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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

Debbie C. Crans*, Bharat Baruah, Allison Ross, Nancy E. Levinger

Department of Chemistry, Colorado State University, 1301 Center Av., Fort Collins, CO 80523, United States

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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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* Corresponding author. Tel.: +1 970 491 7635; fax: +1 970 491 1801.
E-mail address: crans@lamar.colostate.edu (D.C. Crans).

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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

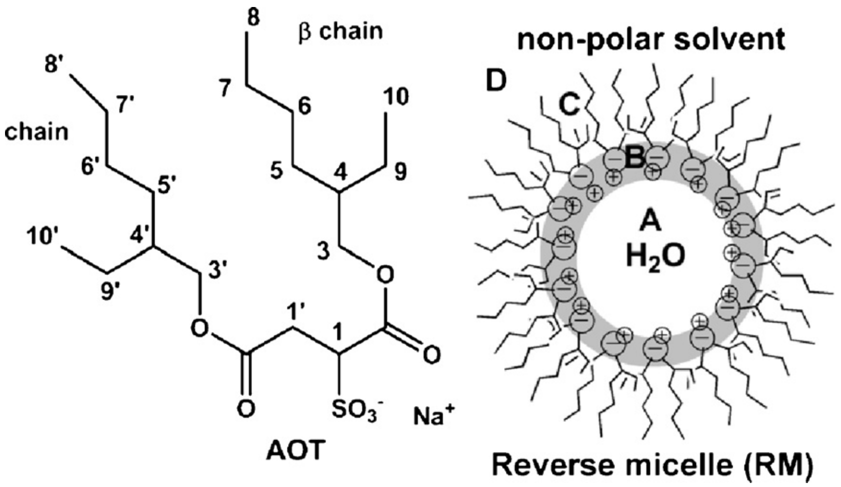

Fig. 1. The structure for AOT is shown as a schematic illustration of an RM based on an AOT/isooctane system with four different environments for solutes; (A) water pool; (B) the aqueous interface; (C) the organic interface; (D) the non-polar organic solvent. The illustration has been adapted with permission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

Table 1
Reverse micellar radii (R_h) and number of V_{10} molecules (n_{occ}) for reverse micelles containing aqueous 10 mM V_{10} or pure water measured using dynamic light scattering at a viscosity of 0.691 cP and a refractive index of 1.391 measured at 826.6 nm and at 25 °C, and in the AOT (0.2 M)/isooctane system [38].

w_0	R_h/nm; V_{10} RMs (pH 6.0)	R_h/nm; H_2O RMs (pH 5.7)	n_{occ}
12	3.6 ± 0.1	4.0 ± 0.1	3
16	4.0 ± 0.3	4.1 ± 0.1	6
20	4.2 ± 0.1	4.5 ± 0.2	11

environment in the tails of the surfactant (Fig. 1C). Finally, a solute can exist in the non-polar organic solvent exclusively, as shown in Fig. 1D.

The RM microemulsions offer solutes an extremely versatile environment as generally described in Fig. 1, from the hydrophobic organic solvent to the transition region at the interface of surfactant and bulk phases, and to the hydrophilic environment in the water pool. The solubility of solutes in these microemulsions therefore differs from those in each of the component parts. These different properties are attributed to the non-conventional and often heterogenous environments created when the non-polar solvent, surfactant and water are mixed, leading to the formation of supramolecular structures. Within the broad range of structures possible for microemulsions, RMs can form regular and well-defined monodisperse structures. RMs are often categorized according to the w_0 parameter, defined as the ratio of the water concentration to the surfactant ($w_0 = [H_2O]/[\text{surfactant}]$) [46,67–70]. Although the structure and size of these nanostructures vary, the w_0 parameter is proportional to the micellar size [66]. In Table 1 we show the data obtained for RMs containing V_{10} [38].

3. Vanadate oligomerization in aqueous solution

Vanadate is a deceptively simple system [2,4–6] until it is recognized that the oxovanadates are in constant rapid exchange in aqueous solution [5] leading to several species present at any given moment [7,71–74]. Vanadate oligomerization reactions are very sensitive to their environment and are readily observed using ^{51}V NMR spectroscopy [5]. As a result, they can be an excellent means of probing the water pool of RMs. Dissolution of sodium metavanadate or sodium orthovanadate in aqueous solution results in the dimerization of vanadate monomer (V_1) to vanadate dimer (V_2), as shown in Fig. 2 [75]. The ratio of V_1 to V_2 formed depends on the environment, including concentration, ionic strength and temperature. The specific protonation state depends on solution pH. For example, various forms of V_1 exist over a broad range of pH values, including VO_2^+ found at acidic pH (<2), $H_2VO_4^-$ and HVO_4^{2-} at approximately neutral pH and VO_4^{3-} found above pH 12. These protonation reactions have previously been studied in detail [7,71–74] and equilibrium is rapidly established in aqueous solution [5]. At neutral pH, formation of the tetramer (V_4) and pentamer (V_5) species are the major species at concentrations above 1 mM. These oligomers are cyclic and form only two different protonation states for the V_4 species ($V_4O_{12}^{4-}$, $HV_4O_{13}^{5-}$), and the V_5 species ($V_5O_{15}^{5-}$, $HV_5O_{16}^{6-}$) [2,5,8,9,76–80]. Minor species also form and linear trimers and tetramers have been reported in a limited pH range [77].

In a limited range around pH 9.0 two additional species have been reported, namely the linear V_3 and V_4L. These species each contain two different V atoms and both types have been observed by ^{51}V NMR spectroscopy demonstrating that these species do not exchange as rapidly as other isomers [81].

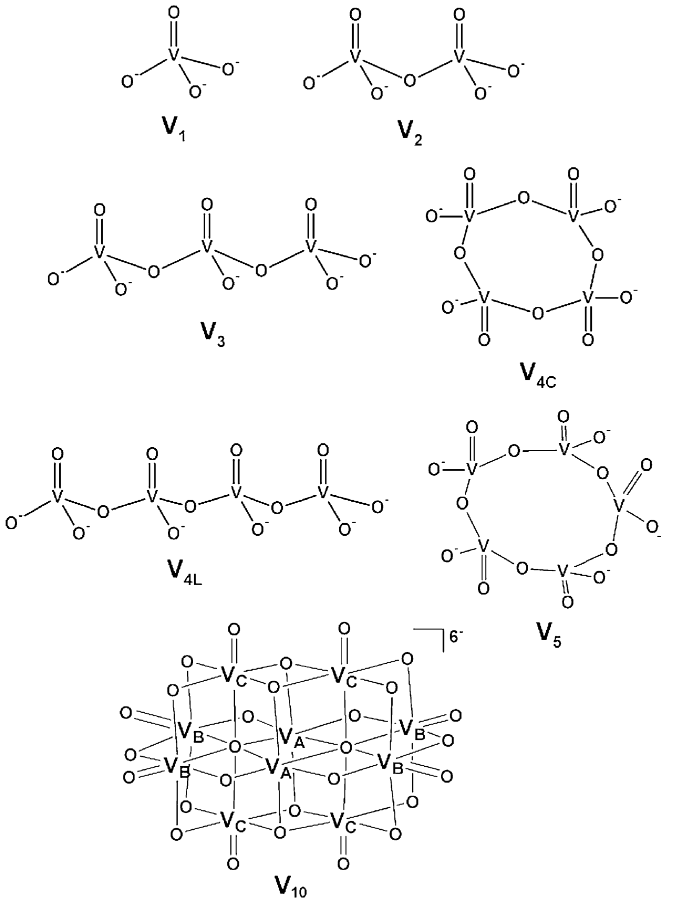

Fig. 2. Representative vanadate oligomers; (V_1) monomer; (V_2) dimer; (V_4 or V_4C) tetramer; (V_5) pentamer; (V_3) linear trimer; (V_4L) linear tetramer.

Despite our ability to distinguish the many different protonation states of vanadate oligomers through their associated ^{51}V NMR chemical shifts, the oligomerization process complicates proton transfer studies of the simple oxovanadates. Evidence exists that the proton concentration within the water pool of the RM differs from the bulk aqueous solution used to form the microemulsion [82–85]. Studies that specifically probe the proton transfer reactions in these systems are therefore desirable. We have explored proton transfer reactions using the decavanadate molecule (V_{10}), an stable oxovanadate at acidic pH [2,3,81]. V_{10} is a compact oxovanadate that differs somewhat from the rapidly exchanging oxovanadates, both structurally, with respect to stability and orange color [2,3,81,86]. In a pH range of 3–6, V_{10} is the most thermodynamically stable species and also exists outside this pH range due to its slow rate of decomposition. For example, aqueous solutions at neutral pH of orange V_{10} remain orange for up to 3 days.

4. Vanadate dimerization in AOT/isooctane RMs

We recently employed the vanadate dimerization reaction as a tool to characterize the water pool in an AOT/isooctane RM system [40]. ^{51}V NMR signals showed interactions with the surfactant interface as reflected by changes in the chemical shifts, intensity of signals and linewidth. The spectra in Fig. 3 show an upfield shift for the V_1 signal with decreasing RM size compared with a downfield shift for the V_2 species [40]. Increasing linewidths are also observed when the oxovanadates are in the RMs. These observations are consistent with an increase in the oligomerization reaction rate between the two oxovanadates, being faster than in aqueous solution.

In addition, as the size of the water pool decreases, the ratio of $[V_2]/[V_1]$ species increases. The concentration of V_2 is gener-

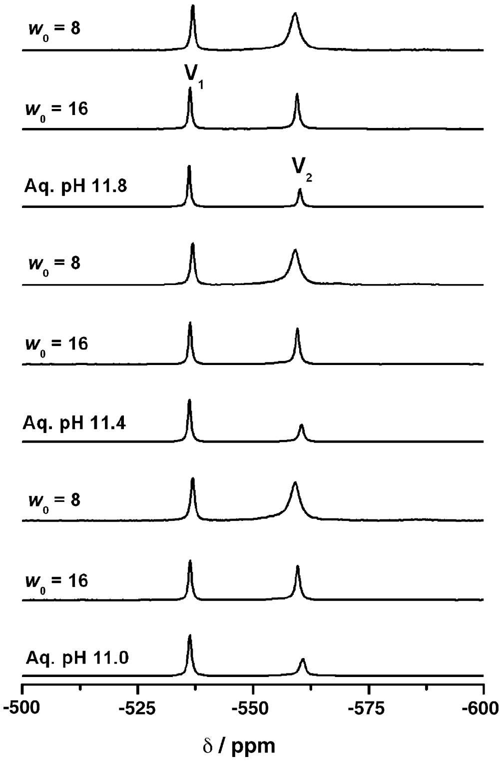

Fig. 3. ^{51}V NMR spectra of 150 mM NH_4VO_3 in 1 M AOT/isooctane. Samples are prepared in phosphate buffer at pH 11.0, 11.4 and 11.8. The ^{51}V NMR spectra are shown in aqueous solution for w_0 sizes 8 and 16. Additional details are described elsewhere [40].

ally closely linked to the specific conditions in solution. Higher concentrations of V_2 in the alkaline pH range are observed with a decrease in pH and suggest that the proton concentration is higher in the smaller RMs. In the smaller reverse micelles V_1 and V_2 are closer to the interface, suggesting that the proton concentration is higher near the interfaces consistent with literature sources [82–85].

The possibility that the observed changes are at least in part due to confinement of the vanadate solution cannot be ruled out [40]. One alternative interpretation is that the interface favors interaction with higher negatively charged species, i.e. V_2 rather than V_1. Given the fact that surfactant counterions are believed to associate closely with the negatively charged AOT interface, such association could be more reasonable than initially considered. Furthermore, an increase in proton concentration in the smaller RMs would result in an increase of V_2 over V_1 as observed in Fig. 3. These studies provide a framework that should be investigated in the future, perhaps using surfactants neutralized with different cations.

These studies showed that the effects of the RM vary depending on w_0 size and effects observable in aqueous solution were recognized as changes in pH and ionic strength. We concluded that the proton concentration of a vanadate solution was slightly lower for larger RMs ($w_0 > 12$), than for the smaller RMs, possibly because the oxovanadates are located nearer the interface in the small RMs [66,74,80,82].

5. Vanadate oligomerization in AOT/isooctane RMs

In the neutral to alkaline pH region, the vanadate oligomerization reaction in aqueous solution forms mainly V_4 and V_5 species [2,4,5,81]. In Fig. 4 we show the ^{51}V NMR spectra of solutions with initial pH values ranging from 8.6 to 10.4 added to microemulsions. At pH 10.4, the signal for the aqueous solution is broader than the signals in the $w_0 = 16$ and 8 RMs, with additional signals reflecting the presence of linear oxovanadates in addition to V_1 and V_2 species. Upon addition to the RMs ($w_0 = 16$ and 8) these species are no longer present and the amount of V_2 increases to yield a speciation pattern not commonly achieved in aqueous solution [2].

At pH 9.8, the spectrum shows that V_1, V_2, V_4 and V_5 are present with V_4 as the major species and on addition of this solution to the RMs, the distribution of species change. As the size of the RM is decreased, significantly less V_4 is observed with a speciation profile not commonly observed for aqueous solution. This reflects the unique environment within the microemulsion and a conversion from the tetramer (V_4) and pentamer (V_5) to the smaller V_1 and V_2 species generally suggests an increase in pH.

At pH 9.4, V_4 is the major species and is readily observed in the ^{51}V NMR spectra although low concentrations of V_1, V_2 and V_5 presumably exist in these solutions. Placing this solution in a RM of $w_0 = 16$ results in a ^{51}V NMR spectrum indistinguishable from the aqueous solution at pH 9.8. Addition of this solution to $w_0 = 8$ results in a ^{51}V NMR spectrum with a speciation profile not commonly observed in aqueous solution, again emphasizing the unique environment in the microemulsion.

At pH values of 8.6 and 9.0, V_4 and V_5 are the major species in solution and V_1, V_2, and V_5 are present at much lower concentrations. Placement of these solutions in the RMs increases the contribution of the V_5 species. For the smaller w_0, the linewidths of the signals in the ^{51}V NMR spectra are dramatically increased with some chemical shift differences, suggesting that the environment and location of these species have changed.

At pH 6.8–8.0, V_4 and V_5 are the major species in solution, with V_1 and V_2 being minor species to the point that in most of the spectra signals for these species do not exceed the threshold of observation. Adding these solutions in the RMs increases the contribution of the V_5 species. For the smaller w_0 the linewidths of the signals in the ^{51}V NMR spectra have dramatically increased and slight chemical shift differences suggest that the location and environment of these cyclic species have changed. Interestingly, in this pH range there is little variation in speciation, although at the smaller w_0 size a significantly higher concentration of V_5 is present.

In summary, these observations demonstrate that the microemulsion environment is unique and the distribution of vanadate oligomers in this system is not always reproduced in aqueous solution at a different pH. We attempted to use the speciation in a quantitative manner for predicting pH, but found in several cases speciation changes consistent with differences in other factors such as those observed with changes in ionic strength and temperature. Specific studies using two variables together, namely pH and temperature decrease was attempted. The spectra obtained showed speciation that was significantly closer to that observed when considering only pH but not exactly that found in the RMs. The possibility to determine the changes using a multidimensional surface with the variables including speciation, pH, size of micelle, ionic strength and temperature was not attempted. Some trends are observed within the smaller RMs as they appear to favor the higher oxovanadates with overall higher charge but not higher charge density. Increasing the ionic strength of the solution and addition of organic solvent favors the higher oxovanadates [87]. However, the magnitude of the changes observed in the RMs environment would require larger quantities of organic solvent in the aqueous pool than is possible. Other changes in speciation such as a higher V_2–V_1 concentration have not been observed in aqueous solution, and report on a unique environment in the RMs. Combined, these results document the fact that microemulsions provide a unique environment with unprecedented speciation and coordination chemistry.

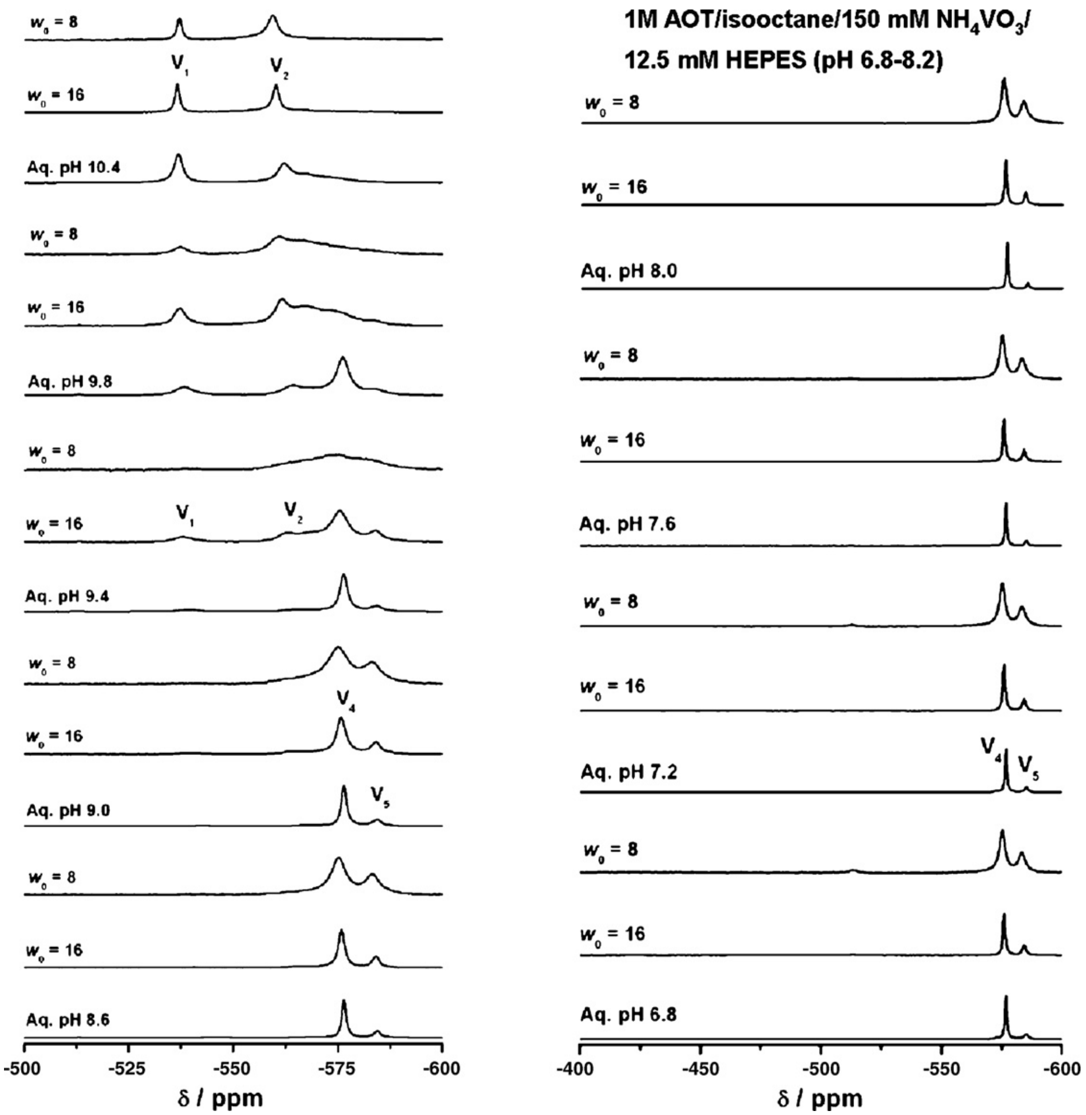

Fig. 4. 78.9 MHz ^{51}V NMR spectra of 150 mM NH_4VO_3 in 1 M AOT/isooctane. The ^{51}V NMR spectra are shown in aqueous solution and for w_0 8 and 16. Samples are prepared in (left) 12.5 mM glycine buffer and (right) 12.5 mM HEPES at pH 8.6, 9.0, 9.4, 9.8 and 10.4 (unpublished data).

6. Proton transfer reactions of decavanadate in AOT/isooctane RMs

Proton transfer reactions were investigated using V_{10} as a probe, as the ^{51}V NMR signals for decavanadate are sensitive to the protonation state, shown in Eqs. (1)–(3) [9,10,81]. The V_{10} species represents an alternate though related probe [86,88], to the simple labile oxovanadates. This structurally robust anion offers an advantage in that it undergoes less oligomerization reactions at acidic pH and is the only observable species present in the pH range 3.5–6.5. Therefore, the highly charged inorganic anion V_{10} was used to probe the water environment in RMs at different pH values and of different sizes, formed from AOT in isooctane. No significant changes were observed until the small w_0 sizes were reached, when the V_{10} starts to feel the AOT interface of the RMs. If the highly charged V_{10} remained in the water pool of the microemulsions, little change would be anticipated until the RMs are reduced in size [38,39]. Calculations predict that the V_{10} oligomer resides (well solvated) in the water pool of reverse micelles for $w_0 > 10$. The chemical shifts show that the environment for V_{10} only very slowly approaches that of bulk water even at $w_0 = 20$–30 [39]:

$$V_{10}O_{28}{}^{6-} + H^+ \rightleftharpoons HV_{10}O_{28}{}^{5-}, \quad pK_1 = 5.5\text{–}6.0 \tag{1}$$

$$HV_{10}O_{28}{}^{5-} + H^+ \rightleftharpoons H_2V_{10}O_{28}{}^{4-}, \quad pK_2 = 3.1\text{–}3.7 \tag{2}$$

$$H_2V_{10}O_{28}{}^{4-} + H^+ \rightleftharpoons H_3V_{10}O_{28}{}^{3-}, \quad pK_3 \approx 2 \tag{3}$$

Experiments were conducted with V_{10} solutions prepared for a range of pH values and added to a solution of AOT in isooctane [38]. ^{51}V NMR spectra were recorded for the AOT/isooctane system and compared with spectra recorded from aqueous solutions. Fig. 5 shows the ^{51}V NMR spectra of solutions from pH 3.1 and 7.0 respectively. Distinct changes in solute environment were observed when an acidic stock solution of protonated V_{10} was placed in a reverse micelle, (Fig. 5, left). The ^{51}V NMR chemical shifts show that the V_{10} in the RMs deprotonates consistent with a decrease in proton concentration for the water pool. Only a small change in the chemical shifts was observed at pH 7.0, suggesting that the environment did not change significantly for V_{10}. Our results indicate that a proton gradient may exist inside the reverse micelles, leaving the interior neutral while the interfacial region is acidic, shown in Fig. 6 [38].

Additional studies were carried out to confirm that the line broadening in the ^{51}V NMR signals observed for these oxovanadates as the w_0 size decreases is due to reducing tumbling rates because of association with the surfactant interface [81]. Further-

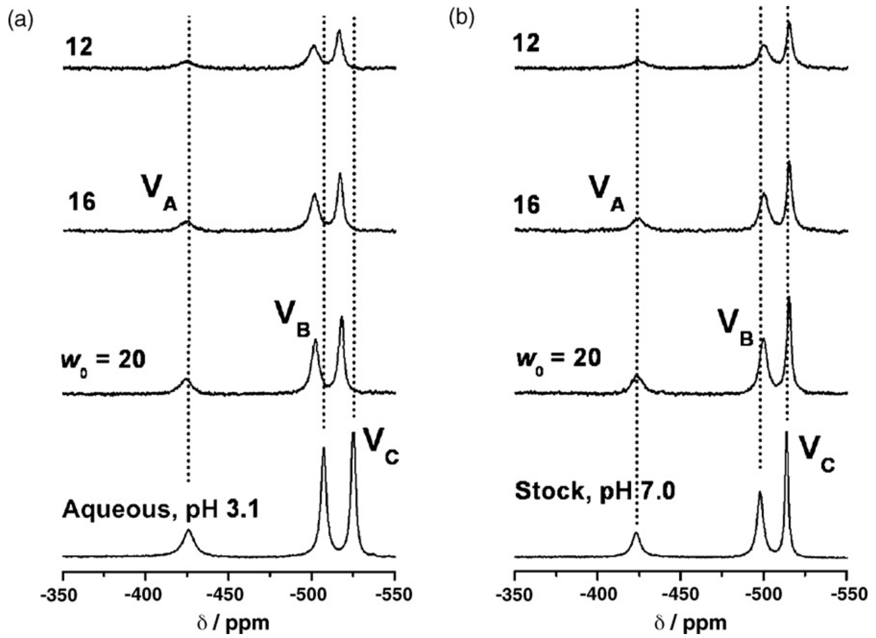

Fig. 5. Representative ^{51}V NMR spectra of V_{10} (a) in stock 10 mM (100 mM V atoms) solution at pH 7.0 and inside reverse micelles created with pH 3.1 stock solution; (b) in 10 mM stock solution at pH 3.1 and inside reverse micelles created with the pH 7.0 stock solution. Adapted from Ref. [38] with permission.

more, IR spectroscopy was used to investigate the OD stretching region for various small RMs prepared with 5% HOD in H_2O. The spectrum shown in Fig. 7 displays a qualitative view of the water pool features inside the RMs and significant shifting and broadening of the OD peak is observed. Spectra were obtained for RMs of $w_0 = 6$ containing V_{10} and compared with those of only water. It can be seen that the spectrum containing V_{10} is very close to the spectrum of $w_0 = 2$ containing only water. Due to the small size of the $w_0 = 2$ RM, almost all of the associated water is in contact with the interface. The similarity of the spectrum to that of the RM where $w_0 = 6$ containing V_{10}, suggests the oxovanadate causes significant perturbation of the associated water in the RM [39].

The studies with V_{10} have provided unique information on the micellar water pool with regard to protonation reactions and hydrogen bonding. Our results are different from studies using 4-aminophthalimide (4-AP) [89] and nitroxide spin probes (*x*-DSA, C8-TEMPO) [90] that suggest the water pool for RMs of $w_0 = 20–30$ has reached bulk water properties [38]. Time-resolved IR studies showed that small, if any, differences were found between bulk water and the micellar water pool for vibrational energy relaxation

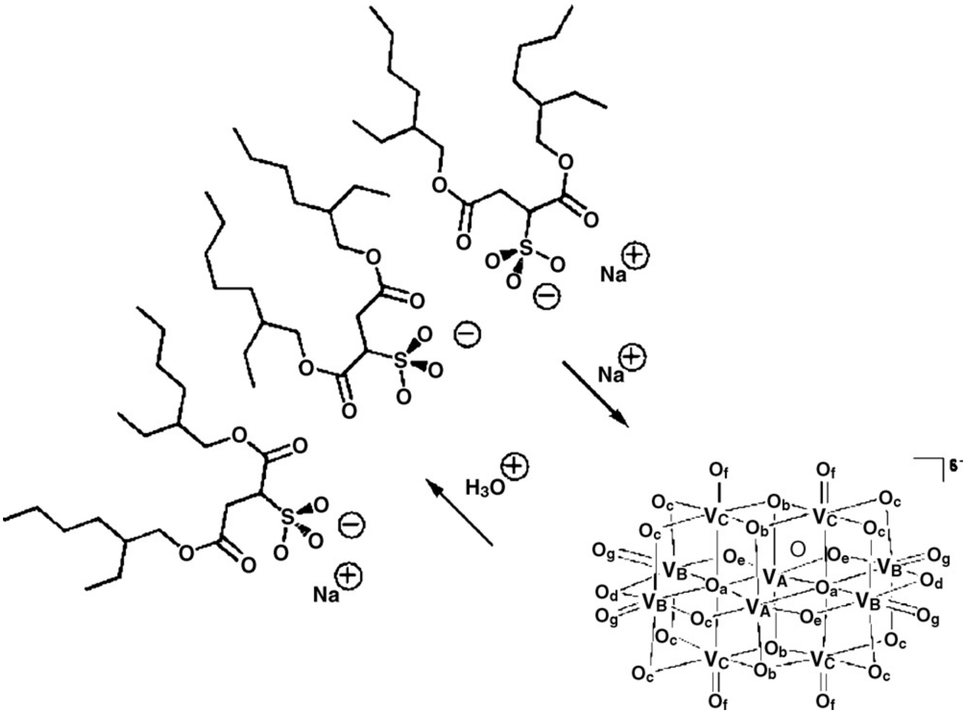

Fig. 6. Schematic depiction of the location of V_{10} with respect to the reverse micelle interface, including counterions. Adapted from Ref. [38] with permission.

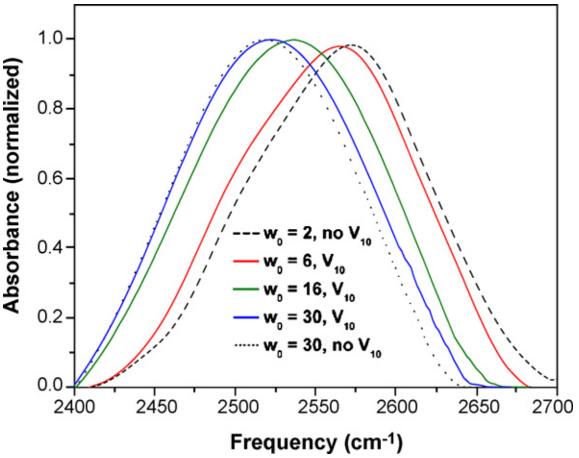

Fig. 7. Background-subtracted FTIR absorption spectra of the OD stretch mode of 5% HOD in different size RMs. Adapted from Ref. [39] with permission but redone by Dr. Pabitra Chatterjee.

for azides [91]. When micellar interior water surrounds V_{10} in the RM it differs from water in the interfacial region [38,39,70]. The difference between both types of water is generally accepted to be associated with differences in the interactions of water with the surfactant head groups, the counter cations [70] and hydrogen bonding [92,93].

7. Concluding remarks

This review describes the chemistry of oxovanadates in microemulsions and reverse micelles, with a focus on the chemistry of these species relating to coordination chemistry. Vanadate dimerization is enhanced in an AOT/isooctane system in part due to the location of the oxovanadates in the micellar water pool. Vanadate oligomerization is also enhanced in an AOT/isooctane system and the larger oligomers are favored in the microemulsion. The responses of vanadates to pH in bulk solution can be correlated to their characteristics in RMs, allowing one to describe the pH profile of confined water in a qualitative manner. Attempts were made to quantify the effects, however, the complex nature of the vanadate equilibria with contributions from pH, temperature, ionic strength and vanadium concentration proved to be too complex and only qualitative information was obtained. Because it is structurally robust, decavanadate V_{10} takes on a special role in the study of RM core water in part because it exhibits multiple protonation equilibria that can be monitored by ^{51}V NMR. V_{10} is located deep in the water pool and deprotonates when acidic stock solutions are used. The extent of the protonation reaction varies with the size of w_0; with the smaller w_0 values increasing the proton concentration at the interface and thus supporting more OH^- ligands over O^{2-} ligands. Solvation and ion pairing may in part be responsible for these observations and will be investigated in the future.

As stability and kinetics of metal complexes are sensitive to their environment, the unique environment in microemulsions can impact the coordination chemistry of metal complexes in a manner not observed in conventional solvent systems. Ranging from the hydrophobic organic solvent, polar surfactant and aqueous water pool, the solutes have many possibilities for ideal solvation in this heterogenous environment, allowing chemistry to take place that has not been observed elsewhere. Such a unique environment may prove to be a very useful tool in synthetic chemistry and structural biology. RMs have recently been used as model systems for membrane proteins with a view to investigating the fundamental physical properties of biomolecules embedded in a complex medium [94].

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