

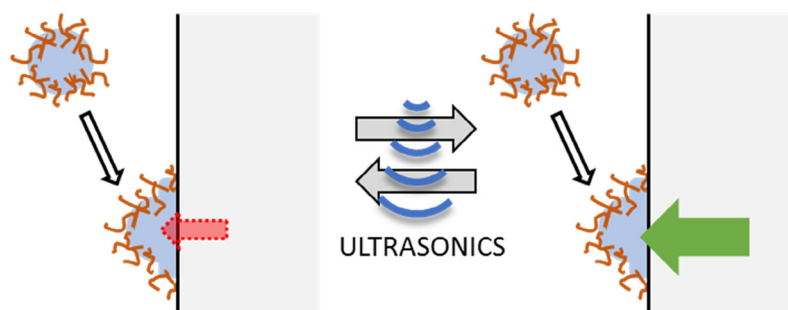
# Acoustic activation of water-in-oil microemulsions for controlled salt dissolution

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## GRAPHICAL ABSTRACT



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## ABSTRACT

**Hypothesis:** The dynamic nature of the oil-water interface allows for sequestration of material within the dispersed domains of a microemulsion. Microstructural changes should therefore change the dissolution rate of a solid surface in a microemulsion. We hypothesize that microstructural changes due to formulation and cavitation in an acoustic field will enable control over solid dissolution rates.

**Experiments:** Water-in-oil microemulsions were formulated using cyclohexane, water, Triton X-100, and hexanol. The microstructure and solvation properties of Winsor Type IV formulations were characterized. Dissolution rates of  $\text{KH}_2\text{PO}_4$  (KDP), were measured. A kinetic analysis isolated the effect of the microstructure, and rate enhancements due to cavitation effects on the microstructure were characterized by measuring dissolution rates in an ultrasonic field.

**Findings:** Dispersed aqueous domains of 2–6 nm radius dissolve a solid block of KDP at 0–10 nm/min. Dissolution rate is governed not by the domain-surface collision frequency but rather by a dissolution probability per domain-surface encounter. Higher probabilities are correlated with larger domains. Rapid and reversible dissolution rate increases of up to 270× were observed under ultrasonic conditions, with <20% of the increase due to bulk heating effects. The rest is attributed to cavitation-induced changes to the domain microstructure, providing a simple method for remotely activating and de-activating dissolution.

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## 1. Introduction

Controlling the dissolution rate of materials is an important chemical processing problem with applications in drug delivery,

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separations, and solid surface dissolution. For water-soluble materials, water-solvent blends or temperature control offer limited control over rates. One approach for achieving control of dissolution rate is to use a microstructured fluid whose structural properties can be altered by formulation or external activation. If the external activation is rapid and reversible, true temporal control over surface dissolution rates can be achieved.

In this study, we investigate temporal control of the dissolution rate of a solid salt surface in a microemulsion. Microemulsions are mixtures of immiscible oil and water with microscopic phase interfaces stabilized by surfactant (and optionally a cosurfactant). The structure, formation, and applications of microemulsions are well-covered in the literature and we will only briefly describe them here [1,2]. A microemulsion is formed when a surfactant lowers the interfacial tension by a factor of  $10^4$ – $10^5$ , which drives an increase in interfacial area by a similar factor. The increase in interfacial area disperses one of the phases into a large number of nanoscale domains. The microstructure forms spontaneously based on free-energy minimization, so microemulsions are thermodynamically stable and will not spontaneously separate into multiple phases even after long times. The thermodynamics of microemulsion formation have been described previously [1,3–5].

Microemulsions can be classified based on the number of microscopic phases formed. Winsor Types I–III have multiple macroscopic phases. We sought a Winsor Type IV water-in-oil system, which is a macroscopically isotropic solution composed of many nanoscale domains of water dispersed in a continuous phase of oil [6]. The microscopic phase structure of these Winsor Type IV formulations can be exploited with the chemical processing convenience of an isotropic fluid.

Microemulsions have been used in a wide number of research and consumer applications [7]. Many of these applications are driven by the ability of a microemulsion to segregate a solute into the dispersed domains, which is useful for drug delivery [8], templated synthesis of nanoparticles [9–12], and separation or extraction processes [13]. The dynamic fusion and fission of dispersed domains forms the basis for the mechanism by which segregated solute disperses throughout a solution. Our focus is not on the overall dispersibility of a solute nor on the impact of domain-domain interactions on the dispersal kinetics. We aim to use the dynamic nature of microemulsions to control dissolution that occurs when dispersed domains interact with a solid surface. Control over the rate at which a solid material dissolves into the dispersed domains would allow accurate and quantitative movement of material from a solid phase into a liquid phase. In this study, we test this concept by investigating the movement of a water-soluble material (salt) from a solid surface to the dispersed aqueous domains of a microemulsion. Previous studies have used microemulsions to extract salts from a solid surface [14–16], and we expand this work by using a kinetic approach to investigate the relative contributions of domain density and domain microstructure on dissolution rate.

The concept of using a microemulsion to temporally control dissolution has been previously reported within the context of abrasive-free polishing slurries. Matsuda et al. first reported the use of microemulsions for polishing copper [17]. In that system, the aqueous domain was doped with a copper etchant and the applied pressure from a polishing pad increased the removal rate by more than  $100\times$ . Several recent studies have used microemulsions as a polishing slurry for potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ , KDP), a water-soluble salt, with the applied polishing pressure increasing the dissolution rate by  $3\times$ – $20\times$  [18–20]. These systems utilize forces that are localized to interfaces (e.g., shear between moving solid surfaces) to “activate” dispersed aqueous domains and facilitate transport from the solid phase to the dispersed domain.

In this work, we extend this concept to include volumetric activation—achieved through an acoustic field—of the dispersed aqueous domains. We also use the highly water-soluble KDP as a sensitive probe for this activation and show that dissolution rates can be rapidly and reversibly enhanced by more than  $100\times$ , providing a large dynamic range for turning dissolution “on” and “off.”

The composition of the microemulsion controls its solvation properties, microstructure, and ultimately the dissolution rate.

## 2. Materials and methods

### 2.1. Microemulsion synthesis

All formulations were synthesized with cyclohexane (99.5%, Sigma-Aldrich), Triton X-100 (4-(1,1,3,3-tetramethylbutyl) phenyl-polyethylene glycol, laboratory grade, Sigma-Aldrich), 1-hexanol (98%, reagent grade Sigma-Aldrich), and de-ionized water ( $18.2\text{ M}\Omega\text{-cm}$ ). Reagents were used as-received without further purification. Triton X-100 and 1-hexanol were first mixed in a 3:2 mass ratio to form a master surfactant/cosurfactant mixture. The master surfactant was added to cyclohexane and mixed by shaking for 30 s in a capped bottle. Water was added and the solution mixed by shaking again. All formulations were mixed gravimetrically in the ratios noted in the text in batch sizes of 10–100 g. We did not observe a dependence of the microemulsion formation or performance on batch size.

### 2.2. Dynamic light scattering

Dynamic light scattering (DLS) data was collected on Brookhaven NanoBrook 90Plus PALS detecting  $90^\circ$  scatter from a 640 nm laser. Samples were loaded into a 1-cm path length fused quartz cuvette and allowed to thermally equilibrate to  $25^\circ\text{C}$  for 5 min. Three consecutive scattering measurements were collected, each for an average of 3 min. The diffusion coefficient was computed using the CONTIN algorithm and converted to hydrodynamic radius through the Stokes-Einstein relation. The dispersed domains were assumed to be moving through a medium with the viscosity of cyclohexane (0.89 cP).

We note that the hydrodynamic radius is not the true geometric radius of the dispersed water phase, which may not necessarily have a spherical shape. The Stokes-Einstein relation is based on the low-Reynolds number drag of a hard sphere in a viscous fluid, providing a lower bound to the true geometric radius of the soft and elastic dispersed domains. Although not the true geometric radius, the hydrodynamic radius can be used to determine trends in the size and number density of the dispersed phase domains.

### 2.3. Titration

The salt carrying capacity of KDP (>99.0%, reagent plus, Sigma-Aldrich) was determined by titration of saturated microemulsions with 10 mM NaOH. For these formulations, the water used to make the microemulsion was first loaded with KDP. The loading varied between 15 and 60 mmol KDP/100 g solution. The water was then added to the surfactant/co-surfactant/oil mixture and allowed to settle overnight. Microemulsions in which precipitate was visible were considered saturated and analyzed by titration to the second equivalence point (pH = 9.7). Prior to titration, the salt was partitioned into a bulk aqueous phase by adding an excess of water to a small volume of sample (1–6 mL). For each formulation, a salt-free sample was titrated as a background measurement which was subtracted from subsequent analyses of saturated samples.

### 2.4. Dissolution experiments

The dimensions and weights of KDP monoliths were individually measured. Typical monolith dimensions were  $16\text{ mm} \times 16\text{ mm} \times 5\text{ mm}$ . Samples were immersed in a glass beaker containing microemulsion. The beaker was covered with a watch glass. Some experiments were allowed to rest quiescently

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