RCEU Proposal for Summer 2020

Project Title: Chemical Reactions at the Critical Point of Solution

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Project Summary:

There are numerous pairs of liquids, which are only partially miscible below a characteristic temperature that depends upon the chemical nature of the pair, but which are completely miscible above this temperature. The temperature of onset of miscibility is said to be the critical solution temperature. In general, the physical properties of the binary liquid mixture vary with temperature, pressure, and the mole fraction of one of the components. Such a system is said to have *three degrees of freedom*. Systems with three degrees of freedom exhibit exceptional behavior as the temperature approaches the critical temperature [1]. For example, the heat capacity is observed to grow without bound. This type of behavior can be found in systems as diverse as gases, superconductors, and the binary liquid mixtures. These similarities provide the basis for the principle of *universality* which is thought to govern all critical phenomena.

Unlike the gases and the superconductors, however, the binary liquid mixtures can be used as solvents for chemical reactions. One may readily inquire, "What will be the behavior of the position of chemical equilibrium in a binary mixture as the temperature approaches the critical solution temperature?" We have shown theoretically, and confirmed experimentally, that in all cases exhibiting three degrees of freedom, the temperature dependence of the position of equilibrium diverges toward infinity as the temperature approaches the critical solution temperature [2].

We have measured, for example, the solubility of a solid metal oxide dissolving in a mixture of isobutyric acid + water, a system which has a critical temperature near 26 C, and is described by three degrees of freedom. The dissolution in this case is due to the *acid/base* reaction of *liquid* isobutyric acid with the *solid* metal oxide, which serves as the base. In agreement with the universality concept, the solubility of the metal oxide is strongly affected as the temperature approaches the critical solution temperature.

Our goal for the summer is to carry out an experiment in which solid benzoic acid dissolves in a mixture of 2,6-dimethylpyridine + water. The *solid* benzoic acid should go into solution by acid/base reaction with the *liquid* base, which is 2,2-dimethylpyridine. Whereas in the experiments involving metal oxides dissolving in isobutyric acid + water, the base (i.e. the metal oxide) is in the solid phase and the acid (i.e. isobutyric acid) is in the liquid phase, it is just the reverse in the case of our RCEU proposed experiment The base (i.e. 2,2-dimethylpyridine) is in the liquid phase, while the acid (i.e. benzoic acid) is in the solid phase. *Although the phases are reversed, we predict that near the critical solution temperature, the temperature behavior of the solubility of the solid benzoic acid will mimic the temperature behavior of the solubility of the solid metal oxide. Hence, we expect "universality" to prevail! Our RCEU student will test this proposition.*

References:

1.J. K. Baird, X. Wang, J. R. Lang, P. Norris, *Chem. Phys.* Lett. **729** (2019) pp. 73-78
2.J. K. Baird, J. R. Lang, X. Wang, A. Mukherjee, *J. Phys. Chem. B* **123** (2019) pp.5545-5554.

Student Duties:

In order to control and hold constant the temperature in this experiment, the reaction vessel will be suspended in 14 L water bath located in the Chemical Physics Research Laboratory in MSB 224. The student will learn to operate the thermostat, heating element, and stirrer in this water bath. The temperature in the bath will be measured using a platinum resistance thermometer. The solvent mixture of 2,6-dimethylpyridine + water will be prepared at the critical composition by weighing on an analytical balance. The liquid mixture, along with the reactants, will be added to the reaction vessel. The reaction will be allowed to proceed to equilibrium under conditions of continuous stirring using a magnetically controlled stirring bar. Periodically, the student will extract a sample from the reaction mixture using a seriological pipet. The sample will be titrated to determine the benzoic acid content. The student will plot the benzoic acid content, s, in the thermodynamic form of $\ln s$ vs. $1/T$ and look for the expected divergence in the slope as the temperature, T, approaches the critical temperature.

Tangible Contributions:

The tangible outcome of all academic scientific research is publication. At the end of the summer, Dr. Baird and the student will collaborate on submitting a manuscript for publication in a refereed research journal. Because the experiment has a straightforward design, it may also be possible to describe a simple version of the experiment for publication in the Journal of Chemical Education.

Specific Outcomes:

The activities described above are common to all industrial analytical chemistry laboratories and will help the student to build a CV supporting employment in industry. Specifically, he will understand how to operate temperature measurement and control instrumentation and to make precision weighings and titrations. He will be able to observe the remarkable cloudiness, termed critical opalescence, which occurs in liquid mixtures near the critical point. On the theoretical side, he will be exposed to thermodynamics and the principle of critical point universality.

Student Prerequisite:

CH 123 General Chemistry II or equivalent.

Faculty Mentorship:

The student's laboratory work will be under the direct supervision of Dr. Baird, who is a daily presence in his laboratory during the summer. He will be assisted by Mr. X. Wang, a third year student in the MTS Ph.D. program. The RCEU student will be trained on the thermostat equipment in the Chemical Physics Research Laboratory in MSB 224. Dr. Baird and Mr. Wang will meet daily with the student to discuss both critical point universality theory and the experimental progress. Discussion of the experiment will include both technique, and methods of data reduction.