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Review

Impact of confinement and interfaces on coordination chemistry: Using oxovanadate reactions and proton transfer reactions as probes in reverse micelles

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ABSTRACT

The versatility of the heterogeneous environment in microemulsions and its impact on coordination chemistry is illustrated by the simple reactions of oxovanadates in aerosol-OT (AOT)/isooctane reverse micelles (RMs). In reverse micelles, vanadate dimerization at neutral and basic pH increases compared to bulk aqueous solution, consistent with localizing in the water pool and an increase in the proton concentration. Formation of tetrameric and pentameric oxovanadate also increases at neutral and basic pH in micellar environments, but at some pH values this system achieves oxovanadate mixtures not accessible in aqueous solutions. Proton transfer reactions monitored using decavanadate suggest that the interior of water pools have proton concentration approximating neutral pH values. These results lead to the proposal that a proton gradient from the RM interior toward the periphery is established in these systems, when the initial aqueous solution is acidic prior to RM formation. In addition to solvation, the effect of these RM structures on such simple systems (although less conventional coordination complexes), suggest the potential for application of these systems to direct the coordination chemistry of metals and metal complexes for preparative purposes. For example, in the emerging field of nanochemistry RMs are used as a template for the synthesis of nanostructures.

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1. Introduction

Using oxovanadates as probes we explore the general question of how interfaces and confined environments impact the coordination chemistry of metal complexes. Oxovanadates are a class of oxometalates formed from vanadium metal ions and oxygen ligands [1,2]. Oxovanadates are generally negatively charged anions with size dependence based upon the number of vanadium atoms and the specific structure of these species. The simplest oxovanadate, commonly referred to as vanadate, exists in three protonation states (HVO_4^{2-}, $H_2VO_4^{2-}$ and VO_4^{3-}) in aqueous solution [1–4]. This simple oxovanadate undergoes a range of oligomerization and deprotonation reactions [4–11]. Oxovanadates are of interest due to the analogy between vanadate and phosphate, the inhibition by vanadates of enzymes, the catalytic potential of these complexes and the insulin enhancing properties of vanadium complexes [1–3,12–14]. Although the oxovanadates may not be the prototype of a coordination complex as defined by Werner,

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the great diversity of coordination complexes [15] should include these molecules produced from metal ion and oxygen ligands. Applications of coordination complexes cover a wide range with examples from hydrometallurgy [16], specialty chemical applications such as oxo group functionalization of the uranyl dication [17], analytical applications in environmental clean-up [18], trace level metal ion detection [18,19] and organic synthesis through applications in catalysis with organometallic coordination compounds [20] to radiopharmaceuticals [21], diagnostic imaging and therapy [22,23], applications in nanoscience [24], bioinorganic models to study structure and function of enzymes [25,26] and medicinal applications as anti-cancer drugs [27–29], anti-diabetic agents [2,30,31] and potential anti-HIV agents [32,33]. Recently, researchers have noted the clinical and commercial aspects of metals, metal complexes and the chemistry of coordination complexes in microheterogenous environments such as RMs. This new frontier may prove critically important, because as we show here the micellar environment extends the chemistry observed under conventional conditions.

The coordination number and ligand coordination to a metal ion in a complex are important factors contributing to the stability and kinetic properties of a complex. In general, properties of coordination complexes are sensitive to pH, ionic strength, temperature and solvation. How interfaces impact these factors depends on the specific interface and fundamental properties of the coordination complexes. Here, we describe the impact of confined media and surfactant interfaces on simple vanadium oxovanadates, as corresponding information on vanadium complexes has not yet been determined to the same level of detail. Effects considered are complex geometry, reaction equilibria and rates of reactions. Few coordination complexes associated with lipid or surfactant interfaces have been reported [34–37] but vanadium in the 5+ oxidation state forms a range of oxovanadates that can be readily investigated using ^{51}V NMR spectroscopy and studies with these complexes are available in greater detail [38–42]. Properties relating to the chemistry of oxovanadates in RMs appear to be affected by the surfactant interface. This may support unconventional chemistry not readily observed in aqueous solution and is demonstrated by the syntheses of nanostructures within a micellar template [43].

2. Reverse micelles (RMs)—a versatile microemulsion

Microemulsions form from mixtures of non-polar solvent, surfactant and polar solvent, usually H_2O [44–48]. The specific properties of the system depend on the non-polar solvent, the surfactant and the ratios of the different components. Microemulsions form from a range of non-polar solvents, especially alkanes such as isooctane and cyclohexane, aromatic solvents such as benzene and toluene, halogenated solvents and supercritical liquids [44,46]. Various surfactants such as negatively charged bis(2-ethylhexyl)sulfosuccinate (aerosol-OT, AOT) [46], positively charged cetyl trimethylammonium bromide (CTAB) and chloride (CTAC) [49] and non-ionic surfactants such as polyoxyethylene(5) nonylphenyl ether (Igepal CO-520) and polyoxyethylene(4) lauryl ether (Brij-30) [50] form an array of structures from micelles to reverse micelles (RMs) and more complex structures. Finally, although most microemulsions include water as the polar solvent, other polar solvents such as glycerol, ethylene glycol, formamide, dimethyl sulfoxide and dimethyl formamide have been used. Recently, researchers have explored microemulsions formed with room temperature ionic liquids as the polar phase.

RMs have been used for a wide range of applications. The heterogenous environments available in RMs can present an alternative to phase transfer catalysis [51]. Confinement in an RM environment can strongly influence the outcome of catalytic reactions [51–59]. For example, Backlund et al. [53] have synthesized chiral esters with high optical purity from racemic substrates using commercially available lipases in microemulsion environments [53]. Correa et al. observed enhanced reaction rates for the nucleophilic aromatic substitution of 1-fluoro-2,4-dinitrobenzene with *n*-butylamine and piperidine when reactants were in RMs compared to bulk solution [54]. RMs have also been widely used as media to form metal nanoparticles useful for catalysis applications [60–64]. We have recently investigated the oxidation of ascorbic acid in RMs catalyzed by oxygen or by vanadate and found the ascorbate reactivity being related to the location of the reaction components [65]. Most of the work described in this paper will relate to the conditions obtained when the components form RMs in an AOT/organic solvent system.

RMs are self-assembled nanosized structures of surfactants or lipids in which an aqueous water pool is surrounded by an organic solvent, Fig. 1. These ternary or higher order systems support environments that range from very hydrophilic to very hydrophobic. The interior water pool is very hydrophilic and in larger RMs has properties that resemble that of bulk water (Fig. 1A). At the interface of the water pool with the surfactant the environment can be very polar if the surfactant is charged. The illustration shows an RM formed using a negatively charged surfactant, with the accompanying positively charged counterions (Fig. 1B). If a solute is able to penetrate the interface further, it can reach a more hydrophobic

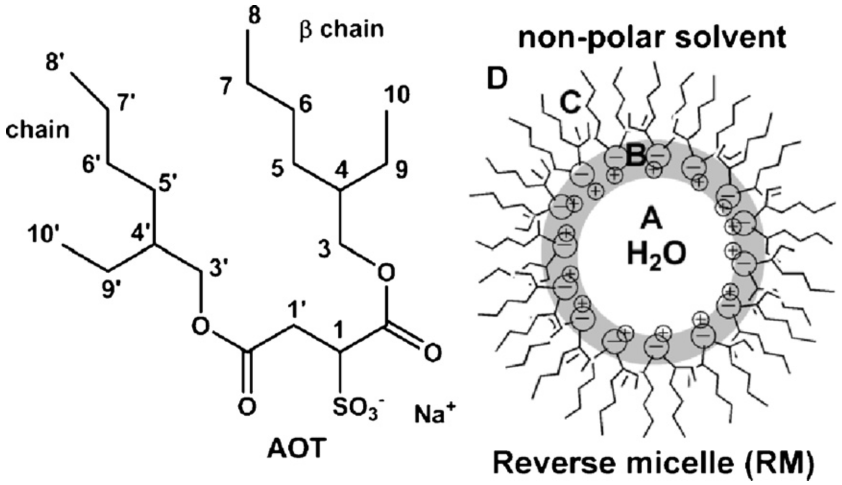

Fig. 1. The structure for AOT is shown as a schematic illustration of an RM based on an AOT/isooctane system with four different environments for solutes; (A) water pool; (B) the aqueous interface; (C) the organic interface; (D) the non-polar organic solvent. The illustration has been adapted with permission from Ref. [66].