This annual report encompasses the third year of grant activity. The broad goal of the project is to characterize the pre-transition droplet formation (PTDF) phenomenon that has been observed in pseudobinary liquid-liquid systems. Four objectives were delineated in the original proposal to meet this goal:

A. Assess the effect of extrinsic impurities on PTDF.
B. Explore the effect of isotopologue abundance percentages on PTDF.
C. Physically isolate pre-transition droplets and determine their composition.
D. Explore PTDF in liquid-liquid systems featuring Coulombic interactions.

Progress continued on the first objective, and work was begun on the fourth objective.

**OBJECTIVE A:** In the previous two years, preparatory work for extrinsic impurity doping tests was completed by measuring the phase behavior of the aniline + cyclohexane (ACH) liquid-liquid system. The compound 2-picoline was selected as a dopant. Two full sets of ACH doped with 2-picoline were prepared by the synthetic method. The stock aniline was doped with either 12 or 16 mole percent 2-picoline, while the cyclohexane was not doped (APCH). Each set thus had a dopant concentration that varied systematically with aniline composition. Over the past year a second 12 mole percent 2-picoline set was prepared to correct for a mixing issue in the first set, and two additional full sets were prepared at 4 and 8 mole percent 2-picoline. Figure One presents the coexistence curves measured for these APCH systems.

The critical composition $x_C$ of each system was determined from analysis of 90° laser light scattering data, and the corresponding critical temperature $T_C$ was then interpolated from the coexistence curve. The $T_C$ values decreased by $-2.16$ K per mole percent of 2-picoline dopant, and the $x_C$ values in mole fraction aniline shifted $-5.98 \times 10^{-3}$ per mole per cent of 2-picoline dopant. The shift in critical point is identified by the gray dashed line in Figure One, and followed the universal linear relation predicted by Jacobs (Phys. Rev. A 1986, 33, 2605) for perturbed liquid-liquid systems.

The entire APCH liquid-liquid coexistence surface was modeled using simple scaling theory and the observed impurity-induced shift in the critical point. The predicted coexistence lines are shown as dashed lines in Figure One. The model predicts greater miscibility at higher aniline compositions and less miscibility at lower aniline compositions than was actually observed. A residual plot (not shown) reveals that the deviations are linear, and both theoretical and experimental work are underway to improve the agreement.

**Figure One:** Coexistence curve data for the (aniline + 2-picoline) + cyclohexane liquid-liquid system. Green circles: 0% 2-picoline; yellow circles: 4%; gray circles: 8%; red circles: 12%; blue circles: 16%. Dashed lines are predicted from an impurity model for the coexistence curves and the observed critical point shift.

**Figure Two:** Difference in pre-transition droplet formation onset $T_{dr}$ and bulk phase transition temperature $T_{cx}$ as a function of composition displacement from the critical point for all five (aniline + 2-picoline) + cyclohexane data sets. The color code for the data points is the same as in Figure One.
Pre-transition droplet formation was observed in all A\textsubscript{p}CH data sets. The quantitative behavior of PTDF was identical to the PTDF behavior observed in the two-component ACH. Figure Two shows the difference in temperature between the onset of PTDF and the bulk liquid-liquid phase transition, \( T_{\text{onset}} - T_{\text{cx}} \), as a function of sample composition relative to the critical composition, \( x - x_c \). The onset and slope of all three curves appear to be the same, so the conclusions are that extrinsic doping has no effect on PTDF, and PTDF behavior shifts with the corresponding shift in critical composition.

**OBJECTIVE D:** The behavior of PTDF in liquid-liquid systems with an ionic component was explored in two ways:

*Ionic Extrinsic Dopant:* Two sets of isobutyric acid + water (IAW) samples were prepared. One set was undoped; all samples in the second set were doped with 0.03 \textit{m} KCl. The undoped IAW set has not been tested yet, but two other full IAW sets tested in this lab a decade ago did not exhibit PTDF. The KCl-doped IAW set was tested and did not exhibit PTDF either. Addition of KCl made the IAW system less miscible, shifting the maximum of the coexistence curve to higher temperature and out to a mole fraction richer in isobutyric acid. This observation was consistent with literature data, where the new maximum was assumed to be the new critical composition. However, analysis of the 90° laser light scattering data shows that the critical composition actually shifts in the other direction, towards a lower mole fraction in isobutyric acid. The magnitude of the \( T_{\text{cx}} \) shift due to KCl dopant must vary with isobutyric acid composition, much in the way that 2-picoline affects the ACH coexistence curve. Experiments to quantify this behavior are underway. A different IAW sample set, not part of this project, has exhibited greater miscibility (lower \( T_{\text{cx}} \) values) over time due to the formation of unknown degradation products. Intriguingly, the critical point observed for the 0.03 \textit{m} KCl doped system falls in line with this other different IAW system on a Jacobs plot. An additional higher molality KCl-doped IAW system will be prepared to confirm this behavior.

*Ionic Liquid Component:* Four different liquid-liquid systems containing an ionic liquid were evaluated for PTDF by making small set of samples, eight compositions per system distributed around the literature critical points:

- \([\text{C}_4\text{mim}][\text{BF}_4]\) + Aniline: Contrary to two literature articles, this system was completely miscible over the relevant composition and temperature ranges that were tested.
- \([\text{C}_6\text{mim}][\text{BF}_4]\) + Water: This system initially exhibited a liquid-liquid coexistence curve, but was unstable and became miscible over the span of a few hours. Some samples may have been shown PTDF.
- \([\text{C}_2\text{mim}][\text{NTf}_2]\) + 1-Propanol: The measured coexistence curve agreed with literature data, and three samples exhibited PTDF. Preliminary evaluation shows that the quantitative onset of PTDF (as in Figure Two) occurs at smaller values of \( x - x_c \) and has a steeper slope than other systems. However, the coexistence curve is much narrower on the mole fraction coordinate, implying that quantitative evaluation of all PTDF data should perhaps use a composition coordinate scaled by the coexistence curve amplitude.
- \([\text{C}_{10}\text{mim}][\text{NTf}_2]\) + Benzene: The measured coexistence curve agreed with literature data, but the system did not show evidence of PTDF.

After this preliminary work, a full set of \([\text{C}_2\text{mim}][\text{NTf}_2]\) + 1-propanol samples were prepared. Data collection and analysis of these samples are currently taking place.

**IMPACTS:** In Fall 2017, two undergraduates who worked during Summer 2017 (MM, TK) presented a poster titled “Impurity Effects on Liquid-Liquid Binary Systems” at the 26\textsuperscript{th} Murdock College Science Research Conference. Two undergraduates (MM, KR) subsequently worked on this project during the 2017-2018 academic year, and results from this project were central to their Senior Theses. Two undergraduates (DH, AW) worked on the project in Summer 2018. Both students attended the 73\textsuperscript{rd} Northwest Regional Meeting of the American Chemical Society, but did not present. The PI gave an oral presentation discussing outcomes of this project at the conference. The talk was titled “Plait Point Behavior in the Aniline + Cyclohexane + 2-Picoline Ternary Liquid System”.

**THREE-YEAR PROJECT OUTCOME SUMMARY:**

- **Objective A:** PTDF behavior is **unaffected** by extrinsic impurity doping.
- **Objective B:** PTDF behavior is **unaffected** by isotopologue enrichment and substitution.
- **Objective C:** Physical extraction and characterization of PTDF droplets is **still in progress**.
- **Objective D:** PTDF behavior shows **no correlation** with the presence or absence of Coulombic interactions in liquid-liquid mixtures. Quantitative comparison of PTDF (such as in Figure Two) may require scaling the composition coordinate by coexistence curve amplitudes.