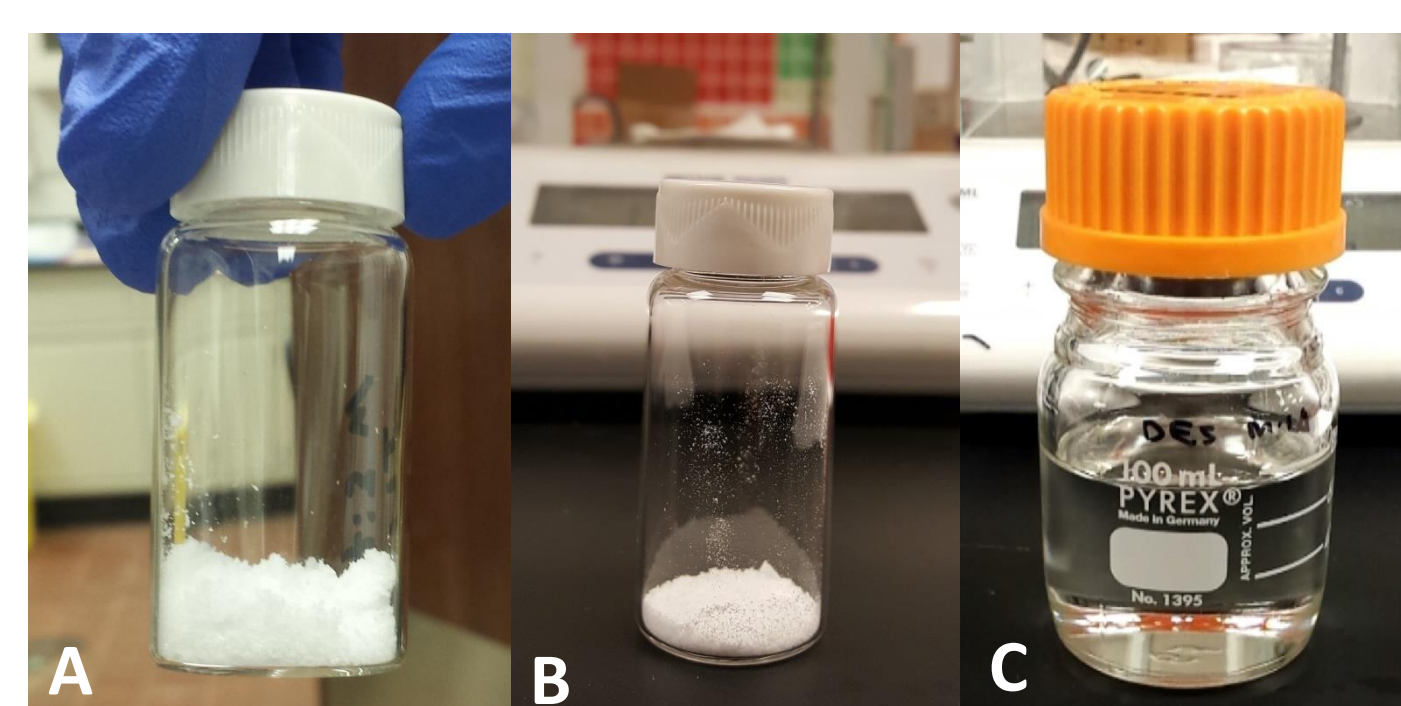


Figure 4: At room temperature, both DL-menthol (A) ($T_m = 36.82^\circ\text{C}$) [4] and lauric acid (B) ($T_m = 43.29^\circ\text{C}$) [4] are solid, but combined, the mixture (C) of the two compounds forms a DES that is liquid, ($T_m = 13.84^\circ\text{C}$) [4] due to its melting point depression

Liquid-Liquid Extractions

A liquid-liquid extraction is a separation technique based on the relative solubility of a compound in two immiscible phases, an organic phase and an aqueous phase. The system of the two solvents is made up of an organic solvent, such as kerosene or hexane, and an aqueous (water-based) solvent.



Figure 5 (left): An example of a solvent system for a liquid-liquid extraction. The top organic layer is kerosene, while the bottom layer (shown in red) is an aqueous buffer with pH = 4. As shown in the figure, a sharp boundary separates the two phases.

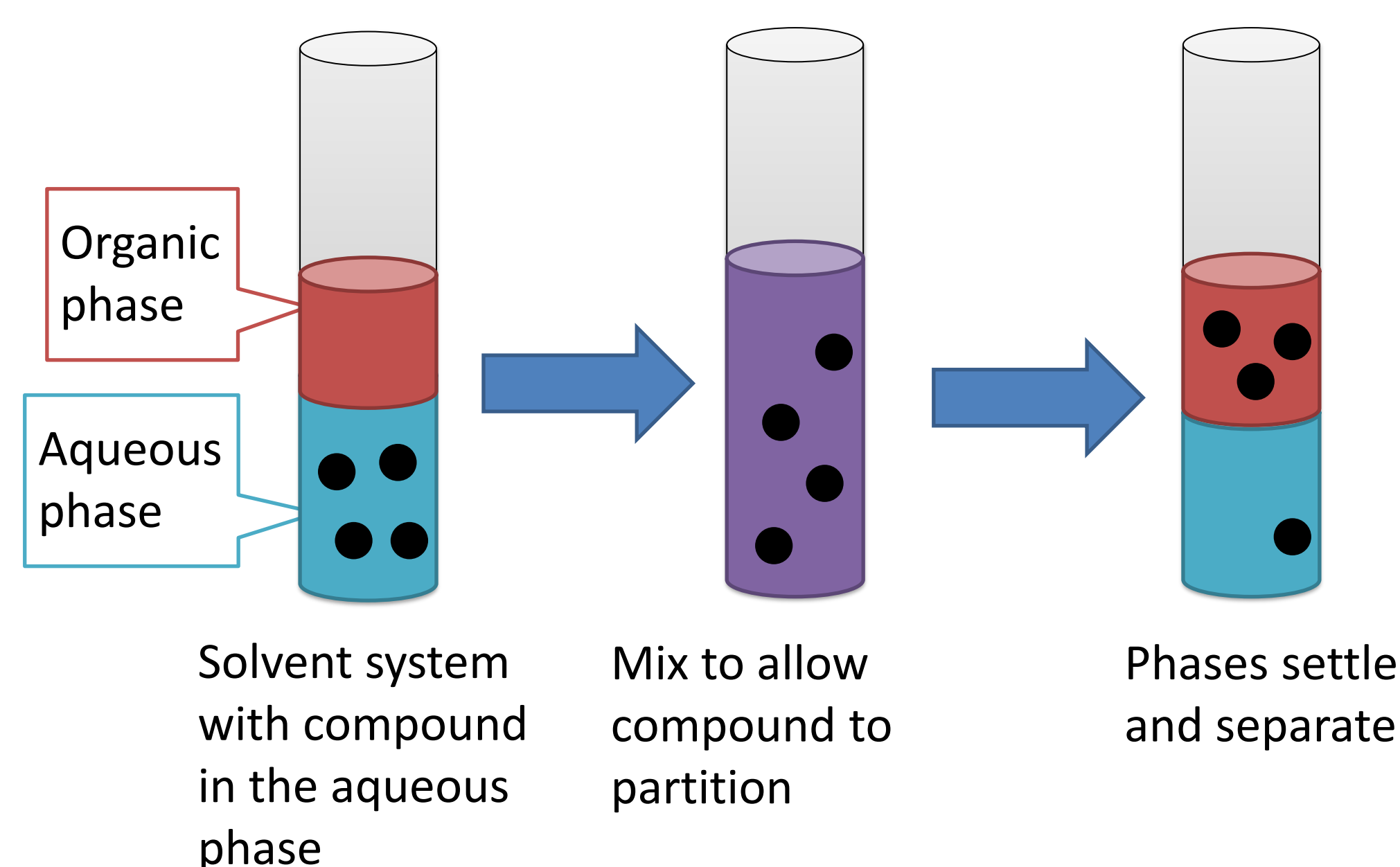


Figure 6: Schematic of a liquid-liquid extraction, where the black dots represent the compound of interest.

In this experiment, radioactive ^{201}Tl (EC , $t_{1/2} = 3.04$ d) is initially added to the aqueous phase, composed of HCl acid. After the organic phase is added, the mixture was mixed at 3000 RPM for 5 minutes and centrifuged at 4400 RPM for 1 minute. In later experiments, Tl(I) is oxidized to Tl(III) with Br_2 water.

$$D = \frac{A_{org} V_{aq}}{A_{aq} V_{org}}$$

Figure 7: Equation representing the distribution ratio, where A is activity, V is volume, aq is aqueous phase, and org is organic phase

Experimental Procedures

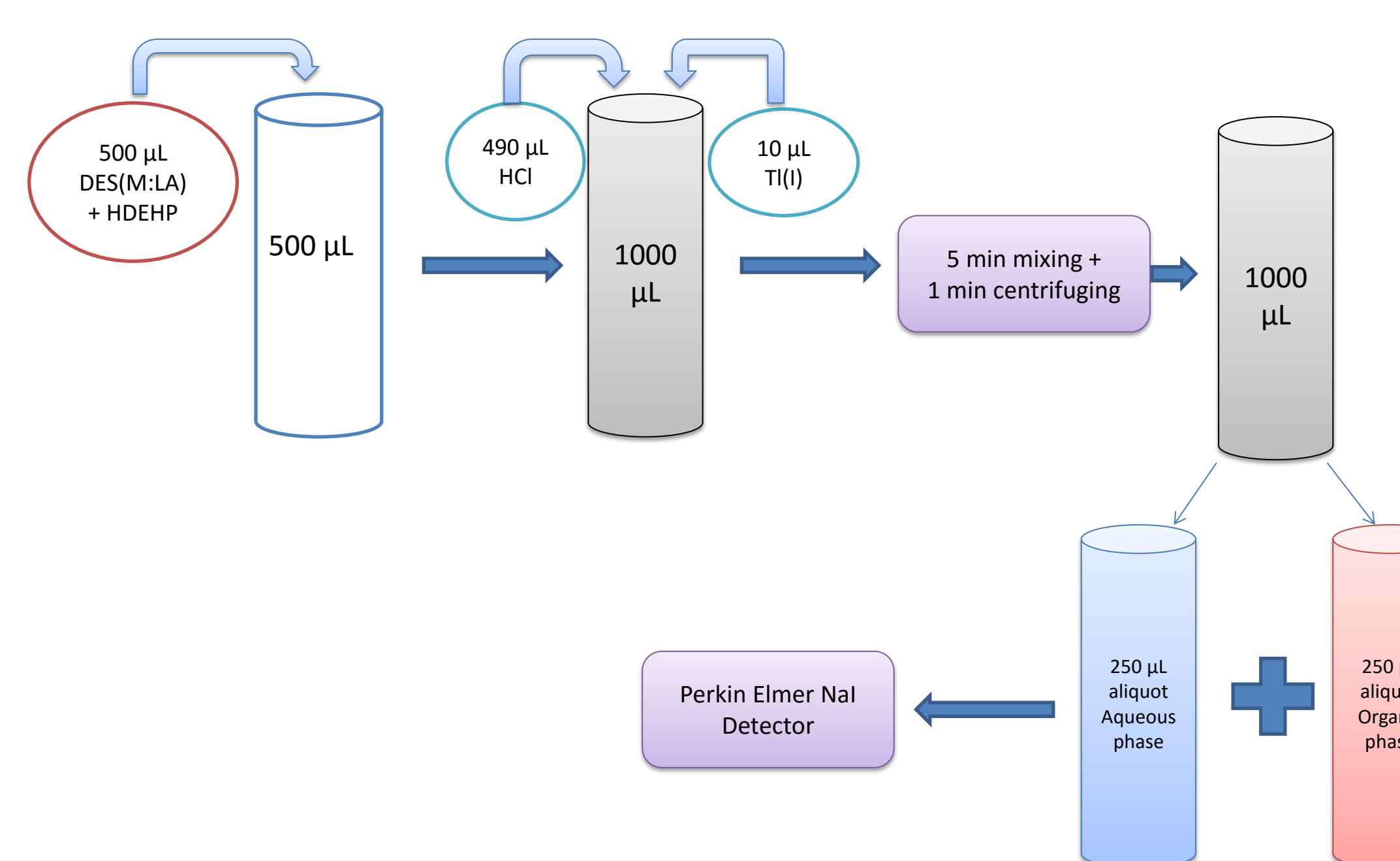


Figure 8: Experimental procedure used for the study of thallium extraction[4]

Results

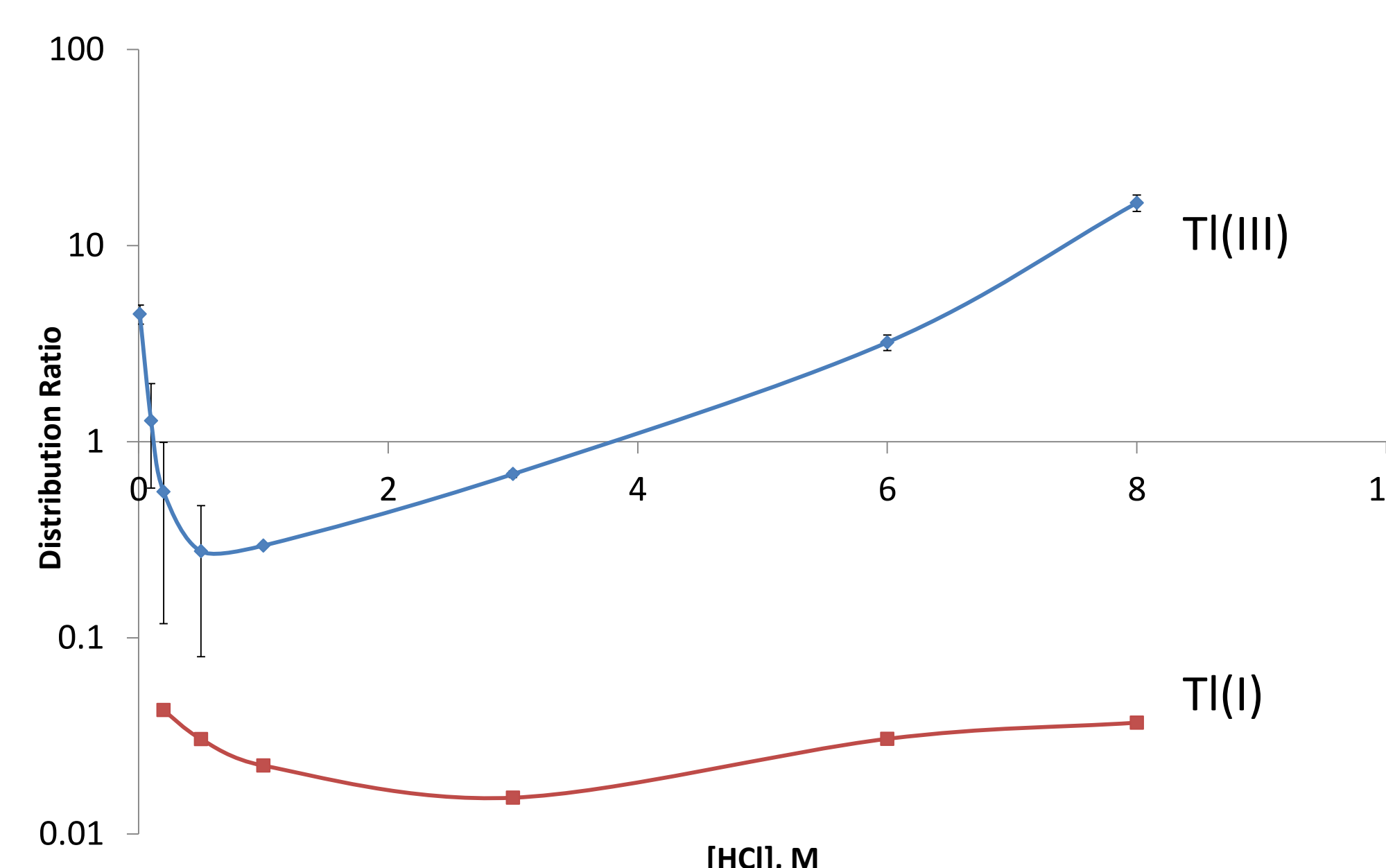


Figure 9: Distribution ratio of Tl(I), shown in red, and Tl(III), shown in blue, for extraction from HCl into the pure DES (M:LA)

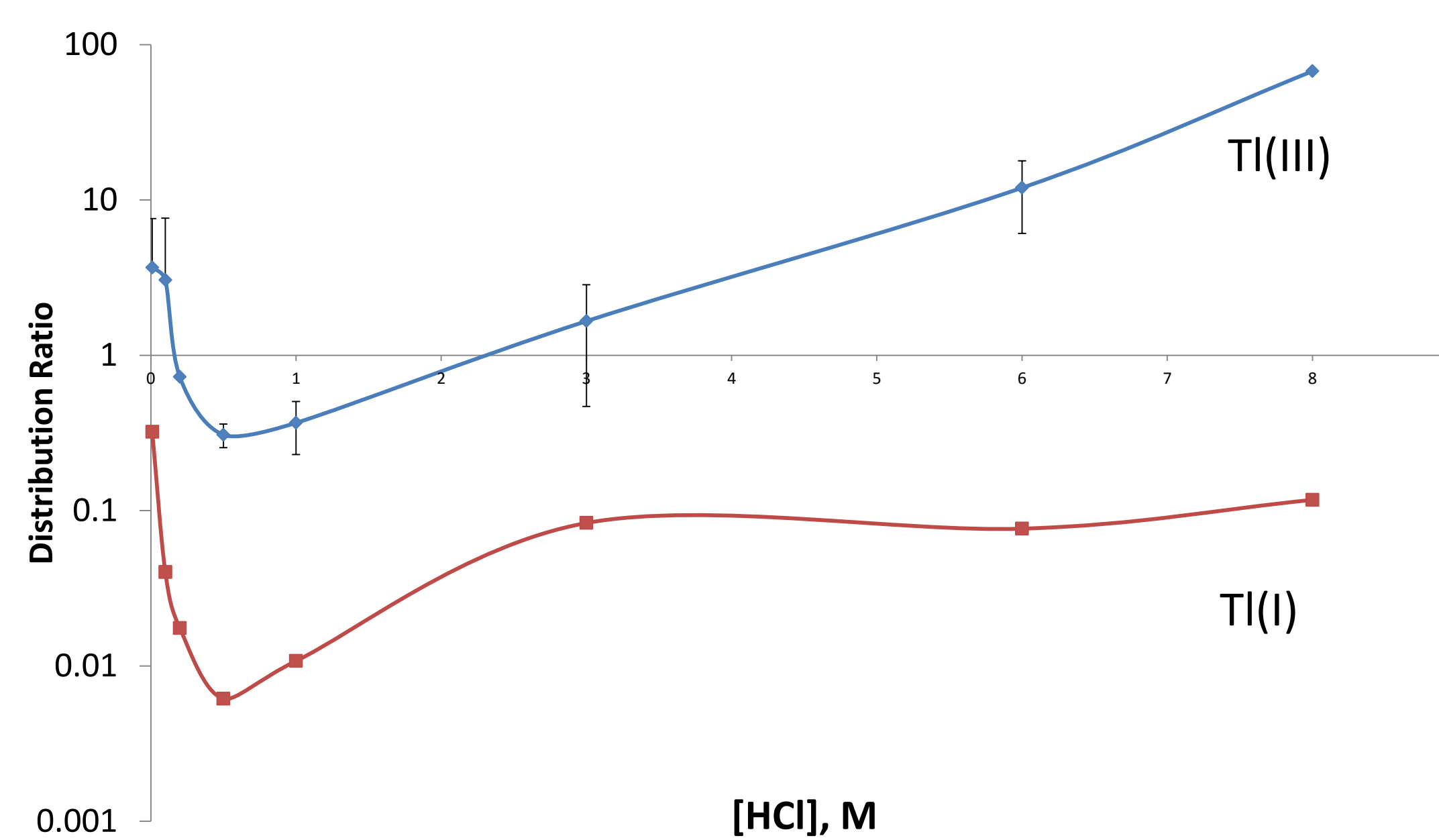


Figure 10: Distribution ratio of Tl(I), shown in red, and Tl(III), shown in blue, in from HCl into the DES (M:LA) containing 30% HDEHP

Results

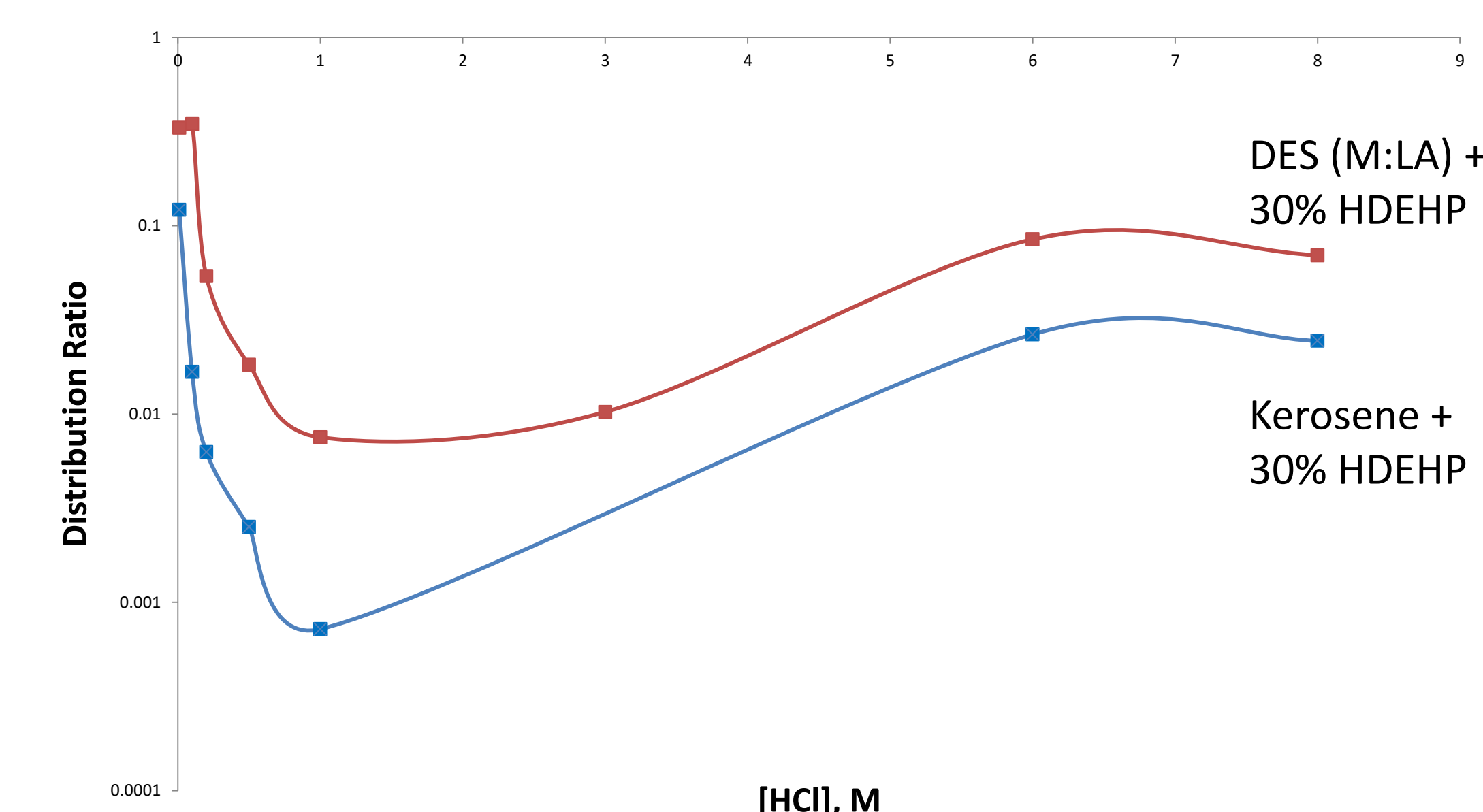


Figure 11: Comparison of the distribution ratio of Tl(I) extraction between HCl and 30% HDEHP in DES (M:LA), shown in red, and 30% HDEHP in kerosene, shown in blue

Conclusion

The distribution ratio for Tl(I) in the investigated systems, both with and without HDEHP, are all below 1.0, showing a low percent recovery. However, the DES M:LA with 30% HDEHP system extracted Tl(I) better than 30% HDEHP in kerosene. In contrast, the extraction of Tl(III) was significantly better with the DES M:LA system, both with and without HDEHP added. The difference in behavior of Tl(I) and Tl(III), as well as the previous work done on In ($D > 3000$) [4], could potentially be exploited in a future experiment on the chemical behavior of element 113.

Acknowledgements

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References

- (1) Conover, E. <https://www.sciencenews.org/blog/science-ticker/four-newest-elements-periodic-table-get-names> **2016**
- (2) Tereshatov, E. E.; Boltoeva, M. Yu.; Mazan, V.; Volia, M. F.; Folden C. M., III *J. Phys. Chem. B* **2016**, *120* (9), 2311–2322.
- (3) Tereshatov, E. E.; Boltoeva, M. Yu.; Folden, C. M., III *Solvent Extr. Ion Exch.* **2015**, *33* (6), 607–624.
- (4) Tereshatov, E. E.; Boltoeva, M. Yu.; Folden, C. M., III accepted to *Green Chem.* **2016**, doi:10.1039/C5GC03080C