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Thermodynamics of Deuterium Oxide Separations in Aqueous Two-Phase Systems

The goal of this seedling project was to ascertain the ability of Organic-Aqueous Two-Phase systems to enhance the separability of deuterium from protium. Such a technology represents a novel and benign process for the recovery of hydrogen isotopes via liquid-liquid extraction. This process could, in principle, be employed as a tool for low cost deuterium oxide preparation for nuclear science studies.

The overall goal of applying organic-aqueous two-phase systems in deuterium separation is to apply a technology known as “Organic-Aqueous Tunable Solvents”, or OATS, toward ternary systems containing H_2O and D_2O. The principle of OATS is the combination of an aqueous phase (in this case comprised of H_2O, HDO, and D_2O), a miscible organic solvent (such as acetonitrile or tetrahydrofuran), and an easily-removable antisolvent (a compound soluble in one phase but not the other, such as CO_2). The potential benefits of application of OATS to deuterium oxide separation is the fact that such systems are tunable to a great extent, allowing wide variation of the hydrophilicity and hydrophobicity of each phase.

The scope of this seedling project is to demonstrate the thermodynamic differences between H_2O-organic-antisolvent systems and D_2O-organic-antisolvent systems as a proof-of-principle for the use of OATS in deuterium separation and to serve as a source of data for the preparation of further proposals.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

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Thermodynamics of Deuterium Oxide Separations in Aqueous Two-Phase Systems

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Abstract: The thermodynamic behavior of aqueous-organic-toluene ternary systems where aqueous components are water (H_2O) and deuterium oxide (D_2O) and organic components are acetonitrile (MeCN), tetrahydrofuran (THF), and 1,4-dioxane (DIOX) have been recorded. Preliminary data has been taken for each ternary system to establish the concentration along the spinodal line where Gibbs energy is minimized. In pursuit of this goal, simple laboratory techniques using common equipment was used to benchmark thermodynamic measurements against values reported in the literature. The impact of deuterium on aqueous two-phase separations was determined for each combination of solvents.

FY2020 Objectives

- Develop SRNL Hazard Assessment to allow work with organic solvents in nonradiological facilities
- Develop cost-effective analytical techniques to measure concentrations of multiphase mixtures in thermodynamic equilibrium
- Develop simple experimental protocols to facilitate thermodynamic measurements with commonly-available laboratory tools
- Benchmark experimental protocols and analytical techniques against literature data to verify accuracy
- Determine the phase equilibria of H_2O-organic-toluene ternary systems
- Determine the phase equilibria of D_2O-organic-toluene ternary systems
- Quantify the impact of deuteration on phase separation in aqueous two-phase systems

Introduction

One of the most important non-radiological compounds used in the nuclear industry and the nuclear research field is deuterium oxide (D_2O), also known as "Heavy Water". D_2O is produced around the world using a variety of inefficient separation techniques that employ dangerous chemicals, high energy expenditures, and large waste volumes. Among these production techniques, the most favored leverage slight differences in the chemical characteristics of O-H and O-D bonds to effect a marginal separation via thermodynamic equilibria. The challenges of hazardous chemicals, high cost of production, and inefficient separation make the large-scale production of D_2O a daunting task. Despite the availability of stockpiles of D_2O, the absence of an efficient domestic source of heavy water has often been critiqued by subject matter experts in the nuclear and national security arenas.[1]

The practice of using Organic Aqueous Tunable Solvents (OATS) as a vehicle for tunable separations is well documented and has been established as a robust solvent extraction process. The principle behind OATS is relatively simple: a water-miscible organic solvent (e.g. acetonitrile) is combined with water to form a single liquid phase. Upon necessity, an antisolvent (a compound exclusively soluble in one of the two solvents) is added such that a phase split is induced. In the case of OATS, this antisolvent is usually CO_2, which can be easily removed by depressurization to restore single-phase behavior. Once a second phase is formed.[2]

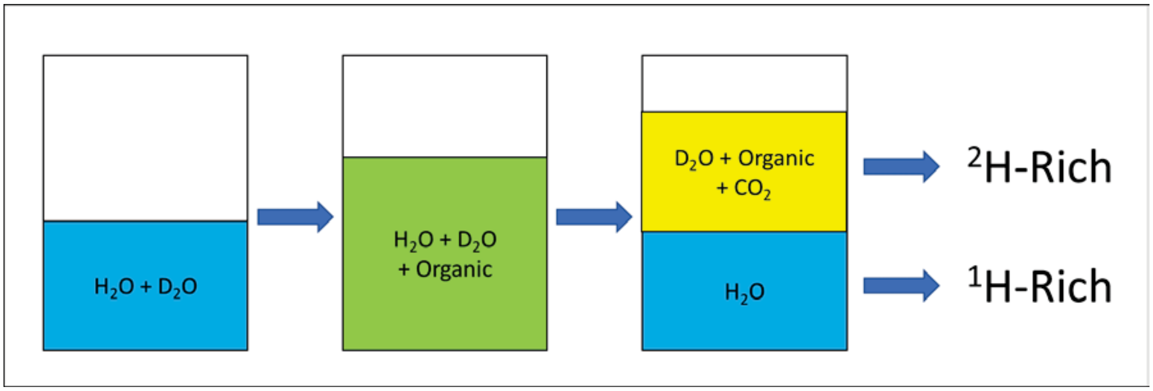

Figure 1. Simplified flowchart of OATS thermodynamics as applied to deuterium separation.

The objective of this program was to perform preliminary scoping studies to ascertain the applicability of OATS processing to the separation of D_2O from H_2O. In particular, the goal of this research was to measure the ternary phase behavior of aqueous-organic-toluene systems and determine the impact (if any) of deuteration on phase separation and critical solution compositions.

Approach

The approach taken throughout this research program may be summarized in three objectives. The first objective was to develop testing protocols and analyses that would allow for low-cost, non-complex measurement of organic concentrations necessary to understand the ternary thermodynamic equilibria of OATS solvents and D_2O. The second objective was to perform measurements of concentrations along the spinodal line for aqueous-organic-toluene ternary systems in the presence and absence of deuterium (toluene was employed as an antisolvent for scoping purposes; use of pressurized CO_2 would necessitate higher design and planning costs). The third objective was to quantify the differences in thermodynamic equilibria between systems containing H_2O and D_2O in order to ascertain the feasibility of OATS to serve as a separation tool for deuterium oxide processing.

Figure 2. Thermo Genesys 10S UV/Vis Spectrophotometer used in organic concentration measurement. Photo from Thermo Fischer.

Results and Discussion

Using common laboratory glassware (i.e., 2- and 4-dram vials, beakers, disposable pipettes, etc.), a simple procedure for determining metastable ternary concentrations (defined as the region between the spinodal and binodal curves of a ternary mixture) was developed that allowed for a significant reduction in the time and financial cost of thermodynamic measurements. While the accuracy of this method is diminished compared to traditional tie-line measurements of biphasic systems, we were able to show that the data achieved using this technique is comparable to data reported in literature using conventional measurement techniques.[3]

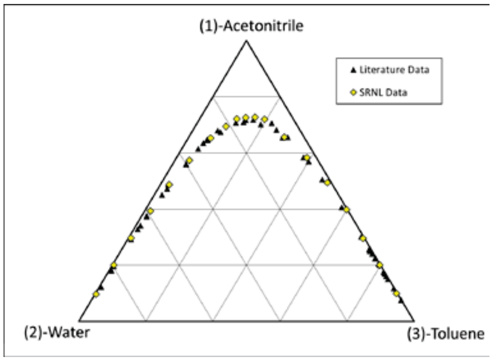

Figure 3. Ternary phase diagram of $MeCN$-H_2O-Toluene equilibria.

In these ternary combinations, the number of components involved in any experiment is three (aqueous, organic, and antisolvent). However, the number of available phases is assumed to be two (two distinct liquid phases; the vaporization of organics and water was assumed to be negligible for the purposes of these scoping experiments). For this reason, temperature and pressure alone are not able to fully specify the properties of a mixture (the Gibbs phase rule indicates that the system is underspecified). Therefore, a measurement of at least one component's concentration is necessary to fully characterize each biphasic mixture. For this purpose, a benchtop UV/Vis spectrophotometer was used to measure the concentration of the antisolvent in each of the biphasic mixtures. This measurement necessitates only a small sample of the organic rich phase followed by large dilution into the organic solvent of choice before measurement. Throughout this work, the spectra of toluene between 200 and 300 nm was considered for quantification, with useful peaks occurring at 262 and 269 nm.

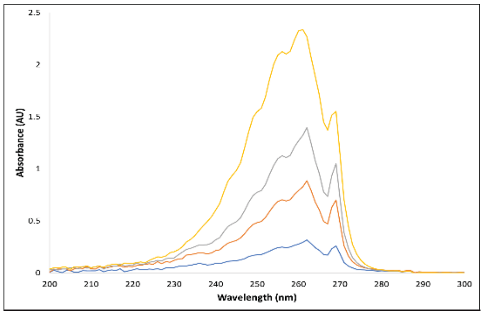

Figure 4. UV/Vis spectra of toluene in Tetrahydrofuran.

Once all of the necessary data had been collected, comparisons were drawn between ternary systems containing H_2O and ternary systems containing D_2O. Generally speaking, differences in spinodal line concentrations are observable when H_2O and D_2O are interchanged. However, the differences at the conditions achievable at this scale are notably small, suggesting that further investigation should be made at different conditions (e.g., temperature).

FY2020 Accomplishments

The following accomplishments were achieved as a result of this work:

- A Hazard Assessment was successfully developed that will allow future work with OATS materials and deuterium oxide with minimal modification.
- A simple dilution protocol was developed for rapid determination of toluene in organic solvents using a benchtop UV/Vis spectrophotometer.
- A quick, low-cost experiment was designed to allow rapid determination of ternary phase equilibria by observation of the cloud points at the metastable regions. This experimental technique was successfully benchmarked against conventional methods reported in literature and found to be capable of similar accuracy.

- Phase equilibria of aqueous (H_2O and D_2O), organic (MeCN, THF, and DIOX), and toluene ternary phase behavior was measured.
- Separability of deuterium via OATS was demonstrated on a small, unoptimized scale using toluene as a surrogate antisolvent.

Future Directions

Results from this research suggest that differences in H_2O and D_2O separation at room temperature, while quantifiable, are suboptimal compared to those achieved at lower temperatures (based on literature studies with D_2O and acetonitrile). While the direction of this optimality may not be universal (optimum temperatures in D_2O-THF-CO_2 separations may occur at higher temperatures), it is clear that temperature variation studies are needed to fully refine and optimize OATS as a D_2O separation process. Furthermore, it is desirable to transition from using the surrogate toluene to using an effective OATS antisolvent (such as CO_2 or propane). While this transition would include the development of testing equipment capable of handling high pressures, the use of a gaseous species greatly simplifies the measurement of phase equilibria concentrations (the degrees of freedom according to the Gibbs phase rule are decreased when a substantial vapor phase is introduced).

To this end, the following steps are recommended as a trajectory for future work:

- A pressure vessel capable of temperature control and optical measurements (e.g., compatible with a cathetometer) should be constructed to allow for non-destructive measurements of ternary phase equilibria across a wide range of temperatures and pressures.
- Equipment for generating high pressures of CO_2 and propane should be procured to facilitate the use of antisolvent at pressures higher than those achievable from standard cylinders.
- Non-destructive phase equilibria measurements should be performed for ternary systems of aqueous (H_2O and D_2O), organic (MeCN, THF, DIOX, and Isopropanol), and antisolvent (CO_2) systems).
- Optimized separation conditions should be used to design a cascade experiment to demonstrate the efficacy of OATS to separate D_2O from H_2O.

References

1. "Isotopes for the Nation's Future: A Long Range Plan"; NSAC Isotopes Subcommittee: **2009**.

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Acronyms

DIOX	1,4-Dioxane
MeCN	Acetonitrile
OATS	Organic Aqueous Tunable Solvents
THF	Tetrahydrofuran
UV	Ultraviolet