**CHEMENG 277 Final Project Proposal**

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1/28/2025

**Description:** Ligand functionalized polymeric membranes (LFMs) are a promising material class that can enable ion-specific separations that are otherwise unachievable using commercially available membranes (e.g. Li+/Na+). The Tarpeh Lab has demonstrated 4-vinylpyridine functionalized LFMs for use in separation of Li+ from Ni2+ in aqueous feedstocks, in which a stronger Ni2+-4-vinylpyridine interaction strength is hypothesized to decrease Ni2+ diffusivity and ion-permeability relative to Li+ ion-permeability.12 A novel application for ion-selective LFMs is the purification of copper sulfate solutions produced from the acidic dissolution of copper scrap and electronics waste, prior to electrowinning. In this application, we hypothesize it is desirable to synthesize LFMs with ligands chosen to hinder Cu2+ ion transport while facilitating transport of contaminants, such as Zn2+. It is therefore desirable to be able to predict the strength of interaction between an ion and an organic ligand to evaluate the practicality of the ligand to achieve a desired separation.

The NIST SRD 46. Critically Selected Stability Constants of Metal Complexes3 dataset includes a vast number of recorded K-values for the stability of ion-ligand complexes in aqueous solution (Figure 1, left). We propose investigation of the NIST SRD 46 dataset for the prediction of ion-ligand interaction strength () based on ligand structure and ion identity. If successful, a predictive model could be generalized to the investigation of unobserved and novel ligand candidates for incorporation into LFMs that exhibit favorable or unfavorable interactions with application-relevant ions.

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| **Figure 1**. (left) Violin plots for values [kcal/mol] calculated from the equilibrium constant, K, for reported aqeuous ion-ligand complexes in a [ML]/[M][L] equilibria for monovalent cations. (right) | |

To-date in a previous class project, a RMSE predictive test error of 0.22 kcal/mol has been achieved employing an XGBoost Regression model trained on a feature set consisting of RDKit Lipinksi package molecular encoding features for each ligand and ion/electrophile quantitative descriptors (Figure 1, right). The trained model has been used to interpolate holes in the NIST SRD 46 dataset and allow for dG prediction between all ions of interest (in the training data) (Figure 2, left). As experimental validation, I have performed sorption experiments employing polymeric materials that are functionalized with the ligand of interest, in this first example, pyridine. A Linear Free Energy Relationship (LFER) exists between the dG observed/predicted within the interpolated NIST Dataset and that we can measure experimentally in the sorption experiments (Figure 2, right). These results demonstrate the promise of rational, ion-selective polymeric material design based on the comparison of ion-ligand dG values (as in the initial dataset).

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| **Figure 2.** (left) Model output. (Right) Linear Free Energy Relationship formed between observed. | |

In this project specifically, I propose continuing to refine the model trained in the NIST SRD 46 dataset and used to interpolate missing observations for ion-ligand interaction dGs, with the main goal of reducing predictive error below 0.22 kcal/mol. I will investigate other model architectures, as well as additional molecular encodings, specifically molecular graphs to feed into graph neural networks. A more accurate prediction of single ion-ligand dG will enable better, more robust LFERs to be formed and aid in ion-selective polymeric material design.

**Works Cited:**

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(2) Abels, K.; Botelho Junior, A. B.; Chen, X.; Tarpeh, W. Ligand Content and Driving Force Effects on Ion-Ion Permselectivity in Ligand-Functionalized Membranes. August 12, 2024. https://doi.org/10.26434/chemrxiv-2024-z6t01.

(3) Burgess, D. R. NIST SRD 46. Critically Selected Stability Constants of Metal Complexes: Version 8.0 for Windows, 2020. https://doi.org/10.18434/M32154.